CHAPTER 7

Cyclopropyl homoconjugation, homoaromaticity and homoantiaromaticity—Theoretical aspects and analysis

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I. INTRODUCTION

Cyclopropyl homoconjugation describes conjugation of a cyclopropyl group with one or several unsaturated groups corresponding to double or triple bonds, cationic centres with empty $p\pi$ orbitals or any other conjugative group. Cyclopropyl homoconjugation is based on the π-character of the cyclopropyl bonds, which is amply documented in the literature[1] and which is discussed extensively in Chapter 2 of this volume by Cremer, Kraka and Szabo[2]. Formally, the single bond of the cyclopropyl group should act as an insulator and lead to an interruption of π-conjugation. As a consequence of the π-character of cyclo-

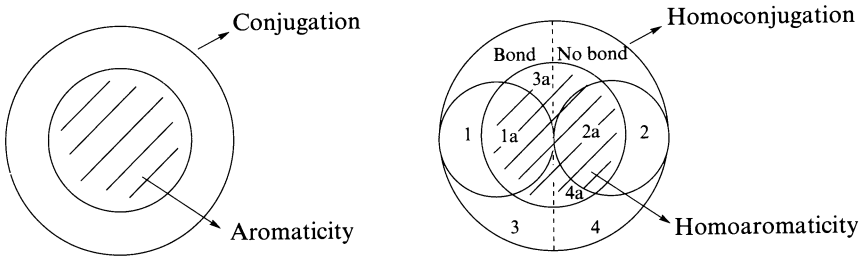
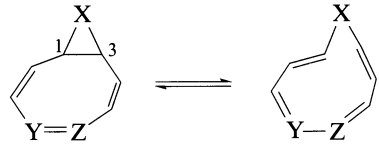


FIGURE 1. Conjugation and aromaticity, homoconjugation and homoaromaticity. Region 1: cyclopropyl homoconjugation ($X = CH_2$); region 2: no-bond homoconjugation ($X = CH_2$); region 3: bond homoconjugation in general ($X \neq CH_2$); region 4: no-bond homoconjugation in general ($X \neq CH_2$). Region 1a: cyclopropyl homoaromaticity ($X = CH_2$); region 2a: no-bond homoaromaticity ($X = CH_2$); region 3a: bond homoaromaticity in general ($X \neq CH_2$); region 4a: no-bond homoaromaticity in general ($X \neq CH_2$). Hence homoconjugation (outer circle) covers regions 1 and 3 (bond homoconjugation) as well as 2 and 4 (no-bond homoconjugation) while homoaromaticity is confined to the inner circle (shaded area) with regions 1a and 3a (bond homoaromaticity) as well as 2a and 4a (no-bond homoaromaticity)

propyl bonds, inclusion of the cyclopropyl ring into a conjugated chain or ring results only in a change in the degree of conjugation but not in its interruption or suppression. In this way the term cyclopropyl homoconjugation expresses homologation of conjugation along a π-chain to systems that include, beside a π-chain or π-cycle, one or several formal σ-bonds of cyclopropyl rings.

Cyclopropyl homoconjugation is a special case of homoconjugation as is indicated in Figure 1. Homoconjugation can be found in molecules **1** or **2**, where $X = CH_2$ and atoms 1 and 3 are connected by a bond (cyclopropyl homoconjugation, region 1 in Figure 1) or just by through-space interactions (no bond homoconjugation, region 2). Molecules **1** and **2** are often connected by a rearrangement process such as the valence tautomeric reaction shown in equation 1. They can also be related as neighbouring forms on the potential energy surface (PES) in the direction of the interaction distance, where either **1** or **2** is located at an energy minimum while the other form is just a transient point on the PES. Cyclopropyl homoconjugation and no bond homoconjugation are strongly related phenomena of one and the same molecular system. Therefore, a review on cyclopropyl homoconjugation must also consider no bond homoconjugation in order to describe, analyse and understand the electronic reasons leading to cyclopropyl homoconjugation.



(1)

(1) **(2)** $X = CH_2$

Homoconjugation can also occur when X in **1** and **2** represents groups other than CH_2. Examples of homoconjugation are known for X = CH, CH_2CH_2, heteroatoms etc. as will be shown in this and the following review article by Childs, Cremer and Elia[3]. All cases with $X \neq CH_2$ are collected in regions 3 and 4 of Figure 1. In general, it is reasonable to distinguish between *bond homoconjugation*, when conjugative interactions are mediated through a bond (regions 1 and 3, Figure 1), and *no bond homoconjugation*, when conjugative interactions are mediated through space rather than through a bond (regions 2 and 4). The exact borderline between these regions is a matter of theoretically based or experimentally based definitions, which we will discuss in this review.

There is another important aspect that has to be considered in connection with cyclopropyl homoconjugation and that becomes clear when considering the homology between conjugation and homoconjugation. Among the many molecules that show conjugation, there is an interesting subgroup of molecules with cyclic conjugation involving $4q + 2$ π-electrons. This subgroup of molecules is aromatic, which means that they are stabilized by cyclic electron delocalization to an extent that can no longer be explained by the conjugative effects typical of polyenes or normal cyclopolyenes. As indicated in Figure 1, aromaticity is the chemically interesting kernel of conjugation, and therefore more than 40 years of chemical research have been devoted to aromatic molecules as is amply documented in many textbooks and review articles[4–10].

In the same way as aromaticity is the interesting core of conjugation, homoaromaticity is the interesting kernel of homoconjugation (shaded area in Figure 1). One can distinguish between cyclopropyl homoaromaticity (region 1a, Figure 1) and no bond homoaromaticity (region 2a). Since chemical research always focuses more on the exceptional cases of chemical behaviour, the actual topic of a review on cyclopropyl homoconjugation has to include cyclopropyl homoaromaticity, which of course is inseparably linked to no bond homoaromaticity. Homoaromaticity is also not limited to $X = CH_2$, and therefore one has to distinguish between bond homoaromaticity in general (regions 1a and 3a) and no bond homoaromaticity (regions 2a and 4a) in general.

Cyclic electron delocalization does not always lead to stabilization. If $4q$ π-electrons are involved it can lead to destabilization and antiaromaticity. Therefore, an integral part of the concept of aromaticity is the concept of antiaromaticity[4–10]. Antiaromaticity is retained to some extent if cyclic delocalization of $4q$ electrons is mediated through homoconjugative interactions. In this case, one speaks of homoantiaromaticity and, according to the classification given above, one can differentiate between cyclopropyl homoantiaromaticity or, in general, bond homoantiaromaticity and no bond homoantiaromaticity.*

Aromaticity has many facets and the question is whether homoaromaticity has a similar manifold of facets. Beside π-aromaticity, there is σ-aromaticity, radial aromaticity, three-dimensional aromaticity, spherical aromaticity and the extension of aromaticity to heteroatomic molecules (heteroaromaticity, compare with Figure 2), not to speak of the many outdated classifications in this connection[10]. The larger class of homoaromatic molecules can be related to π-aromatic compounds although some more sophisticated differentiation may be appropriate. π-Aromatic compounds may have a planar geometry (e.g. benzene, tropylium cation etc.) or a distorted geometry deviating to some extent from planarity (e.g. bridged annulenes). The majority of π-homoaromatic molecules possesses a distorted, non-planar ring geometry (e.g. homotropenylium cation, homocyclopropenium cation, etc.) while only a few (mostly controversial) examples are known with planar geometry and pure $p\pi$, $p\pi$ overlap (see the discussion in Section II).

The term in-plane aromaticity[11] has been used for molecules such as the didehydrophenyl cation (see Section II). However, we stress that the compounds in question are homoaromatic rather than aromatic molecules, which can be directly related to σ-aromaticity[12]. Therefore, the appropriate notation should be homo-σ-aromaticity rather than in-plane aromaticity. The concept of σ-aromaticity is very controversial. One can completely avoid this term by referring to the mode of electron delocalization as was done by Cremer[13]. While π-aromaticity and homo-π-aromaticity are connected with ribbon delocalization of electrons along a conjugative cycle, molecules that have been considered to be either σ-aromatic or homo-σ-aromatic (in-plane aromatic) seem to prefer delocalization of electrons over a surface defined by the participating atoms (see the discussion in

*Some authors have used the term antihomoaromaticity. We think that this term may be misleading since it implies either a system that, despite homoaromaticity, is destabilized or the anti form of a homoaromatic system, which may be considered as the aromatic form itself.

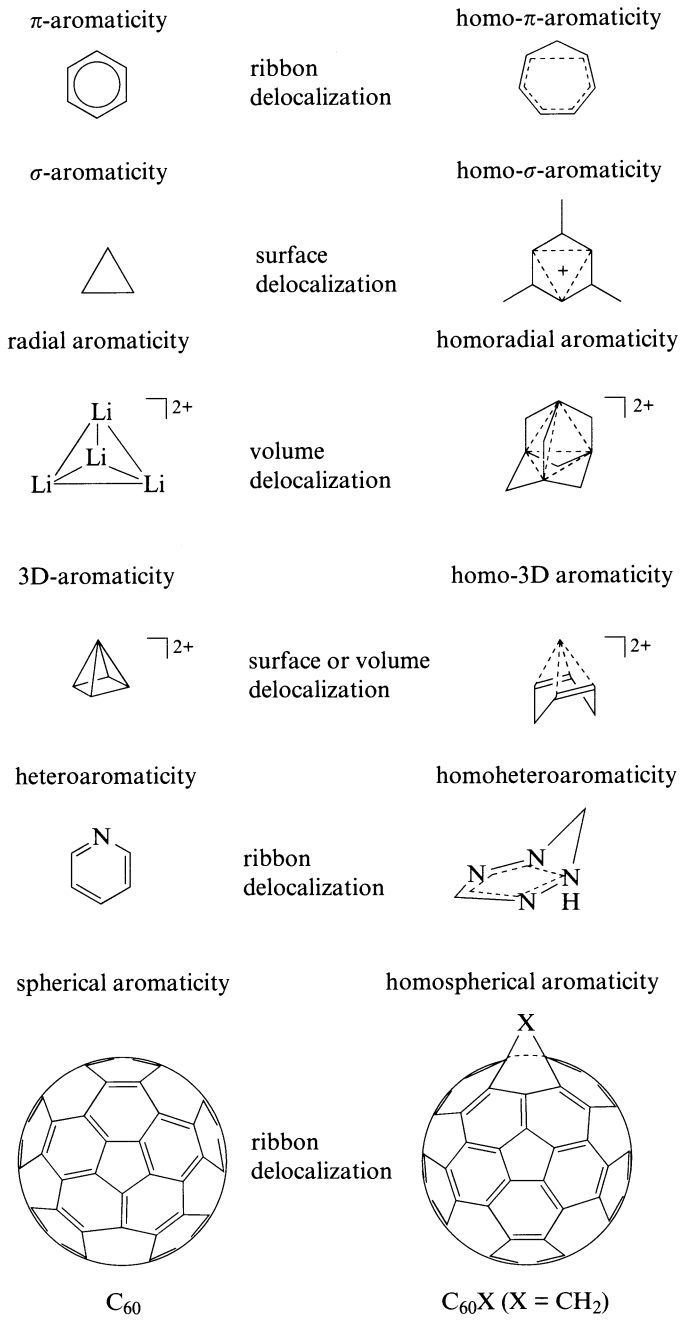


FIGURE 2. Types of aromaticity and homoaromaticity. The preferred electron delocalization mode is given in each case according to Cremer[13]

Chapter 2 of this volume[2]). Therefore, σ-aromatic and homo-σ-aromatic molecules are molecules with surface delocalization of electrons (Figure 2).

Extension of the concepts of ribbon and surface delocalization of electrons to three-dimensions leads to volume delocalization and covers cases of radial aromaticity and three-dimensional (3D) aromaticity[10]. As we will show later the most convicing example of radial aromaticity, namely the 1,3-dehydro-5,7-adamantanediyl cation (Figure 2), is actually an example of homoradial aromaticity. Also, there exist several examples of homo-3D aromaticity that are normally listed under 3D-aromaticity (for an example, see Figure 2). Finally, a number of examples have been investigated that can be classified as homoheteroaromatic systems (Figure 2). It may be only a matter of time until the first molecule with homospherical aromaticity has been synthesized and investigated.

Research on homoconjugative and homoaromatic molecules has been at the centre of organic chemistry for more than 40 years. It was initiated by the epochal investigations of Winstein and his coworkers[14,15] (for a description of Winstein's work, see the following chapter by Childs, Cremer and Elia[3]). Since then it has developed rapidly, as is amply documented in hundreds of publications and research reports. Work on homoconjugation and homoaromaticity was supported by and has influenced important developments in synthesis, kinetics, structure determination, thermochemistry and spectroscopy. The results of this work have improved our understanding of chemical bonding, electronic structure theory, structure and stability and the reactivity behaviour of molecules. Therefore, it has been reviewed in special reports[15–23] and textbooks[6–10] at regular intervals with the latest review appearing in 1994[23].

Any review on cyclopropyl homoconjugation is also a review on cyclopropyl homoaromaticity and has to consider closely related phenomena such as bond and no-bond homoconjugation (homoaromaticity) in general. Furthermore, it will automatically reflect developments, discoveries, problems and ambiguities in the field of aromaticity. While research on aromaticity concentrated in the beginning on planar closed-shell molecules with a clear separation between σ- and π-bonding, studies on homoaromatic molecules led to new dimensions in the realm of aromaticity. First, a clear separation between σ- and π-bonding was no longer possible and one had to realize that partial σ-bonding also leads to conjugation, which, for example, considerably helped an understanding of the electronic structure of bridged annulenes. Also, a formal σ-bond of a cyclopropyl group was accepted as a conjugative element, which could replace a double bond to some extent.

While these new ideas were still understandable against the background of classical bonding theory, it was difficult for a chemist of the fifties and sixties to accept that electron delocalization is not limited to following the framework of bonds but can also occur through space without the transmitting mechanism of any partially or fully developed 2-electron bond. This new mechanism of electron delocalization could only be accepted by inventing the 'homoconjugative (homoaromatic) bond' and by speaking about 'non-classical bonding' and 'non-classical structures'. These terms in a way reflected the difficulties chemists had to preserve classical bonding theory and to comprehend the new type of conjugation through space without bonding[24]. The full acceptance of the new mechanism of electron delocalization required the giving up of dogmas in classical bonding models and therefore it took its time. However, the transition from cyclopropyl homoconjugation to no-bond homoconjugation has led directly to a basic understanding and differentiation of interactions through bond and through space, to a comprehension of the forces acting in transition states, to a distinction between short-range and long-range forces and to improved knowledge about non-bonded interactions in general.

Although our knowledge about the electronic forces that act in homoconjugated molecules has increased considerably during the last 40 years, there is still considerable confusion concerning exactly how to define homoconjugation and homoaromaticity. Several attempts by distinguished reviewers have helped to classify the experimental material, but the synthesis and investigation of new unexpected examples of homoconjugated

and homoaromatic molecules have maintained a constant level of confusion. Questions about homoaromaticity for neutral or anionic molecules[25,26], the range of homoaromatic interactions or the energetic consequences have not thus far been settled satisfactorily[14–23]. These questions can only be answered in a clear way for a limited number of homoconjugated systems which has led to the somewhat provocative opinion[25,26] that the concepts of homoconjugation and homoaromaticity apply just to a relatively small number of molecules and therefore their general value may be questioned. Before accepting these claims, one has to remember that both homoconjugation and homoaromaticity are models and as such their basis is simplification.

A. Models in Chemistry

Models are an important part of organic chemistry and they form the working framework within which a large body of factual material can be organized, understood and used in a predictive manner. Some models such as those of the chemical bond, the division of bonds into σ- and π-types, conjugation, molecular orbitals or electronegativity, have become so engrained that frequently it is forgotten that these are still models.

For a model to be useful and effective it should have three characteristics[27], First, it should have some physical basis. Second, it should be simple and readily understood. Lastly, it should have predictive capability. There will always be failures of simple models to account quantitatively for a particular phenomenon. In these instances it is always tempting to develop a further model as, for example, continues to be done with substituent constants, rather than using the discrepancies to provide valuable insights into the reasons for the discrepancy between the model and the system in question.

The concepts of homoconjugation and homoaromaticity build on the ideas of the chemical bond, conjugation and aromaticity. In this chapter, while refining the concepts somewhat, we seek to retain the simplicity of the original models as developed by Winstein and colleagues[14,15]. We recognize that there will be failures of the models to account for all the properties of the molecules discussed here; however, we feel that the simplicity and predictive power of these models justify their retention as part of the working framework of the organic chemist.

B. Organization of the Chapter

Contrary to previous review articles, we will present our account of cyclopropyl homoconjugation, homoconjugation in general and homoaromaticity in two parts organized in two closely connected chapters. In the current chapter, we will thoroughly discuss the theoretical basis and description of homoconjugation and homoaromaticity. In the following Chapter[3] we will review the history and development of the concept of homoconjugation and homoaromaticity. Following this, experimental and theoretical work on specific homoconjugated and homoaromatic systems will be reviewed on a selected basis where ample use is made of basic considerations and definitions worked out in this chapter.

The remainder of the current chapter is organized into four major sections. In Section II, we will focus on the definition of homoconjugation and homoaromaticity starting from a topological angle of perspective and then proceeding to chemically relevant definitions. In Section III, we will examine the theoretical basis for defining, detecting and characterizing homoconjugation and homo(anti)aromaticity. Various theoretical tools, such as orbital overlap, PMO theory, electron density analysis and energy decomposition, will be discussed to obtain useful descriptions and definitions of homoconjugation and homoaromaticity. Ample reference will be made to the theoretical description of the cyclopropyl group, and this section is closely connected with Chapter 2 of this volume in which the

theory of cyclopropane and the cyclopropyl group is reviewed by Cremer, Kraka and Szabo[2].

Following Section III, there will be a section (Section IV) in which the basic requirements for an *ab initio* investigation of homoconjugated molecules are sketched. As an illustrative example, the *ab initio* investigation of the homotropenylium cation will be described in detail where special emphasis is laid on an assessment of those molecular properties that are a direct reflection of the homoaromatic character of the molecule. The section will close by deriving detailed definitions and requirements for homoaromaticity and homoantiaromaticity that are adjusted to the more recent developments in the field.

The chapter concludes with a reflective section that provides the link between this more theoretically oriented review on cyclopropyl homoconjugation and the following chapter, which will concentrate on specific examples of homoconjugation and homoaromaticity[3]. In addition, we will point out some directions for future work on cyclopropyl homoconjugation and homoconjugation in general.

II. DEFINITION OF HOMOCONJUGATION AND HOMOAROMATICITY—BASIC CONSIDERATIONS.

In terms of homoconjugation, there are two basic starting points for a particular system as illustrated in equation 1 for cyclic conjugated systems with a single interruption. It is possible to start with a closed form, **1**, and consider its conjugation or one can start with an open form, **2**, and consider through-space interactions. Homoconjugation does not require that the closed form consists of a cyclopropyl ring. However, in practice many known examples formally involve a cyclopropane or three-membered ring form as the ring-closed valence tautomer. It is this that has led the editor to include a discussion of homoconjugation in a volume on the chemistry of the cyclopropyl group. It should be stressed that in many systems to be discussed the starting point is an open form and linkage to a cyclopropane can at times seem tenuous.

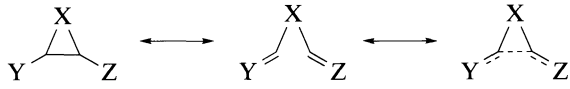
In this and the following review[3], we are concerned particularly with cyclopropyl homoconjugation and not simply the conjugation of a cyclopropyl group to an unsaturated centre. This differentiation may on first sight be confusing, since most authors tend to use these terms synonymously. Clearly, one can take the view that cyclopropyl conjugation is also cyclopropyl homoconjugation. But there are fine differences between these terms, which one can use for a better understanding of homoconjugation in general. In the case of cyclopropyl conjugation, the emphasis is on the conjugative ability of the cyclopropyl group (as indicated in Scheme 1) and therefore the term is suited for the description of conjugation in substituted cyclopropanes.

cyclopropyl conjugation cyclopropyl homoconjugation

SCHEME 1. Difference between cyclopropyl conjugation and cyclopropyl homoconjugation

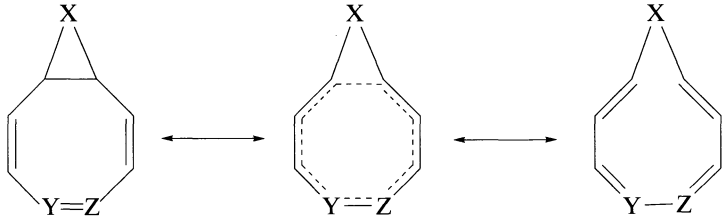
In the case of cyclopropyl homoconjugation, the emphasis is more on the mode of conjugation (i.e. homoconjugation) and therefore this term is better suited for homoconjugated systems including a cyclopropyl ring (Scheme 1). Cyclopropyl conjugation can be considered as a normal phenomenon similar to conjugation in polyenes. Cyclopropyl

homoconjugation implies some changes in the electronic structure of a molecule over and above what one knows about molecules with cyclopropyl conjugation. The distinction is important, since it reduces the huge number of molecules with a cyclopropyl group in conjugation with some unsaturated substituent to a relatively small number of exceptional molecules with cyclopropyl homoconjugation. The focus of our attention is on delocalization of electrons through space or through a cyclopropane bond (equation 2), thus leading to cyclopropyl groups with unusual bonding. Cyclopropyl conjugation does not necessarily embrace this 'transmission' aspect of homoconjugation and its main focus is normally on the effect of a cyclopropane as a substituent.



(2)

Homoconjugation can be a linear phenomenon; that is, one can be concerned with conjugation and electron delocalization through space between the ends of two unsaturated fragments. The special and most important case is where the unsaturated fragment or fragments are combined in a cyclic system such that a through-space interaction potentially leads to a cyclically delocalized system **3** (equation 3), which can be stabilized by homoaromaticity. Structure **3** has to be distinguished from **1** and **2** (equation 1) since the latter have different bonding patterns and geometries. Structure **3** can be considered as a bond–no bond resonance structures **3a** and **3b** which, of course, possess the same geometry as **3** but are different from **1** and **2**.



(3)

(3a) **(3)** **(3b)**

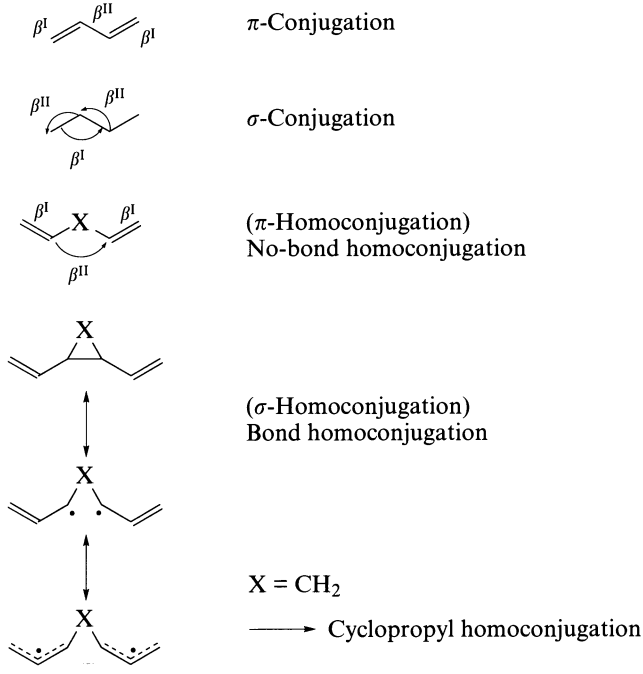
A. From Conjugation to Cyclopropyl Homoconjugation

Since the terms homoconjugation, cyclopropyl-(homo)conjugation, homoaromaticity, etc. are used by different authors in different ways, a review on cyclopropyl homoconjugation requires some clarification of these basic terms.

1. Conjugation

Originally, the term conjugation was used in a topological sense indicating a particular arrangement of bonds[13]. For example, double bond conjugation implies that each pair of double bonds in a conjugated system be separated by only one single bond. Such a bond arrangement leads to significant interactions of the π-MOs of the double bonds and, as a consequence, to delocalized π-MOs. The term conjugation was extended to orbital language where it describes particular orbital interactions (π-conjugation, σ-conjugation) given by the topology of the molecule. Conjugation implies an alternation between stronger and weaker orbital interactions leading to a corresponding alternation of the

resonance integrals β. This is illustrated in Scheme 2 for π- and σ-conjugated systems. (We note that σ-conjugation is superfluous on a topological basis because, topologically, conjugation requires two different bond types.) In the former case, the resonance integrals β^{I} (larger) and β^{II} (smaller) each describe interatomic interactions. In σ-conjugated systems the stronger interactions (β^{I}) are intraatomic and the weaker (β^{II}) interatomic[12].



SCHEME 2. Conjugation versus homoconjugation

2. Homoconjugation

Since conjugation was originally based on a topological definition, one should also initially define homoconjugation in a similar manner. Thus when double bond conjugation is interrupted by a saturated group X (e.g. CH_2, Scheme 2), then conjugation can be restored to some extent by through-space interactions between the double bonds and their associated π-orbitals that are separated by the group X. In this way, a single conjugated system is re-established. The interaction bridging the group X was called homoconjugation because it leads to a system that is iso-conjugate with the unperturbed conjugated π-system. Thus, homologation of the unperturbed conjugated π-system by insertion of a saturated group X leads to the homoconjugated π-system.

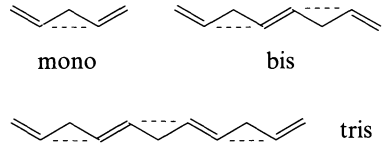
Cyclopropyl homoconjugation is a special case of homoconjugation. It will occur if $X = CH_2$ and there are sufficiently strong interactions between the double bonds such that a bond is formed.

In order to clarify the role of cyclopropyl homoconjugation within the concept of homoconjugation, it is appropriate to classify the various types of homoconjugative interactions according to the following seven critera:

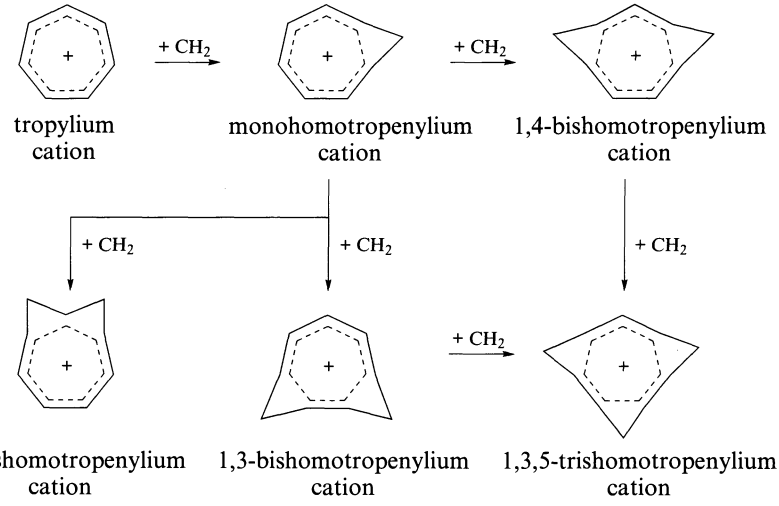
(a) the number of interruptions in the conjugated chain,

(b) the nature of the orbital interactions,
(c) the nature of the saturated group X,
(d) the type of orbital overlap,
(e) the nature and type of the interacting groups in the conjugated systems,
(f) the charge and multiplicity of the molecule and
(g) the state of the molecule in which homoconjugative interactions become important.
These criteria are discussed in separate sections below.

a. The number of interruptions. In principle, any number of interruptions is possible given a long enough conjugated chain. The number of interruptions is specified by the prefix mono-, bis-, etc. as shown in Scheme 3. For example, homologation of the tropylium cation by insertion of a CH_2 group leads to the monohomotropenylium ion (Scheme 4). Introduction of a second CH_2 group will formally yield either 1,2-, 1,3- or 1,4-bishomotropenylium ion. Formally, there is a possibility of inserting a third CH_2 group, which will lead to a 1,3,5-trishomotropenylium ion (Scheme 4). The cations shown in Scheme 4 are clearly related and the nomenclature used above stresses this point. We will use this type of nomenclature throughout this and the following review[3].



SCHEME 3. Mono-, bis- and tris-homoconjugated molecules



SCHEME 4. Mono-, bis- and trishomoconjugation of the tropenylium cation

b. Nature of orbital interactions. Homoconjugative interactions range from weak through-space interactions to normal bonding interactions. Cyclopropyl homoconjugation implies that a cyclopropyl group has been formed, i.e. that the interacting centres are connected by a bond. Some authors have described this situation by the term 'σ-homo-

conjugation' to indicate that the conjugative chain is formally closed by a σ-bond (see Scheme 2). We think that such a term is not appropriate since it disguises the fact that it is actually the partial π-character of the connecting cyclopropyl bond[1,2] that leads to conjugation and also incorrectly implies the existence of π-homoconjugation as being the counterpart of cyclopropyl homoconjugation (see Section A.4 below).

It is more appropriate to couple the term 'cyclopropyl homoconjugation' with bond homoconjugation as the conjugative interactions are mediated by a cyclopropyl bond. The term 'bond homoconjugation' is more general than cyclopropyl homoconjugation since it covers all cases in which a homoconjugated system is formed via a bond, irrespective of whether this bond is part of a cyclopropyl, cyclobutyl or any other ring (compare with Figure 1).

It should be stressed that homoconjugation in general does not necessarily require the existence of a bond. Conjugative interactions can be mediated through space by appropriate overlap between the orbitals involved. Through-space interactions between orbitals have been amply documented in the literature in connection with either homoconjugation or other phenomena[28]. They are clearly a function of the distance R between the interacting centres. Indeed, it is convenient to classify the type of interactions as a function of R (Figure 3). For large values of R, overlap and through-space interactions between the

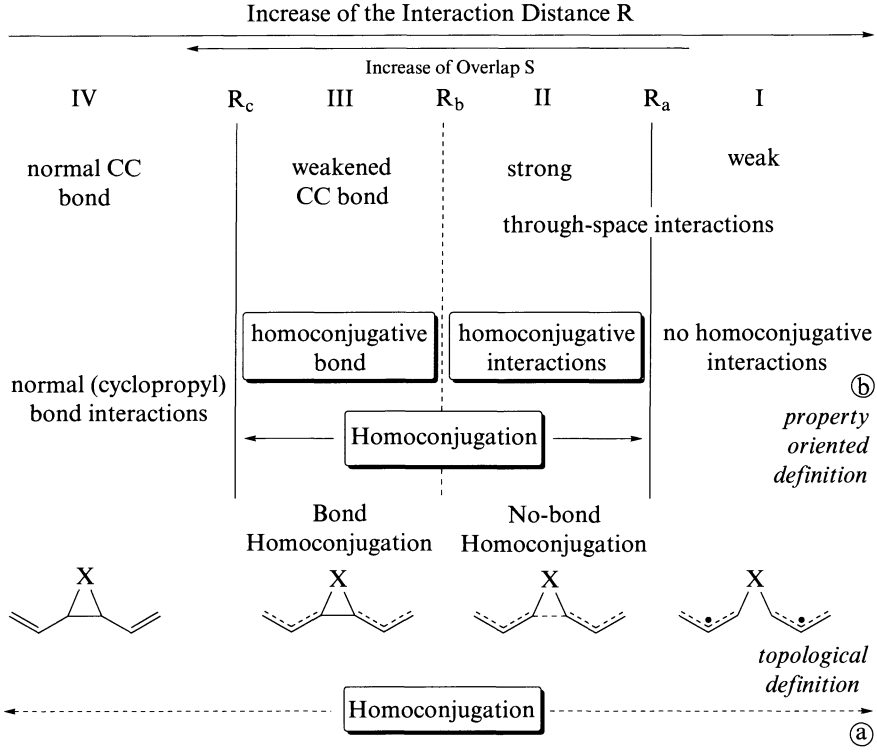


FIGURE 3. Topological (a) and property oriented (b) definition of homoconjugation based on the value R of the distance between interacting atoms in a potentially homoconjugated system. Types of interactions for increasing interaction distance (decreasing overlap S) are given for a hydrocarbon

orbitals involved are weak and probably have little consequence for the properties of a molecule. Although one can speak of homoconjugation in a topological sense, this is not very useful from a chemical point of view as the molecule would not chemically be significantly different from other related molecules with two isolated conjugated systems.

With a decrease of R, a point R_a will be reached at which through-space interactions are sufficiently strong to become chemically significant with the formation of a single homoconjugative system. In this case, we have 'no-bond homoconjugation' (Figure 3).

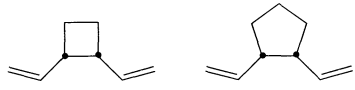
A further decrease of R will lead to the piont R_b (Figure 3) at which a weak bond is established between the interacting centres. At this point no bond homoconjugation turns into bond homoconjugation or, for the special case X = CH_2, into cyclopropyl homoconjugation.

Further reduction in R leads to the point R_c (Figure 3) at which the bond is fully formed and normal cyclopropyl substituent interactions occur. Homoconjugation ceases to be a relevant chemical factor at point R_c and the molecule can be adequately described in terms of a cyclopropyl substituted system.

It is also interesting to note what formally happens when R is further shortened from the point R_c. In the case of cyclopropyl conjugation, significant shortening between the interacting centres will lead to a conversion of the cyclopropyl ring into an ethylene–methylene complex (see Chapter 2)[2]. Conjugation is established at the cost of losing a methylene group from the system.

As shown in Figure 3, a decrease of the interaction distance R leads to a continuous change from weak through-space interactions to no-bond homoconjugation, bond homoconjugation (cyclopropyl homoconjugation), weak bond interactions between cyclopropyl ring and substituent and, finally, normal conjugation. It is not likely that there is any molecule for which such a transition can be monitored by experimental means. Chemical relevance is only achieved in those situations where a global (local) energy minimum exists on the potential energy surface (PES) with a value of R between R_a and R_c that is deep enough to be detected experimentally (see Section II.D).

c. Nature of the saturated group X. For cyclopropyl homoconjugation, X is equal to CH_2. This is the most common case of homoconjugation and the reason homoconjugation is discussed in a volume on the cyclopropyl group rather than in other volumes of *The Chemistry of the Functional Group* series. However, in principle, homoconjugation is also possible for X = CH_2CH_2 or any other group. Bond homoconjugation would then lead to a cyclobutyl ring (cyclobutyl homoconjugation), a cycloalkyl ring or some other ring. Despite speculation on potential homoconjugation involving cyclobutane or higher rings, no experimental evidence is available to indicate the presence of any conjugative interaction between the two double bonds of **4**, **5** or their derivatives. The absence of homoconjugation in these higher systems points to the special electronic properties of the cyclopropyl ring (see Chapter 1 of this volume[2]). However, it is too early to completely exclude the possibility of cyclobutyl or other types of homoconjugation as their potential depends more on the type of orbital interactions involved (see Section 2.d below) and the steric situation of the molecule than on the nature of X.



(4) **(5)**

Considerable homoconjugative interactions could also be retained if X in a homoconjugative system is a heteroatomic group such as NH, O, SiH_2, PH, S, etc. Indeed, it is possible to encounter homoconjugative interactions with almost any heteroatomic group

X provided steric factors are suitable to allow bonding or through-space overlap between the interacting orbitals. The critical factors for homoconjugative interactions are orbital overlap and the difference between the energies of the interacting orbitals. Orbital overlap depends on the geometry (distance *R*, Figure 3) of a molecule, which in turn is a consequence of topological and steric factors such as bridges, rings, tetrahedral and pyramidal centres, etc. Orbital energies depend on the nature of the conjugated sub-chains and also the nature of the group X. In principle, any bridging group X is possible in terms of homoconjugation as long as orbital overlap and similarity of the energies of the interacting orbitals are guaranteed. In order to clarify further these two requirements we must consider the types of orbitals which can be involved in homoconjugative interactions.

d. Type of orbital overlap. One could classify homoconjugative interactions according to the type of the interacting orbitals. However, this would complicate the description of homoconjugation because there are both a large variety of potential interacting orbitals and, moreover, it is not always clear how to describe the orbitals in question. It is far easier to follow the original suggestion of Winstein[14] and to classify the type of orbital overlap rather than the interacting orbitals themselves. For both bond homoconjugation and no-bond homoconjugation, one can distinguish three different possibilities of orbital overlap. These are π,π-, $\sigma/\pi,\sigma/\pi$- and σ,σ-types of overlap. Examples for the various types of overlap are shown in Figure 4.

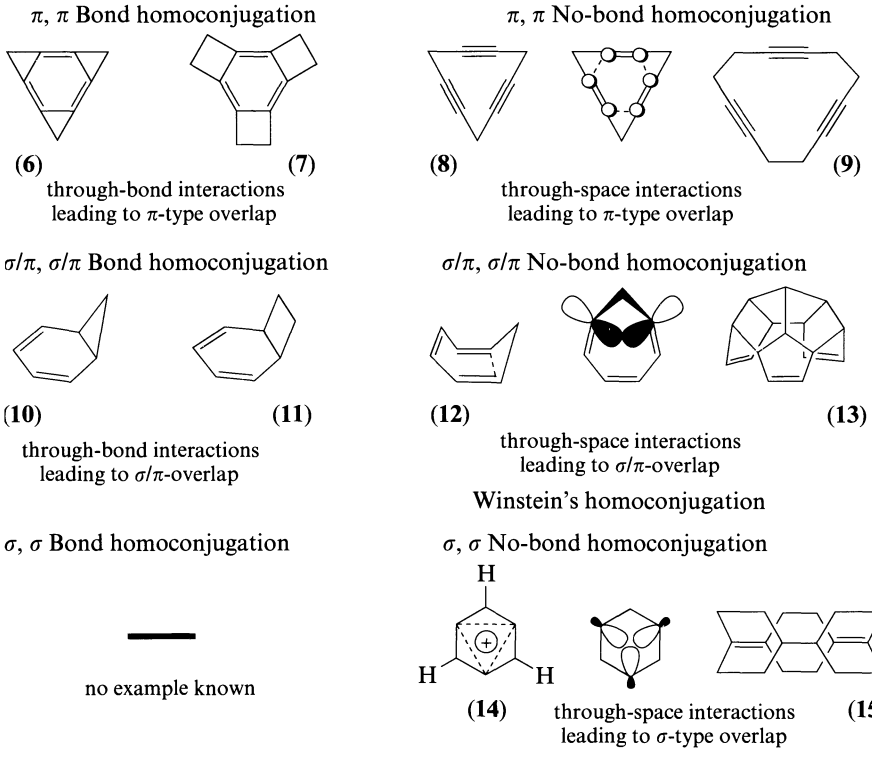


FIGURE 4. Possible types of bond and no-bond homoconjugation classified according to orbital overlap between the interacting centres

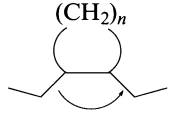
Pure π-type overlap will occur, for example, with tricyclopropabenzene or tricyclobutabenzene. There has been a long-lasting debate as to whether these compounds show a Mills–Nixon effect (alternation of bond lengths enforced by cyclopropane and cyclobutane annelation). However, all existing evidence suggests that the benzene ring with its electron delocalization is fully retained and that ring annelation does not 'freeze out' one of the resonance structures of benzene[29–31]. It may be misleading, therefore, to consider tricyclopropabenzene as a trishomoconjugated system from a chemical point of view. However, since at this point we are only considering homoconjugation from a topological perspective, it is possible to consider tricyclopropabenzene and related systems as potential examples of trishomoconjugated systems with π,π-type overlap.

Calculations suggest that tricyclopropabenzene, **6**, and tricyclobutabenzene, **7**, suffer from large strain energies and, as a result, their valence tautomers, [3]pericyclyne (**8**) and 1,5,9-cyclododecatriyne (**9**), are more stable[32]. Both **8** and **9** are examples of potential π,π-type no-bond homoconjugation. Since the overlap between out-of-plane π-orbitals decreases more rapidly than that between in-plane π-orbitals with increase in the distance R, interactions between the former (leading to π-type overlap) are much smaller than those between the latter (leading to σ-type overlap). As a result, **8** and **9** may be better examples of σ,σ-rather than π,π-type no-bond homoconjugation.

Overlap and through-space interactions are increased as soon as pπ-orbitals are tilted toward each other, thus mixing with σ-orbitals and attaining partial σ-character. This is the situation which Winstein described when he spoke of an overlap situation, which is between σ and π[14]. A $\sigma/\pi,\sigma/\pi$-type overlap can occur for both bond and no-bond homoconjugation as shown in Figure 4. Formal examples of the first case are norcaradiene, **10**, or bicyclo[4.2.0]octadiene, **11**, while the classical example of the second case is cycloheptatriene, **12**. In trienes such as *cis*, *cis*, *cis*-1,4,7-cyclononatriene, triquinacene or C_{16}-hexaquinanacene, **13**, the overlap changes gradually from $\sigma/\pi,\sigma/\pi$-type to σ,σ-type, involving in the latter case the in-plane π-orbitals. C_{16}-hexaquinanacene is a potential example of a σ,σ-type of homoconjugative overlap.

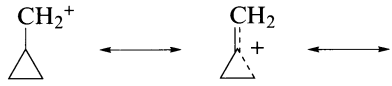
There are several potential examples of σ,σ-type no-bond homoconjugation in the literature, of which the 3,5-dehydrophenyl cation, **14**, is probably best known (see also Figure 2)[33]. If the sp^2 hybrid orbitals at position 1, 3 and 5 point toward the centre of the ring, they can overlap and form a homoconjugative 2-electron–3-centre system. In plane overlap between π orbitals, σ-type overlap can also be expected for tetracyclo-[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene, **15**, in which three double bonds are kept face to face by frames made out of cyclohexane rings[34]. Finally, [3]pericyclyne and 1,5,9-cyclododecatriyne could be considered to be better examples for σ,σ-type rather than π,π-type overlap as mentioned above.

Bond homoconjugation via σ,σ-type overlap is identical with σ-conjugation, and if the latter occurs it cannot be distinguished from the former (Scheme 5). As such it is not reasonable to use the term σ,σ-bond homoconjugation.



SCHEME 5. σ-Conjugation

e. Nature and type of interacting groups. Usually these are conjugated π-systems with one or more C atoms. The simplest such system would be a carbinyl group, $—CH_2^+$, joined to a cyclopropyl ring thus leading to the cyclopropylcarbinyl cation, **16**. Homoconjugation involving the CH_2^+ group and the vicinal three-membered ring bonds leads to a homologue



(16)

of the allyl cation. Similarly, vinylcyclopropane is a homologue of butadiene and divinylcyclopropane a homologue of hexatriene. In principle, any charged or uncharged polyenyl group can function as a sub-group in potentially homoconjugated systems.

Little is known about the extent to which heteroatoms can be incorporated into the conjugated chain of a homoconjugative system. In principle it should be possible to include heteroatoms with lone-pair electrons that can contribute their *n*-type electrons. Alternatively, replacement of the CH_2^+ group by BH_2 or other groups with empty pπ-orbitals should also lead to a retention of homoconjugation (see the next chapter[3]).

Recent investigations by Szabo and Cremer[35] have shown that Si can also participate in homoconjugation and homoaromaticity. This may also be true for atoms such as Ge or Sn. There are many more possibilities of homoconjugative interactions than have been considered thus far in the literature.

f. Charge and multiplicity of the molecule. The total charge of a molecule affects the energies of the interacting orbitals in a homoconjugative system. For example, in the case of the cyclopropylcarbinyl cation, the positive charge at the CH_2 group lowers the energy of the empty pπ-orbital. Interactions with the Walsh orbitals of the cyclopropyl ring are facilitated since they depend on the energy difference between the interacting orbitals (see Chapter 2 of this volume[2]). Charge transfer from the ring to the empty pπ orbital leads to electron delocalization and homoconjugation.

In general, one can expect that positively charged systems are better suited for homoconjugation than neutral or negatively charged molecules. The positive charge is mostly accompanied by relatively low-lying unoccupied orbitals, which can interact with high-lying occupied orbitals. Indeed, homoconjugation and homoaromaticity are best established for cationic systems while they are still controversial for neutral and anionic systems.

Most homoconjugative molecules studied so far represent closed-shell singlet systems with multiplicity $2S + 1 = 1$. Open-shell systems with higher multiplicity are normally very labile and, as a result, can only be studied in detail if electron delocalization leads to significant stabilization of the system in question. In general, homoconjugative electron delocalization cannot guarantee high stabilization energies (see Section III) and therefore homoconjugative effects are too small to be observed in connection with open-shell systems of higher multiplicity.

Nevertheless, there exist a number of free radicals ($2S + 1 = 2$, doublet state), for which ESR measurements suggest non-classical structures as a result of homoconjugative (homoaromatic) interactions. In all cases of radical homoaromaticity considered so far, the radicals in question are actually radical cations. This again emphasizes the important role of a positive charge in connection with homoconjugation[36].

g. The state of the molecule. Homoconjugation has been exclusively detected and investigated for molecules in their ground state. Definitely, it will also play a role for molecules in their excited states, but since excitation energies are normally much larger than homoconjugative stabilization energies, homoconjugation can only be a second-order effect, which will be difficult to detect and to investigate.

The situation will be different if one considers the transition states of chemical reactions. In a bond-forming reaction, the reaction partners will already interact with each other before all bonds are formed, i.e. most of the interactions occur through-space. If the react-

ing molecules both possess conjugated π-systems as in the case of pericyclic reactions, homoconjugative systems can be formed and homoconjugative interactions will lead to a lowering of the energy of the transition state. Examples are the valence tautomeric rearrangements of cyclopentadiene/bicyclo[2.1.0]pentene, cycloheptatriene/norcaradiene, etc. and related reactions.

One could even go one step further and argue that the important aspect of a pericyclic reaction is the through-space interaction between atoms about to form a bond. The situation is similar to that in no-bond homoconjugative systems and therefore pericyclic transition states resemble homoconjugative systems with or (mostly) without bridging between the conjugation partners. As a matter of fact, pericyclic reactions have been amply investigated with regard to the possibility of through-space interactions and electron delocalization in their transition states. The focus of these investigations has not been homoconjugation, but the translation of the Woodward–Hoffmann orbital symmetry rules[37] into the Evans–Dewar–Zimmermann electron counting rules[38]. In this latter approach, emphasis is placed on the identification of aromatic or antiaromatic electron ensembles participating in the formation of bonds in transition states. Typical interaction distances between C atoms, that are about to form a CC bond, are 1.8 to 2.4 Å in a transition state, and therefore one could speak of homoconjugation and homoaromaticity rather than conjugation and aromaticity in an orbital symmetry-allowed pericyclic transition state.

From the seven classification criteria discussed above, it becomes clear that most homoconjugative systems studied so far belong in the class of monohomoconjugated singlet ground-state cations, in which a π-conjugated electron system is closed by σ/π, σ/π overlap. However, the classification given above also shows that many other homoconjugated systems are possible, the question being only which of these many possibilities is of chemical relevance.

B. From a Topological to a Chemical Definition of Homoconjugation

The topological definition of homoconjugation outlined above, although quite useful, does not necessarily say anything about the possible chemical consequences of such a conjugation. If homoconjugation does not lead to any changes in the properties of a molecule that are interesting enough to be investigated, then the classification of the molecules as being homoconjugated is not very useful.

1. The concept of electron or bond delocalization

When homoconjugation leads to electron or bond delocalization, and thereby to a change in the properties of a molecule, homoconjugation becomes chemically relevant. In fact, electrons are always delocalized over the space of a molecule. However, it has turned out that it is extremely useful to consider bonding, lone-pair and inner-shell electrons to be essentially 'localized' in the bond, lone-pair or core region, respectively. This assumption is the basis of the concept of electron or bond localization and reflects the fact that many properties of a molecule can be reproduced in terms of bond or atom contributions. Of course, neither bond localization nor electron localization refers to any observable molecular property. They simply suggest that most molecules behave as if their bonds were localized and that their properties can be reproduced with the help of bond increments. With the concept of bond localization a large body of experimental data on molecular properties can be rationalized, i.e. bond or electron localization is a heuristic concept[13].

Within the concept of bond or electron localization, the meaning of the term electron (de) localization is changed:

Electrons or bonds will be considered to be localized if the properties of the molecule can be explained in terms of bond contributions. If this is not the case, electrons and bonds are considered to be delocalized.

It is clear from this definition that bond (orbital) conjugation is far more common than bond (electron) delocalization. *Conjugation does not always lead to bond delocalization* and, accordingly, it is not correct to use the two terms indiscriminately[13]. It is well known that polyenes are typical examples of double bond conjugation but, as has been demonstrated by Dewar and coworkers[39], their heats of formation as well as other properties can be reproduced by appropriate bond increments. *Thus polyenes are not examples of bond or electron delocalization.*

It is also misleading to consider delocalized π or σ MOs as an indication of bond (electron) delocalization. As canonical MOs are always delocalized, one could localize the MOs and check whether they are all confined to bond regions or whether certain MOs possess long orbital tails outside the bond region. In the latter case, one could anticipate bond delocalization. However, this classification would be wrong since MOs reflect the properties of single electrons. *The concept of bond or electron delocalization is based on the collective properties of all electrons.* Hence, localized MOs with long tails could just indicate π-orbital conjugation and not bond (electron) delocalization.

2. A definition of homoconjugation based on the concept of bond (electron) delocalization

Since conjugation and homoconjugation are parallel concepts, it is logical to base a chemically relevant definition of homoconjugation on the concept of bond (electron) delocalization:

A molecule will be considered to be a homoconjugative system if

(a) *it fulfils the topological requirements of homoconjugation (interruption of a conjugative chain by one or more saturated groups) and*

(b) *if its properties cannot be explained in terms of bond or group contributions of the two separated conjugative systems.*

Homoconjugation thus involves electron and bond delocalization (in the heuristic sense) in the homoconjugative system.

This definition helps to clarify which molecular properties will reflect the homoconjugative character of a system in question. For example, many authors cite ESR hyperfine coupling constants, ionization potentials or calculated orbital energies as indicators for homoconjugation. However, these properties are properties of single electrons that just reflect properties of the orbitals (within the Koopmans approximation) such as σ- or π-conjugation that result from the topology of the molecule. For example, it is not appropriate to speak in the case of norbornadiene of no-bond homoconjugation between the two double bonds based on the fact that the photoelectron spectrum of the molecule indicates a splitting between the π-levels as a result of through-space interactions[40]. The splitting simply reflects the tendency of electrons to delocalize (in the quantum mechanical sense of the word) if spatial arrangement and overlap give them this possibility. Therefore, single electron properties such as ionization potentials can confirm homoconjugation only in the topological sense. This may be considered to be a useful confirmation of the topology and (to some extent at least) of the geometry of the molecule. However, they do not say anything about the chemical consequences of homoconjugation as these result from bond (electron) delocalization mediated by through-space interactions or a cyclopropyl bond.

For example, norbornadiene does not possess a stability that is significantly different from that of a diene without any through-space interactions. Its heat of formation can be

fully reproduced by appropriate group contributions[41]. Therefore, norbornadiene is not an example for bond (electron) delocalization but rather of through-space interactions between double bonds.

Clearly, only those properties of potentially homoconjugated systems that are the collective ones of all electrons can be used to meaningfully assess the extent of bond (electron) delocalization. In principle, these can be energy, geometry, dipole moment, polarizability, NMR chemical shifts, diamagnetic susceptibility, etc. In most cases, some form of the molecular energy has been used to assess the extent of bond (electron) delocalization but other molecular properties such as bond length alternation parameters, NMR chemical shifts or diamagnetic susceptibility exaltation values have also been used. Utilizing these properties in connection with suitable reference compounds, the two distance values R_a and R_c in Figure 3 can be fixed. The distance R_a is that distance for which through-space interactions turn into chemically relevant homoconjugative interactions. Similarly, the distance R_c is that distance for which homoconjugative interactions are replaced by normal bond interactions between cyclopropyl ring and neighbouring groups.

3. The choice of appropriate reference compounds.

Since energy is the most important molecular property for a chemist, the following discussion will focus on the energies of homoconjugative systems. Comparable arguments are valid for the other properties that depend on all electrons of the molecule.

Homoconjugation can lead to a bond (electron) delocalization energy, which reveals an excess stability of the system when compared to suitable reference compounds. *The selection of appropriate reference compounds is essential for the definition of homoconjugation.*

The problem of selection of a suitable reference is of course also found for other basic concepts in chemistry such as aromaticity, strain or even the covalent bond[27]. By choosing the wrong reference compound, a concept can become so vague that it distracts one from viewing the few exceptional observations one wants to describe. This may be illustrated by considering for a moment the description of conjugated systems. If one were to use the CC bonds in ethane and ethene as reference bonds for the description of polyenes, each of these larger molecules would show an appreciable bond delocalization energy. Even the higher alkenes such as propene, butene, etc. would have a bond delocalization energy because they contain at least one $C(sp^2)$—$C(sp^3)$ single bond that is more stable than the $C(sp^3)$—$C(sp^3)$ reference bond of ethane. Strictly speaking by using this definition there would only be one normal alkene, namely ethene.

Dewar and coworkers[39] have pointed out that an adequate description of polyenes has to be based on a set of reference molecules and reference bonds that comprises not only a $C(sp^3)$—$C(sp^3)$ bond, but also $C(sp^2)$—$C(sp^3)$, $C(sp^2)$—$C(sp^2)$ reference bonds in order to separate normal cases of bond conjugation from exceptional cases which show bond delocalization. When this extended set of reference bonds is used, polyenes as well as radialenes and many cyclopolyenes are described as normal conjugated π-systems without any significant extra stabilization from bond delocalization[39].

A similar point has been made by Roth and coworkers[41,42] who investigated potentially homoconjugated systems using a modified MM2 force field, MM2ERW. The latter contained as reference bonds not only $C(sp^2)$—$C(sp^3)$, $C(sp^2)$—$C(sp^2)$, etc. bonds needed for the description of polyenes, but also the $C(sp^2)$—C(cyclopropyl) single bond taken from vinylcyclopropane in order to adequately describe cyclopropyl-substituted compounds **17**–**26** listed in Table 1. With this extended set of reference bonds, Roth and coworkers were able to reproduce experimental heats of formation ΔH_f^0 of polyenes and cyclopropyl-substituted molecules with an accuracy of $\pm$ 0.5 kcal mol^{-1}. In particular, calculated and experimental ΔH_f^0 values of cyclopropyl conjugated molecules such as **20**, **21**, **23**, **25** or **26** (Table 1) agree within 0.1 kcal mol^{-1}. If these molecules were to benefit from

TABLE 1. Comparison of experimental and MM2ERW heats of formation ΔH_f^0 (kcal mol^{-1}) for cyclopropyl conjugated molecules[41]

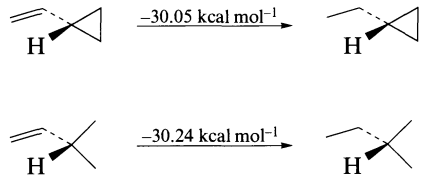
Molecule		ΔH_f^0 (exp)	ΔH_f^0 (MM2ERW)	RE[a]
17		12.7	12.7	0
18		30.9	30.2	0.7
19		44.2	44.4	–0.2
20		30.4	30.4	0
21		48.2	48.7	–0.5
22		9.1	9.2	–0.1
23		37.8	37.8	0
24		0.3	–0.0$_3$	0.3
25		28.9	28.8	0.1
26		56.8	56.9	–0.1

[a]Resonance energies (RE) are all close to zero.

bond (electron) delocalization, ΔH_f^0 (MM2ERW) values (based on the additivity of bond energies) would turn out to be larger than experimental ΔH_f^0 values. The difference between experimental and calculated enthalpies would be the homoconjugative stabilization energy or resonance energy (RE). The reproducibility of experimental ΔH_f^0 values of all the compounds in Table 1 clearly indicates that the degree of cyclopropyl conjugation is similar to that of the reference molecule, vinylcyclopropane. There is no evidence of any special cyclopropyl homoconjugation.

 (4)

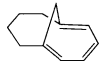
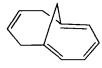
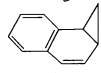
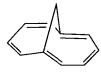
Staley, on the basis of the temperature dependence of the equilibrium in equation 4, has suggested that the stabilization energy resulting from a homoconjugative interaction between a cyclopropyl group and a double bond is 1.1 kcal mol^{-1} [43]. However, this stabilization energy becomes zero when vinylcyclopropane is used as the appropriate reference. This does not mean that π-conjugation vanishes. It simply means that the larger number of homoconjugated systems in a topological point of view is reduced to a smaller number of interesting cases for which homoconjugation leads to exceptional chemical behaviour. Roth and coworkers[41] have underlined this point by noting the similarity of measured heats of hydrogenation of vinylcyclopropane and isopentene (Scheme 6).



SCHEME 6. Heats of hydrogenation of vinylcyclopropane and isopentene[41]

When vinylcyclopropane is used as the key reference compound, the only examples of significant bond (electron) delocalization energies are cyclic homoconjugative systems with potentially aromatic electron ensembles (compare compounds **27–38** in Table 2). For example, norcaradienes **33** and **34** possess small, but significant bond delocalization energies RE of about 3 kcal mol^{-1} (Table 2). Similarly, the RE values of the cycloheptatrienes **30**, **31** and **32** are between 4 and 6 kcal mol^{-1}.

TABLE 2. Resonance energies (RE) obtained from experimental and MM2ERW calculated heats of formation ΔH_f^0 (kcal mol^{-1}) for homoconjugated molecules[41,42]

Molecule		ΔH_f^0 (exp)	ΔH_f^0 (MM2ERW)	RE
27		79.6	69.7	9.9
28		60.0	53.4	6.6
29		50.1	49.7	0.4
30		44.6	48.7	−4.1
31		35.0	39.4	−4.4
32		62.3	68.4	−6.1
33		46.0	49.5	−3.5
34		57.0	60.1	−3.1
35		77.1	94.3	−17.2
36		95.5	101.3	−5.8
37		49.9	51.7	−1.8
38		45.2	44.4	0.8

As the topological definition of homoconjugation is combined with the heuristic concept of bond (electron) delocalization, the concept becomes chemically more relevant since it narrows down the number of possible homoconjugative cases. One result of this more rigorous definition is that homoconjugation without the possibility of cyclic electron delocalization ceases to be an interesting phenomenon. There are hardly any examples of significant homoconjugative bond (electron) delocalization in non-homoaromatic compounds (see the following chapter[3]). In view of this it is not surprising that the terms homoconjugation and homoaromaticity are often incorrectly used as synonyms. Such a usage is inaccurate since homoconjugation is a more general term than homoaromaticity in the same way as conjugation is more general than aromatic conjugation (aromaticity; see Figure 1, Section I).

C. Homoaromaticity and Homoantiaromaticity

Predictions as to the chemical relevance of homoconjugation in the sense of aromatic delocalization of electrons can be made if the topological concept of homoconjugation is connected with an electron count. An electron count can help in suggesting whether a homoconjugative interaction could lead to a change in the stability of the molecule. This is particularly useful if the molecule in question represents a cyclic system that by homoconjugative interactions can form an aromatic or antiaromatic ring system. This is indicated in Figure 5. Homoconjugation connected with an electron count leads to the prediction of potential homoaromaticity, which may or may not be verified by experiment.

Homoaromaticity can be characterized in the same way as homoconjugative interactions by:

(1) the number of interruptions in the conjugated chain,

(2) the nature of the orbital interactions,

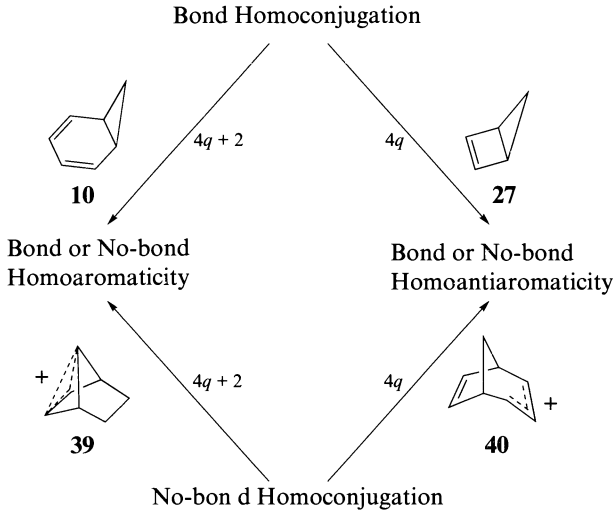


FIGURE 5. From bond and no-bond homoconjugation to bond and no-bond homoaromaticity or homoantiaromaticity. In each case the number of cyclically delocalized electrons ($4q$ or $4q + 2$) is given

(3) the nature of the saturated group X,
(4) the type of orbital overlap,
(5) the nature and type of the interacting groups in the conjugated systems,
(6) the charge and multiplicity of the molecule and
(7) the state of the molecule in which homoconjugative interactions are important.

Hence one can speak of mono-, bis-, tris-homoaromaticity, etc. (1), of bond and no-bond homoaromaticity (2), of cyclopropyl or cyclobutyl homoaromaticity (3), homoaromaticity mediated by π,π-, $\sigma/\pi,\sigma/\pi$- and σ,σ-type overlap (4), homoaromaticity involving heteroatoms, triple bonds etc. (5), neutral, cationic or anionic homoaromaticity as well as radical homoaromaticity (6), homoaromaticity in ground, excited or transition states (7).

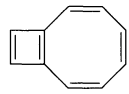
In addition, one can classify homoaromaticity with regard to the number of electrons involved, i.e. 2, 6, 10 or, in general, $4q + 2$ electrons.

Apart from this, it would be appropriate, although never done in practice, to define homoaromaticity with regard to a molecular property (such as energy, geometry, chemical shifts, etc.) in comparison to the reference(s) used. Various molecular properties reflect the special electronic features of homoaromatic systems with different sensitivity. Thus, for example, it is possible that NMR chemical shifts could suggest weak bond (electron) delocalization while an analysis of the molecular energy does not provide any indication of homoaromatic character.

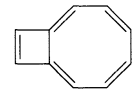
In the case of homoantiaromaticity, characterization is more difficult. Antiaromaticity describes a situation in which electron delocalization leads to destabilization. Clearly, if through-space interactions would close a cyclic system to form an antiaromatic electron ensemble, the molecule would adopt another conformation that would help to avoid antiaromatic electron delocalization. Of course, steric factors may enforce through-space interactions as in **40** (Figure 5). However, simple deformations of the molecule can reduce through-space interactions to an insignificant level.

Formally, no-bond homoantiaromaticity cannot be ruled out. However, *de facto* it will not play any major role in determining the chemistry of $4q$-electron systems.

Similarly, bond homoantiaromaticity may be of little importance. For example, in the case of **27** bond homoconjugation would lead to bond (cyclopropyl) homoantiaromaticity (enforced delocalization of 4 π-electrons). However, it is also possible that homoconjugation could involve the peripheral C—C bonds of the cyclopropyl ring and in this way avoid the formation of an antiaromatic π-electron ensemble and instead form a peripheral aromatic electron ensemble. Cremer and coworkers[27,44], following earlier suggestions by Childs, Winstein and coworkers[45], pointed out this possibility in their investigation of the geometry and electron density distribution of various potentially homoantiaromatic molecules. Their observation is in line with the electronic structure of potentially antiaromatic π-electron systems such as bicyclo[6.2.0]decapentaene, **41**, which avoids the cyclobutadiene structure, **41a**, and instead exists as the peripheral 10-π-electron system **41b**[46].



(41a)



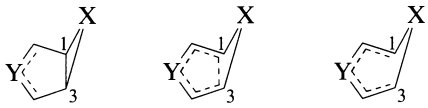
(41b)

There is, however, an important difference between examples **27** and **41**. The later compound forms a Hückel-aromatic orbital system in **41b** while the former compound adopts a Möbius orbital system with $4q + 2$ electrons, i.e. **27** is Möbius antiaromatic although six electrons participate in cyclic delocalization (see Section III. B). This is in line with a destabilizing resonance energy of 9.9 kcal mol^{-1} (Table 2) calculated with the MM2ERW method[41,42].

We conclude that each case of potential bond or, more specifically, cyclopropyl homoantiaromaticity has to be considered separately. Detailed investigations have to clarify whether homoantiaromaticity is of any chemical relevance or whether the molecule has reorganized into a non-homoaromatic electronic structure.

D. Homoconjugation and the Topology of the Potential Energy Surface: From Homoaromaticity to Frozen Transition States

The potentially homoaromatic system **42** can adopt three different structures: **42a**, **42b** and **42c**. The bicyclic structure **42a** corresponds to the situation of bond or cyclopropyl homoconjugation leading to the delocalization of $4q + 2$ electrons and, therefore, to bond or cyclopropyl homoaromaticity. Structure **42c** represents a monocyclic form with weak 1,3-through-space interactions that do not lead to homoconjugation and, accordingly, this structure can be considered to possess an open π-electron system. Finally, structure **42b** corresponds to a no-bond (homoconjugative) homoaromatic system characterized by strong through-space interactions and cyclic electron delocalization.



(42a) **(42b)** **(42c)**

$X = CH_2$, $Y = (CH)_n^q$ $(q = +1, 0, -1)$

In Figure 6, one-dimensional cuts through the PES in the direction of the 1,3-interaction distance R in **42** are shown. Either structures **42a**, **42b**, **42c** or all three of them can occupy stationary points on the potential energy surface (PES) and, according to the topology of the PES, different chemical situations can be distinguished.

Situation 1. A minimum exists only for the bicyclic structure **42a**. The PES may in fact be less steep in the direction of a hypothetical form **42b** because of the possibility of slightly stabilizing through-space interactions.

Situation 2. A minimum exists only for the open from **42c**. The PES may again be less steep in the direction of a hypothetical form **42b** because of the possibility of slightly stabilizing through-space interactions.

Situation 3. There is only a minimum for the non-classical form **42b**. The importance of homoaromaticity is reflected by the curvature of the PES at the minimum **42b** (steepness of the PES).

Situation 4. Two minima exist on the PES which correspond to the classic forms **42a** and **42c**. Interconversion of these forms leads to a transition state, which corresponds to the non-classical form **42b**.

There are further possibilities, namely that **42a**,**b** or **b**,**c** or **a**,**b**,**c** occupy two or three minima on the PES. Although these possibilities cannot be fully excluded, they are not likely since the characteristic interaction distances R are very similar and therefore would imply minima on the PES that are very close to each other. Small geometrical changes would lead from one minimum to the other and, since small geometrical changes normally imply small energy changes, one of the minima may be just a shallow energy well that is chemically not detectable. Hence, for all practical purposes, the possibilities 1 to 4 outlined above would seem to be the most likely.

Situation 1 (**42a**) corresponds to cyclopropyl homoconjugation (cyclopropyl homoaromaticity), the subject of this review article. Situation 2 (**42c**) may be only interesting in

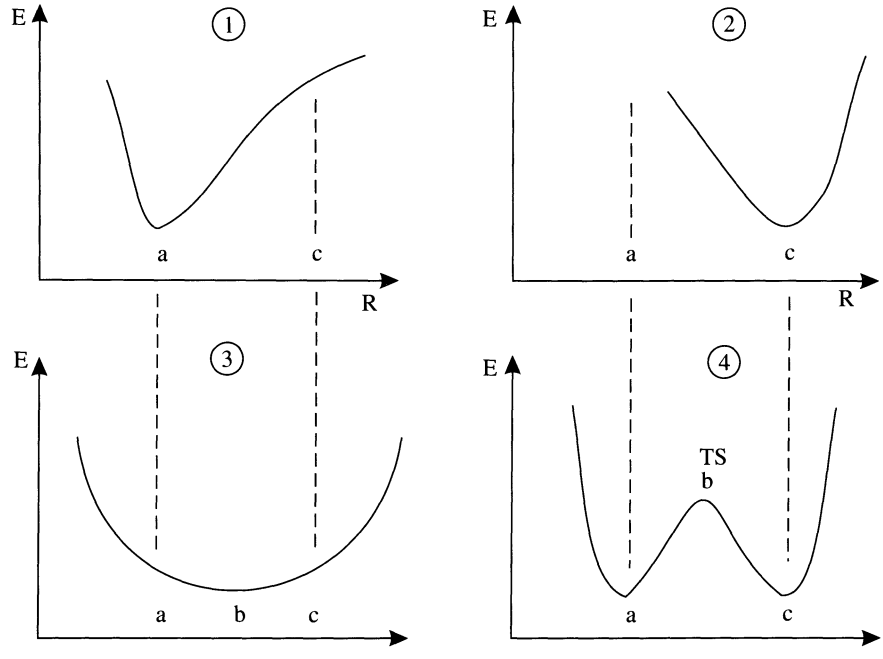


FIGURE 6. One-dimensional representations of the potential energy surface (PES) of molecule **42** shown as a function of the interaction distance *R*. Situation 1 corresponds to the bicyclic molecule **42a**, situation 2 to the open monocyclic molecule **42c**, situation 3 to the no-bond homoaromatic molecule **42b** with non-classical structure and situation 4 to a valence tautomeric equilibrium between **42a** and **42c** with the homoaromatic form **42b** being the transition state. See text

connection with weak through-space interactions while situation 3 (**42b**) represents an example of no-bond homoconjugation and no-bond homoaromaticity.

Situation 4 corresponds to a valence tautomeric rearrangement between the homoconjugative form **42a** and the open monocyclic form **42c** as already discussed in connection with equation 1. The transition state of the rearrangement may be stabilized by no-bond homoconjugation. This has been discussed in various ways using orbital symmetry and electron counting models (see Section II.A)[37,38]. Situation 4 represents an example of an aromatic transition state since, in the terminology of the Dewar–Evans–Zimmermann rules, one cannot distinguish between aromaticity and homoaromaticity (Section II.A). However, as the interaction distances in a transition state are normally outside the range of typical bond lengths, it would be most appropriate to speak in cases corresponding to situation 4 of a homoaromatic or a homoantiaromatic transition state.

It is interesting to consider further the relationship between situations 3 and 4. Situation 3 will be reached if the transition state in 4 is sufficiently stabilized so that its relative energy drops below those of the valence tautomeric forms **42a** and **42c**. In other words, situation 3 corresponds to a *frozen transition state*[47]. *A no-bond homoaromatic compound is simply the realization of a frozen TS.*

This relationship explains some of the fascination that homoaromaticity had, and still has, for chemists. Knowledge about transition states is very important for an understanding of chemical reactions, yet it is the most difficult information to obtain experimentally.

Concepts such as the 'frozen transition state'[47] or the 'frozen reaction path' (Bürgi–Dunitz reaction path)[48] were developed to obtain direct experimental information on transition states. So far, all attempts have failed to realize a frozen transition state experimentally, Cremer and coworkers[49-58] have shown that a no-bond homoaromatic compound (PES situation 3), such as the homotropenylium cation, corresponds to a frozen transition state, and therefore its investigation provides ample information about the properties of transition states.

III. THEORETICAL ASPECTS OF DEFINING, DETECTING AND DESCRIBING HOMOCONJUGATION AND HOMOAROMATICITY

Cyclopropyl homoconjugation can be easily detected and described as long as one retains its topological definition. This also holds to some extent in the case of no-bond homoconjugation. However, as soon as one has to assess the chemical relevance of homoconjugation and to determine a homoconjugative bond (electron) delocalization energy, one needs, as mentioned in Section I, suitable reference compounds for comparison.

The problem of the reference compound is inherent to most chemical concepts[27]. By definition *a suitable reference compound is a compound that possesses the same properties as the target compound with the exception of the electronic and structural features to be investigated.* In most cases, such a compound cannot be found since changes in the (electronic) structure automatically lead to changes in all properties and hinder meaningful comparison. This is the reason why many chemical concepts are discussed at a qualitative rather than a quantitative level. In fact, as has been forcefully described by Binsch, attempts to quantify a concept very often lead to the collapse of the whole concept[59]. This potential collapse-by-quantification problem exists for the concepts of homoconjugation and homoaromaticity just as it does for the concept of aromaticity.

Homoaromaticity as a chemical concept is based on the concepts of aromaticity and homoconjugation. In its simplest form aromaticity is an electron counting concept. Thus if there are $4q + 2$ π-electrons in a planar (or nearly planar) cyclic system, then this is considered to be aromatic*.

At the simplest level (Section I), homoconjugation can be based on a topological footing. At more sophisticated levels, aromaticity as well as homoconjugation are treated as orbital concepts. This means that in the case of homoaromaticity one has to check whether the structure (geometry) and topology of the molecule in question allow through-space overlap to close a cyclic π-system and whether available π-electrons occupy bonding rather than antibonding π-orbitals. If this is the case, a homoaromatic bond (electron) delocalization energy (resonance energy) can result that should reflect the stability of the compound in question. Alternatively, a bond equalization index, diamagnetic susceptibility exaltation or some other property could define the homoaromatic character of the compound. In this way, homoaromaticity is generally easier to describe than homoconjugation as the latter does not necessarily lead to a significant bond (electron) delocalization energy (see above).

The experimental assessment of homoaromaticity is often based on working definitions of homoaromaticity that are influenced by the context of the experimental measurements and available reference data. Such a working definition may be incompatible with other definitions, be limited to a small set of related compounds and frequently be rather vague with regard to a general understanding of homoaromaticity. However, it can be useful to

*This prediction is only correct when the π-electrons fill an aromatic subshell of MOs. As soon as antibonding MOs are filled, aromatic stabilization is no longer guaranteed. Thus, trioxacyclopropane, the cyclic isomer of ozone, possesses 6 π-electrons, but 4 of them occupy antibonding MOs and, therefore, the molecule is relatively unstable.

apply these working definitions of homoaromaticity when research is focused on a limited series of compounds. Difficulties arise as soon as one tries to translate experimental assessments of homoaromatic character so that they comply with a more general quantitative assessment of the phenomenon. Conclusions about homoaromatic character based on some isolated observations can cease to be pertinent within a general concept of homoaromaticity.

In the following, rather than discussing the many definitions of homoconjugation or homoaromaticity that have been expressed by various experimentalists, we compare the few theoretically based attempts to derive a more general definition of homoaromaticity.

A. Winstein's Definition of Homoaromaticity

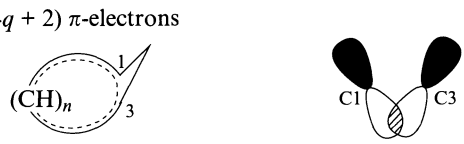
A first basis for the definition of the term homoaromaticity emerges out of Winstein's impressive work[14,15]. Winstein was careful not to restrict homoaromaticity to just those cases where the carbon framework of an aromatic system is interrupted by a single atom bridge but rather generalized the situation to include other possible bridges such as the $-CH_2CH_2-$ group[14,15]. According to Winstein, the key issue is the presence of an appropriate geometry for orbital overlap through-space rather than the number and type of intervening atoms. As for the nature of the interactions through-space, Winstein speaks of 'electron delocalization across intervening carbon atoms'[14,15] when he defines homoconjugation and homoaromaticity in general terms, thus avoiding any specification of the electronic forces leading to homoconjugative interactions. At other places, e.g. when he discusses the norbornenyl cation and related compounds, Winstein speaks of 2-electron 3-centre bonding and the existence of 'partial (homoaromatic) bonds of bond order between 0 and 1'[14,15]. Formulations such as the latter have led various authors to state that a basic requirement of Winstein's definition of homoaromaticity is the existence of 'a 1,3 bond closing the cyclic conjugation'[44].

However, in order to set Winstein's assessment of a homoaromatic bond into the correct context, one has to consider the understanding of chemical bonding at Winstein's time, which was predominantly based on Hückel MO (HMO) theory. Within HMO theory, the definition of a chemical bond is vauge[60]. A chemical bond between neighbouring atoms is imposed by setting a resonance integral for this particular atom,atom interaction to a preselected value. Solution of the HMO equations leads to a matrix of atom,atom interaction indices which are called 'bond orders' irrespective of whether or not they correspond to an interaction for which a resonance integral has been set. In case of no-bond homoconjugative interactions, small 'bond orders' ≥ 0 were calculated which were considered as an indication of a covalent bond. As a result, even for relatively large homoconjugative interaction distances weak 'homoaromatic bonds' were predicted by HMO theory.

In view of the vague knowledge of bonding in the sixties, we consider it more appropriate to stress Winstein's general understanding of homoaromaticity, which covered both bond and no-bond homoaromaticity[14]. Winstein's requirements for homoaromaticity can be listed as follows:

The potentially aromatic system **43** *with* $(4q+2)$ π*-electrons will be homoaromatic if*:

1. *the system is closed by electron delocalization across the homoconjugatively connected atoms,*
2. *the interaction or bond index of the 1,3 link is between 0 and 1,*
3. *orbital overlap of the participating p-AOs at centres 1 and 3 is neither* σ *nor* π *but intermediate between these two (Scheme 7) and*
4. *the* $(4q+2)$ π*-electrons are fully delocalized over the resulting closed cycle, thus leading to net stabilization.*



(43) σ/π overlap

SCHEME 7. σ/π-Overlap in the homoaromatic hydrocarbon **43**

Setting out the requirements for homoaromaticity in this manner, it should be easy to distinguish homoaromatic from non-homoaromatic molecules. Clearly, an appropriate geometry or structure of the species in question is required. This pertains not only to the appropriate placement of the AOs at the homoconjugative centres but also to the structural changes associated with the cyclic delocalization of $(4q + 2)$ π-electrons. This cyclic delocalization should also be reflected by the stability of the system and its spectroscopic properties, including in particular its NMR spectrum.

Although Winstein's definition set the basis for an understanding of the phenomenon, neither experimental nor theoretical tools were available at his time to quantitatively assess the chemical consequences of homoaromaticity or to clearly distinguish between homoaromatic molecules and molecules with normal cyclopropyl–substituent interactions or molecules that experience just some weak through-space interactions. Even today, a detailed definition of geometric and electronic requirements for homoaromaticity is still outside the possibilities of a modern theory of homoconjugation. This becomes particularly clear when considering Winstein's requirement of a homoaromatic net stabilization energy (point 4). Throughout Winstein's early work he repeatedly stressed delocalization energy and stability of homoaromatic systems[14,15]. However, the homoaromatic stabilization energy is much smaller in magnitude and even more difficult to define than the aromatic stabilization energy. Hence, even modern theory has its problems when it comes to puffing substance into the basic requirement of homoaromaticity as formulated by Winstein. We will show this in the following by considering the various steps that have been taken in the last 25 years to obtain a more quantitative assessment of homoconjugation and homoaromaticity.

B. Description of Homoconjugative Interactions in Terms of Orbital Overlap

Various authors have tried to define overlap values S at which through-space interactions may lead to homoconjugative interactions[61]. Although S can be related to resonance integrals and bond energies[62], it is in general not possible to give a specific value of S for any atom–atom interaction at which bonding starts. Similarly, it is difficult to define on the basis of overlap values a generally applicable rule that predicts the change from weak through-space interactions to homoconjugative (or homoaromatic) through-space interactions. Nevertheless, a serious attempt has been made to develop at least a working condition for the description of homoaromatic CC interactions. This involves an assessment of π,π overlap in a situation where a molecule is distorted from planarity and considerable mixing between σ- and π-orbitals occurs.

Haddon solved this issue by employing a π-orbital axis vector (POAV) analysis in which the orientation of a pπ-orbital is determined with regard to the σ-bonds and to neighbouring pπ-orbitals in a conjugated system[63]. The POAV is perpendicular in the case of a planar π-system but has to be approximated by POAV1 or POAV2 for a non-planar π-system. In the first case (POAV1) the POAV is assumed to form equal angles to the three σ-bonds at the same atom, while in the second case (POAV2) it is given by the direction of that hybrid orbital which is orthogonal to the σ-orbitals (see Figure 7).

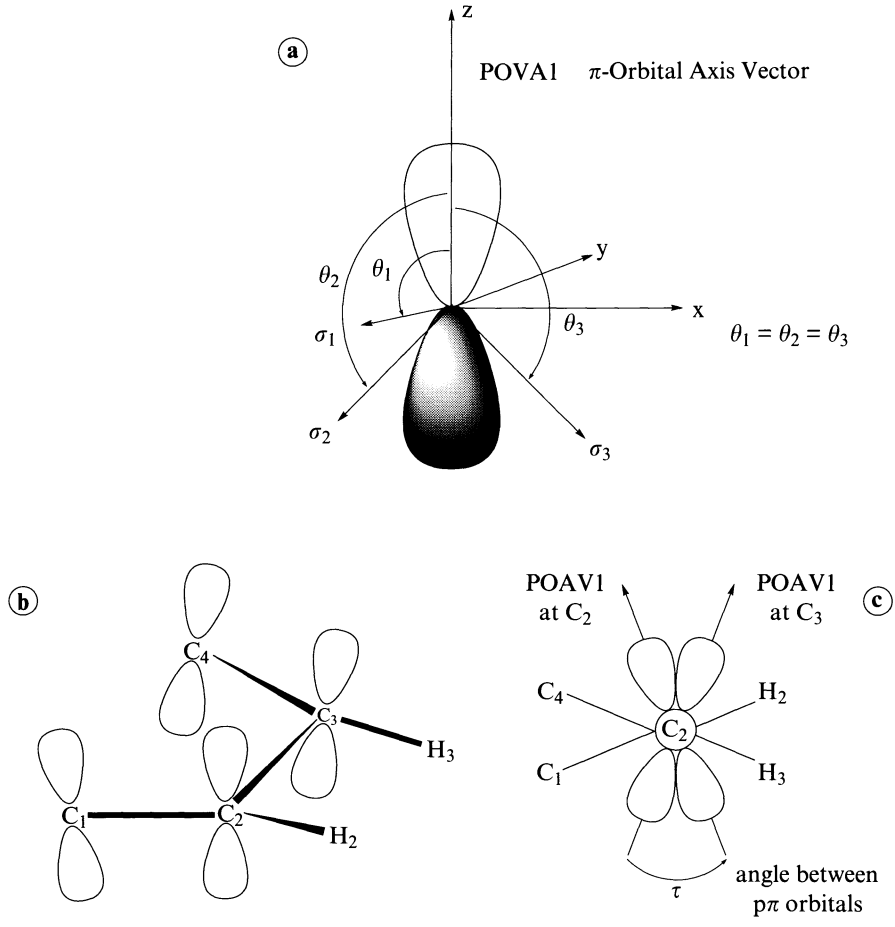


FIGURE 7. (a) Definition of the π-orbital axis vector (POAV1). The angles θ_1, θ_2 and θ_3 between π-orbital and σ-bonds are equal. (b) Part of a distorted π-system. (c) The misalignment between the POAV1 at C2 and that at C3 is measured by the angle τ

On a quantum chemical basis, the latter definition is preferred, although in practice descriptions with either POAV1 or POAV2 are similar. Both definitions re-install the σ–π separability in non-planar systems. However, the π-orbital is now a hybrid orbital rather than a pπ-orbital that is locally orthogonal (POAV2) to the σ-orbitals at the same atom. With the POAV analysis, any misalignment of p-orbitals in non-planar geometries can be determined by the dihedral angle τ between two POAVs (see Figure 7). In addition, the total overlap between the orbitals of two neighbouring atoms in non-planar geometries can be divided into a σ-part (S_σ) and a π-part (S_π).

As a reference value for S_π, Haddon suggested the pπ,pπ overlap integral S^B between nearest neighbours in benzene (R = 1.3964 Å, S_π^B = 0.246) and to define the fractional overlap $\eta = S_\pi/S_\pi^B$. The fractional overlap reflects the degree of pπ,pπ overlap that has developed for a given bond. A π-bond is fully developed for values of η close to 1, while

chemically relevant non-bonded overlap can be expected for smaller η values. A value of $\eta = 0.2$ was taken as a suitable threshold value above which pπ,pπ overlap becomes significant. This value was based on the second-nearest-neighbour overlap integral in benzene ($\eta = 0.14$) and corresponds to about $S = 0.05$[63].

With these definitions, useful descriptions of non-planar π-systems and potentially homoconjugated systems have been developed. The descriptions are particularly attractive to experimentalists because orbital overlap is accepted as a major contributing factor to bonding and it is easy to visualize. Although Haddon did not formally define homoaromaticity in his work[63] one can use his threshold value of S to define homoaromaticity in the following way:

A potentially aromatic system X with $(4q + 2)$ π*-electrons will be homoaromatic if*

1. *the system is closed by a 1,3 homoconjugative interaction with* $\eta = S_{13}/S^B > 0.2$,
2. *the misalignment between the* π*-AOs at centres* 1 *and* 3 *is larger than* $0°$ *but lower than* $90°$ *thus leading to orbital overlap between* σ *and* π *and,*
3. *the* $(4q + 2)$ π*-electrons are fully delocalized in the resulting homoconjugative cycle.*

This definition covers both bond and no-bond homoaromaticity with a clear distinction between the possibility of insignificant through-space interactions with $\eta < 0.2$.

It is interesting to apply this definition, which is a clear improvement over Winstein's original definition of homoaromaticity, to a particular case, namely the homotropenylium cation.

1. The homotropenylium cation as a test case

The homotropenylium cation is the *prima facie* example of homoaromaticity, and therefore any useful definition of homoaromaticity has to cover this example. Haddon has calculated [at the HF/6–31G(d) level of theory using 5 d functions] the PES of the homotropenylium cation as a function of the 1,7 interaction distance by optimizing the geometry of the molecule for fixed values of R (1,7)[64]. The results of his POAV analysis are summarized in Figure 8.

As can be seen from Figure 8, the fractional overlap η remains significant over the whole range of the PES between R (1,7) = 1.6 and 2.6 Å. Using Haddon's definition of homoaromaticity, homoaromatic interactions have already started at 2.6 Å ($\eta = 0.2$) and rapidly develop to a homoaromatic bond with decreasing R (1,7) distance. At the equilibirium distance [R(1,7) = 2 Å, see Section IV.B], $\eta = 0.75$, at R (1,7) = 1.85 Å a C(1)C(7) π-bond comparable to those in benzene seems to be fully developed ($\eta = 1.0$) and for further decrease of C(1)C(7) to 1.6 Å the π-bond becomes similar to that of ethylene in terms of overlap ($\eta = 1.5$). Another feature that indicates homoaromaticity is the equilibration of η values of all ring bonds in bond length regions that correspond to the equilibrium geometry. Finally, the ring (bond) current J of the homotropenylium cation was shown to attain a maximum in the region 1.6 to 1.8 Å at a point close to the equilibrium value of R(1,7)[64].

The description of the homotropenylium ion on the basis of the POAV analysis confirms the homoaromatic character of the cation. However, the analysis suggests in addition some consequences of homoconjugative delocalization, which are difficult to accept. These are:

1. The overlap parameter η suggests homoaromatic delocalization of electrons for a large range of distances (1.6 to 2.6 Å). This is also found for other molecules and, as a result, molecules such as bridged annulenes with interaction distances of 2.4 Å and more are all described as being homoaromatic[63]. The result is that Haddon's overlap-based definition of homoaromaticity becomes as general as the topology-based definition.

2. The results for the homotropenylium cation suggest that CC interaction distances of up to 2 Å and more lead to a homoaromatic bond. This is in agreement with some of

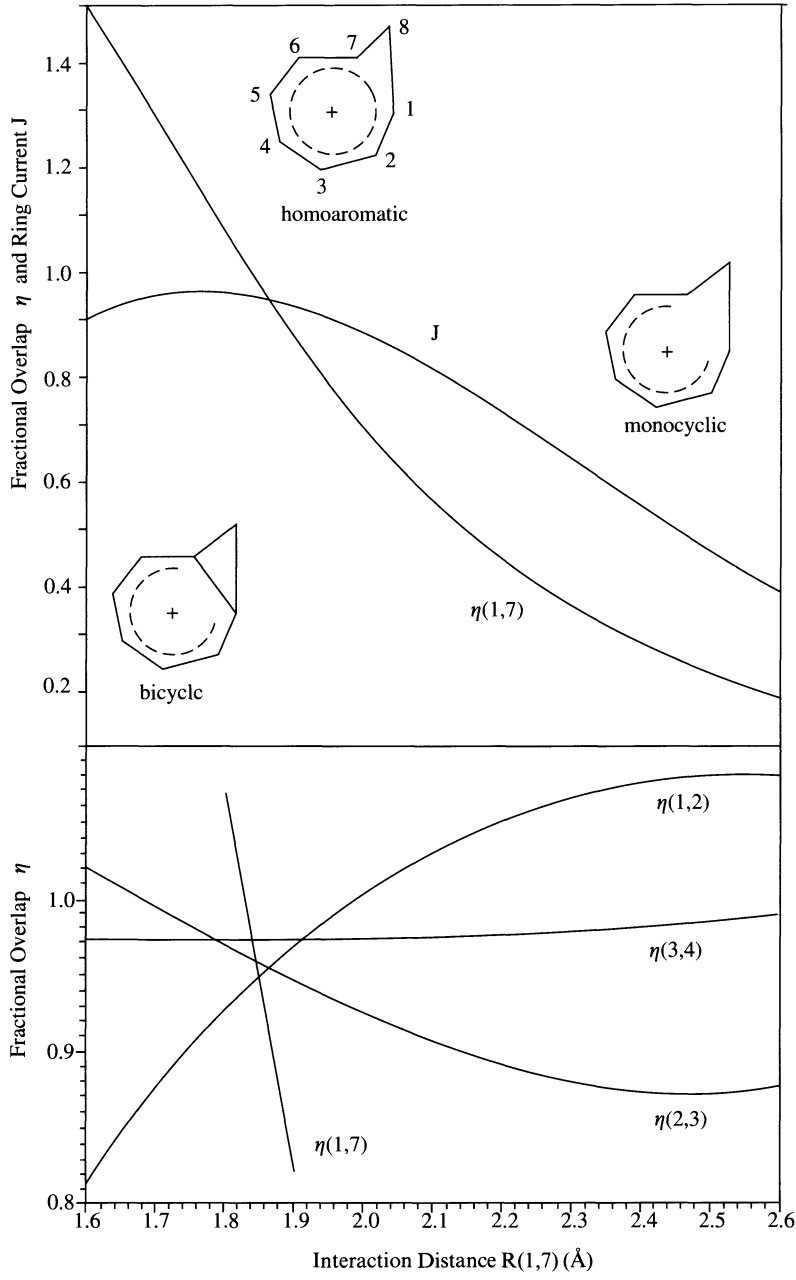


FIGURE 8. Homotropenylium cation. Dependence of ring current J (uncorrected for area) and fractional overlaps η(C1,C7) = η(1,7), η(C1,C2) = η(1,2), η(C2,C3) = η(2,3) and η(C3,C4) = η(3,4) on the 1,7 interaction distance according to 3D-HMO calculations of Haddon[63]

Winstein's predictions, but in clear contradiction to other observations which suggest that CC bonds are dissolved at much shorter distances.

3. In view of the calculated bond lengths for the homotropenylium cation it is difficult to accept that the 1,7 interaction should be the strongest π-bond in the cyclic system[62].

These difficulties seem to stem from the definition of the overlap parameter η. This parameter is based on the next-neighbour pπ,pπ overlap value in benzene according to equation 5:

$$\eta = \{S(s,s) + S(s,p\sigma) + S(p\sigma,p\sigma) + S(p\pi,p\pi)\}/S^{B}(p\pi,p\pi) \quad (5)$$

where the inclusion of $S(s,s) + S(s,p\sigma) + S(p\sigma,p\sigma)$ indicates that the π-orbitals of the POAV analysis always possess an admixture of σ-character in case of non-planar π-systems. For a given $R > 1.3$ Å, $S(p\sigma,p)$ is considerably larger than $S(p\pi,p\pi)$ and, as a result, the overlap parameter is artificially increased with increasing pyramidalization (non-planarity) of the interacting π-centres. This unwanted effect can only be balanced by calibrating η with $S^{B}(s,s)$, $S^{B}(s,p\sigma)$, $S^{B}(p\sigma,p\sigma)$ of benzene weighted according to the appropriate hybridization ratios.

Apart from the definition of η, the fixing of a threshold value for η is arbitrary because it does not combine this value with any observable property of the molecule (energy, geometry, etc.). In addition, the determination of η does not help to distinguish homoconjugated interactions from homoconjugated bonds, i.e. it does not specify point R_b in Figure 3. In summary, the use of fractional overlap values for the description of homoaromatic character is misleading since it exaggerates the magnitude of these interactions.

C. The PMO Description of Homoaromaticity

Early MO descriptions of homoaromatic compounds were based on Hückel MO (HMO) theory. Through-space interactions between interacting C centres were modelled by assuming a value for the resonance integral β. For example, in the case of the homotropenylium cation, Winstein took β (C1,C7) = 0.5 β_0 and obtained a resonance energy comparable to that of the tropenylium cation[14]. He concluded that, despite the insertion of the CH_2 group into the π-system of the tropenylium cation, delocalization of π-electrons is largely retained.

Inclusion of a saturated group into a π-system leads to a perturbation of π-delocalization and therefore a qualitative MO description of homoaromatic compounds is best done on the basis of perturbational MO (PMO) theory[28,65]. Almost at the same time, several researchers independently formualted the PMO description of homoaromatic compounds[66–73]. Haddon showed that stabilization energies resulting from homoaromatic interactions decrease with increasing ring size, which means that increased stability due to homoaromatization will be readily offset by steric and strain effects. Hence, homoaromaticity can only be observed for relatively small rings. Other qualitative insights were gained as to the influence of substituents, a second homoconjugated linkage and ring annelation[68,71].

Hehre[66,69] and independently Jörgensen[72,73] pointed out that the Möbius and Hückel description of homoconjugated molecules (Figure 9) is consistent with the assumed homoaromtic and homoantiaromatic character of these compounds. However, it was also realized that in the general case such a classification might not be sufficient to describe subtle differences in orbital interactions, which determine the homo(anti)aromatic character of a molecule.

With the increasing possibilities of doing semi-empirical or even small basis set *ab initio* calculations on homoconjugated compounds, PMO theory was used both to predict and to rationalize the results of quantum chemical calculations on potentially homoaromatic

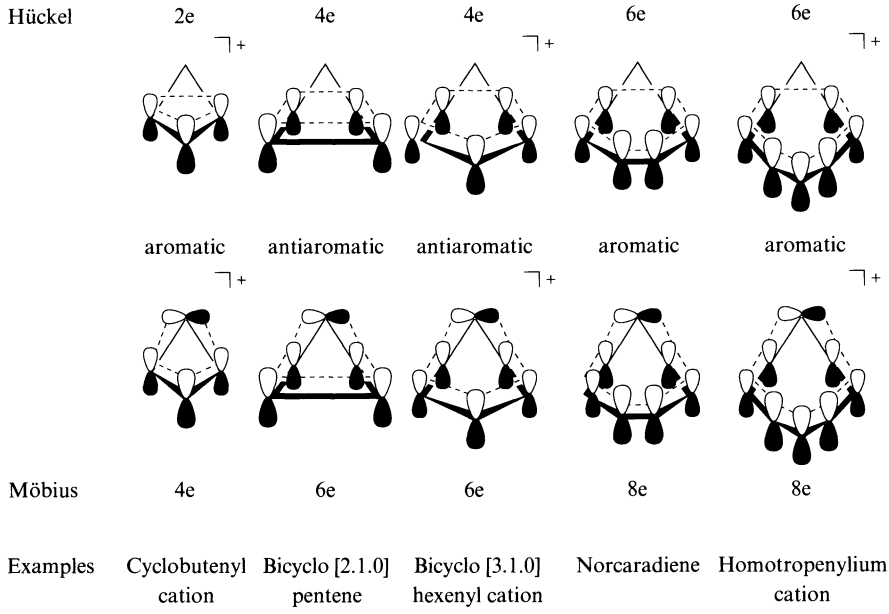


FIGURE 9. Hückel and Möbius orbital systems for homoconjugated molecules. In each case, the number of participating electrons (e) is given and classification according to aromatic or antiaromatic character indicated

molecules[66,69,72,73]. Various ways of dissecting a homoconjugated compound into fragments were considered and the PMO analysis of frontier orbital interactions between the fragments was used to predict the stability of the system in question and to classify the molecule as being homoaromatic or homoantiaromatic. For example, molecules with cyclopropyl homoconjugation were dissected into cyclopropyl and polyene units. For the cyclopropyl unit, bonding and antibonding Walsh MOs (compare with Section III of Chapter 2 of this Volume)[2] were considered, while for the polyene unit π(HOMO) and π(LUMO) were included into the analysis.

As shown in Figure 10 for the cases of bicyclo[2.1.0]pentene and bicyclo[3.1.0]hexenyl cation, four-electron w_S–π(HOMO) or w_A–π(HOMO) interactions are always destabilizing. They are partially or fully balanced by stabilizing two-electron w_A–π(HOMO) or w_S–π(HOMO) interactions, where overlap between interacting orbitals and the difference in orbital energies must be considered to give reliable predictions on whether four-electron destabilizing or two-electron stabilizing effects dominate the relative energy of the compound in question. For example, for bicyclo[2.1.0]pentene the former effect is larger than the latter and, accordingly, the molecule is destabilized and can be considered as homoantiaromatic (see Section II.D). However, for the bicyclo[3.1.0]hexenyl cation, stabilizing two-electron interactions are larger because they involve the much lower-lying π(LUMO) of the allyl cation [compared to π(LUMO) of ethene], and therefore the bicyclo[3.1.0]hexenyl cation might be even slightly stabilized according to PMO theory. Hence the classification of the bicyclo[3.1.0]hexenyl cation as being homoanti- or nonaromatic will be quite problematic if one analyses it just by PMO theory (Figure 10).

Although the PMO analysis becomes increasingly complex for larger systems, some useful predictions can be made from simplified orbital interaction diagrams. For the

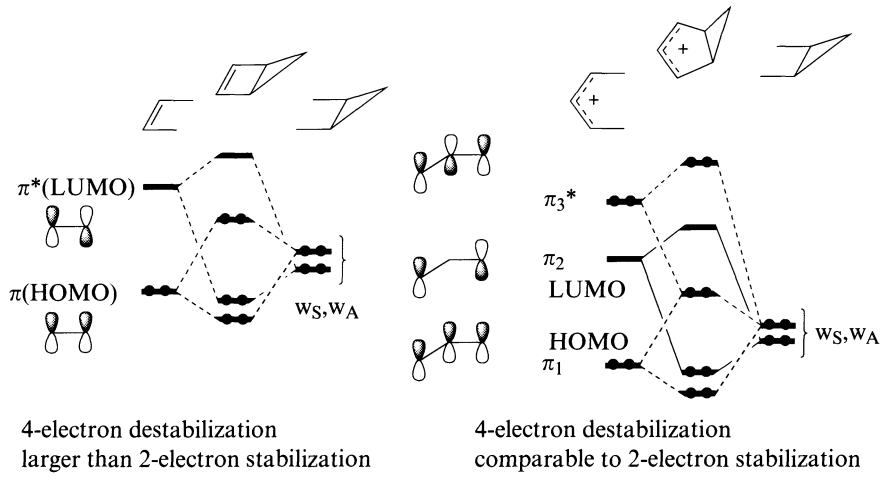


FIGURE 10. PMO interaction diagrams for the frontier orbitals of bicyclo[2.1.0]pentene (left) and bicyclo[3.1.0]hexenyl cation (right) according to Jörgensen[73]. The Walsh orbitals of the cyclopropyl ring are denoted by w_s and w_a, electrons by dots. Compare with Figure 11

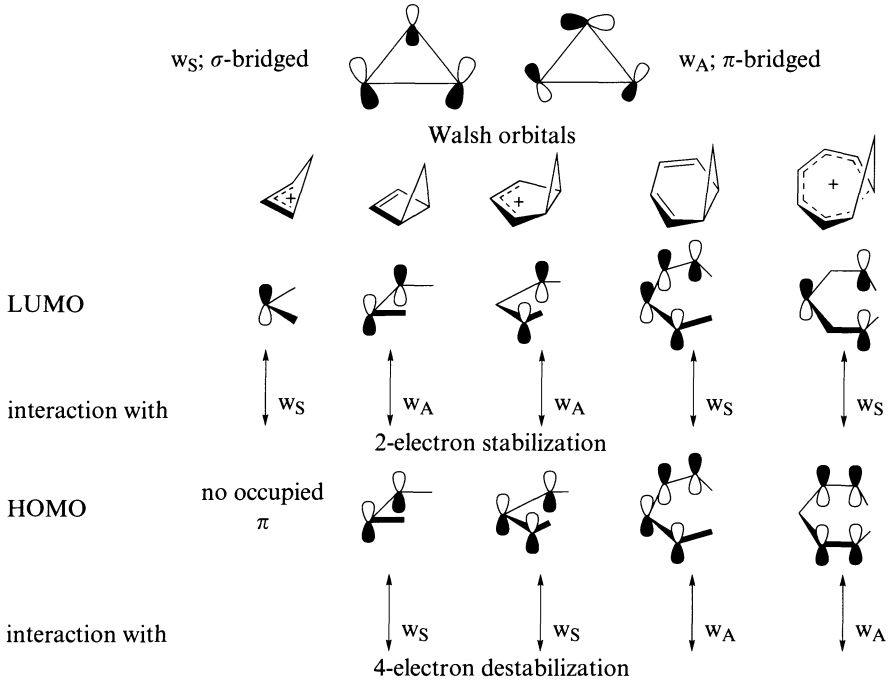


FIGURE 11. Frontier orbital interactions in homoconjugated molecules classified according to stabilizing 2-electron and destabilizing 4-electron interactions (compare with Figure 10)

potentially homoaromatic compounds in Figure 11, Walsh MO w_S is involved in the stabilizing interactions, which means that negative charge is transferred from the fusion bond of cyclopropyl to π(LUMO) of the polyene system. This leads to

(1) a lengthening of the fusion bond,
(2) a delocalization of negative (or positive) charge and
(3) bond equalization in the polyene (note that negative charge is transferred into the C=C antibonding MO of the butadiene unit of norcaradiene; Figure 11).

Also, the bonds between the polyene and the cyclopropyl ring are shortened due to bonding primary overlap between w_S of cyclopropyl and π(LUMO) of the polyene.

If the antibonding Walsh MO is involved in the two-electron stabilizing interactions (bicyclo[2.1.0]pentene and bicyclo[3.1.0]hexenyl cation, Figure 11), then charge transfer to π(LUMO) of the polyene will lead to

(1) lengthening of the cyclopropyl bonds adjacent to the fusion bond,
(2) a shortening of the fusion bond,
(3) delocalization of negative (and positive) charge and
(4) bond equalization in the polyene (note that negative charge is transferred into the C=C antibonding MO of the ethene unit of bicyclo[2.1.0]pentene; Figures 10 and 11).

In summary, PMO theory predicts that two different situations can occur: For the potentially homoaromatic compounds of Figures 10 and 11, electron delocalization takes place in the cyclopolyene part of a formally bicyclic compound. As a result of charge transfer, the fusion bond lengthens and may finally open up so that a formally monocyclic compound with homoaromatic character is formed. The degree of electron delocalization, the exact structure (geometry) and the degree of homoaromaticity depend on the nature of the π(LUMO) of the polyene as well as on strain and steric effects invoked by geometry changes accompanying homoaromatic electron delocalization.

In the potentially homoantiaromatic molecules of Figure 11, electron delocalization occurs along the periphery of a bicyclic system, involving in this way $4q + 2$ rather than $4q$ electrons. Since, however, the corresponding orbital system is of Möbius rather than Hückel type (Figure 9), delocalization of $4q + 2$ electrons leads to overall destabilization rather than stabilization.

Jörgensen[72,73] also applied PMO theory to cyclobutyl-fused analogues of the molecules shown in Figure 11. He observed no significant orbital interactions between the degenerate pair of cyclobutane HOMOs and the π-MOs of the polyene unit in line with observations Haddon had made[68]. Hence, cyclobutyl homoconjugation leading to homoaromaticity was excluded by Jörgensen. In fact, he suggested the use of cyclobutyl-fused molecules as suitable (similarly strained) reference compounds for cyclopropyl homoconjugated molecules with potential homoaromaticity or homoantiaromaticity (see Section III.G)[73].

D. Description of a Homoconjugative Bond by Bond Orders and Other Interaction Indices

It has been always tempting to use bond orders as descriptors for homoconjugative or homoaromatic interactions. For example, PMO theory predicts typical changes in the bond order due to homoconjugative interactions. An increase or decrease of the bond order depends on the number of electrons involved and the dominance of either 2-electron 2-orbital stabilizing or 4-electron 2-orbital destabilizing interactions[28,65,71]. This led Jörgensen suggesting the use of π-bond orders obtained by semi-empirical methods as a gauge for homoaromaticity[72]. A basic problem of this approach is that for both bonding and non-bonding situations, bond orders larger than zero can be obtained. Therefore, it would be appropriate to speak of atom,atom interaction indices and to use the term bond

order only for true bonding situations. However, since no generally applicable criteria are known to define a bond via its bond order, the latter term has to be used indiscriminately for both bonding and non-bonding situations, which of course considerably reduces its value.

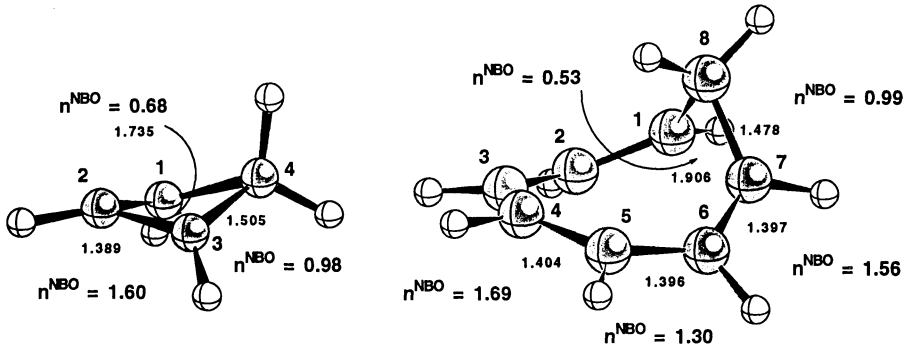
As typical of many other attempts to describe homoconjugative interactions with the help of bond orders, we mention here recent investigations of Williams, Kurtz and Farley[74]. These authors used various semi-empirical methods (MNDO, AM1, MINDO-CI, AM1-CI) to study cycloheptatriene, 1,6-methano[10]annulene, elassovalene and some other potentially homoaromatic compounds. For the 1,6 interactions in cycloheptatriene and 1,6-methano[10]annulene, small bond orders < 0.1 were calculated suggesting the absence of homoconjugative interactions although homoaromatic character is generally accepted in the case of the 1,6-methano[10]annulene. The authors concluded from this that bond orders seem to be of no use as possible discriminators of homoconjugative interactions[74].

As an alternative to using bond orders Williams, Kurtz and Farley suggested using the two-centre energy terms E (AB) (A and B are interacting atoms) that one obtains upon partitioning of semi-empirical NDO energies into mono- and bicentric contributions. This procedure was originally suggested by Fischer and Kollmar[75] and later used by Dewar and Lo[76], who showed that E (AB) provides a measure of bond strength. A negative value of E (AB) implies strong bonding between atoms A and B while positive values indicate destabilizing interactions between A and B. Also, calculated E (AB) values correlate with the corresponding bond lengths R (AB) as has been shown by various authors[76,77].

Williams and coworkers[74] found that E (AB) values, contrary to bond orders, lead to reasonable predictions with regard to the homoconjugative or homoaromatic character of systems such as 1,6-methano[10]annulene or semibullvalene provided the semi-empirical MNDO or AM1 method is connected with limited Configuration Interaction (CI) of the 2×2 or 4×4 type. However, Dewar and Lo[76], who studied various Cope rearrangements with the help of two-centre energies at the MINDO/2 level, found that E (AB) values are actually too large (four times normal bond energies) to provide a reliable measure of bond strength. In the case of CC bonds their zero-point value can be found in the region stretching from 2.2 to 3 Å depending on the semi-empirical method used. Apart from this, energy partitioning into mono- and bicentric terms cannot be extended to *ab initio* methods because of the occurrence of a large number of 3- and 4-centre energy terms which lead to a sizeable contribution to the energy.

In recent years, one has frequently based the analysis of bond orders on natural bond orbitals (NBO) and natural localized MOs (NLMOs)[78]. Calculations of NBO bond orders for homoaromatic systems such as the cyclobutenyl (**44**) or the homotropenylium cation (**45**)[79] lead to significant bond orders of 0.5–0.7 (Figure 12) for the homoconjugative interactions C1,C3 (R = 1.74 Å) and C1,C7 (R = 1.91 Å), respectively, thus supporting Winstein's expectation of partial bonds[14]. Inspection of the NBO bond orders of Figure 12 also reveals that they are strongly alternating along the closed homoaromatic cycles, predicting bond strengths that do not parallel the corresponding small changes in the bond lengths. It seems that *the NBO analysis pushes the homoaromatic system in the direction of a bicyclic structure with considerable bond alternation* rather than the bond equalization caused by homoaromatic electron delocalization (see Section IV.B).

These deficiencies of the NBO analysis in the case of homoconjugated molecules seems to result from two critical steps of the method[78]: (1) Atomic densities are spherically averaged, which means that anisotropies of the atomic densities caused by neighbouring atoms can only be re-introduced by an orthogonalization process. (2) The occupancy-weighted symmetric orthogonalization procedure used in the NBO analysis enforces the best Lewis structure, i.e. it seeks the next classical structure and, accordingly, may not be suited for describing a homoaromatic system with a non-classical structure.



(44) (45)

FIGURE 12. NBO bond orders n^{NBO} of homocyclopropenium (**44**) and homotropenylium cation (**45**) obtained from HF/6-31G(d) calculations[79]. MP2 bond lengths (in Å) are also given[49,56]

A better description of homoaromatic systems is provided by bond orders based on the virial partitioning analysis of the total electron density distribution, which we will discuss in the next section.

E. The Electron Density Based Definition of a Homoconjugative Bond

A more promising attempt to define a homoconjugative bond has been made by Cremer and coworkers[27,44,49–58] on the basis of *ab initio* calculations and the topological analysis of the electron density distribution ρ (**r**)[80]. The distribution ρ (**r**) takes a characteristic form in the case of molecules. At the positions of the nuclei, ρ (**r**) attains maximal values. In the off-nucleus direction, ρ (**r**) decreases exponentially and approaches zero for large **r**. This is different if one considers the region between two nuclei belonging to bonded atoms. In this region, ρ (**r**) adopts fairly large values. *The nuclei are connected by a path of maximum electron density* (*MED path*). Any lateral displacement from the MED path leads to a decrease in ρ (**r**). The position **p** of the minimum of ρ (**r**) along the MED path is a point which can be used to characterize the density distribution in the internuclear region. The position **p** corresponds to a maximum of ρ (**r**) in the directions perpendicular to the path, i.e. it is a first-order saddle point of ρ (**r**) in three dimensions.

Bader and coworkers[81] have shown that the saddle point **p** is fully characterized by the first and second derivatives of ρ (**r**) with regard to **r**: The gradient of ρ (**r**), $\nabla\rho$ (**r**), vanishes at **p** and two of the three eigenvalues (curvatures) λ_i (i = 1,2,3) of the Hessian matrix of ρ (**r**), i.e. the matrix of second derivatives, are negative. The curvatures λ_1 and λ_2 perpendicular to the MED path are negative while the curvature λ_3 along the MED path is positive due to the minimum of ρ (**r**) in this direction.

If one analyses the gradient of ρ (**r**) not only at the point **p** but also at other points in molecular space, then the gradient vector field of ρ (**r**) will be obtained[81]. The gradient vector ρ (**r**) always points in the direction of a maximum increase in ρ (**r**). Thus, each such vector is directed toward some neighbouring point. By calculating $\nabla\rho$ (**r**) at a continuous succession of points, a trajectory of $\nabla\rho$ (**r**), the path traced out by the gradient vector of ρ (**r**), is obtained.

In the gradient vector field of a diatomic molecule AB (or any general molecule), one can distinguish three types of trajectories: First, there are just two trajectories that connect the

nuclei of bonded atoms and the intermediate saddle point and, in this way, define the MED path. Then, there is a class of trajectories which all terminate at the saddle point **p** and form a surface S (AB) perpendicular to the MED path separating the regions of the two bonded atoms. The surface S (AB) is called the zero-flux surface and can be considered as an interatomic surface. Finally, there is a class of trajectories which terminates at the nucleus and forms the basin of the corresponding atom.

Analysis of the electron density distribution ρ (**r**) of numerous molecules has revealed that there exists a one-to-one relation between MED paths, saddle points **p** and interatomic surfaces on the one side and chemical bonds on the other[27,81,82]. However, low-density MED paths can also be found in the case of non-bonding interactions between two molecules in a van der Waals complex[82]. To distinguish covalent bonding fron non-bonded or van der Waals interactions, Cremer and Kraka have given two conditions for the existence of a covalent bond between two atoms A and B[82,83]:

1. *Atoms A and B have to be connected by a MED path.* The existence of a MED path implies a saddle point **p** of the electron density distribution ρ (**r**) as well as a zero-flux surface S (AB) between atoms A and B (necessary condition).

2. *The local energy density H (**p**) is stabilizing*, i.e. it must be smaller than zero (sufficient condition).

The local energy density H (**r**) in the bonding area is defined by equation 6[82,83]:

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) \tag{6}$$

where G (**r**) is a local kinetic energy density and V (**r**) is the local potential energy density. The distribution V (**r**) is always negative while G (**r**) is always positive. If H (**r**) is negative, then the local potential energy density V (**r**) will dominate and an accumulation of electronic charge in the inter-nuclear region will be stabilizing. In this case, the MED path and saddle point **p** correspond to bond path and bond critical point and can be used to characterize the covalent bond[27,82,83].

If H (**r**) is zero or positive in the inter-nuclear region, then there will be closed-shell interactions between the atoms in question, typical of ionic bonding, hydrogen bonding or van der Waals interactions[81].

If one correlates the calculated electron density at the bond critical point **p** and the CC bond distance R for a variety of hydrocarbons, a linear relationship will be obtained which holds for both single, double, triple, aromatic and homoaromatic CC bonds. On the basis of this relationship, a bond order n(CC) has been defined according to equation 7[80,82]:

$$n = \exp\{a[\rho(\mathbf{p}) - b]\} \tag{7}$$

where the constants a and b have been determined by assigning Lewis bond orders of 1, 2 and 3 to ethane, ethene and acetylene.

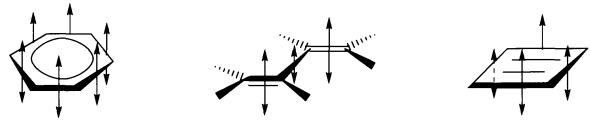
Another insight into the nature of a covalent bond is provided by analysing the anisotropy of the electron density distribution ρ (**r**) at the bond critical point **p**[80]. For the CC double bond, the electron density extends more into space in the direction of the π orbitals than perpendicular to them. This is reflected by the eigenvalues λ_1 and λ_2 of the Hessian matrix, which give the curvatures of ρ (**r**) perpendicular to the bond axis. The ratio λ_1 to λ_2 has been used to define the bond ellipticity ε according to equation 8[80]:

$$\varepsilon = \lambda_1/\lambda_2 - 1 \tag{8}$$

The value of ε is a measure of the anisotropy of ρ (**r**) at **p**. A direction has been assigned to ε, namely the direction of the soft curvature given by the eigen vector associated with λ_2. This direction is called the major axis of λ[80]. It is normally indicated by a double-headed arrow.

Although a distinction between σ and π electrons is no longer appropriate when analysing ρ (**r**), it is nevertheless appealing to relate the bond ellipticity ε to the π *character* of a double bond[80,82].

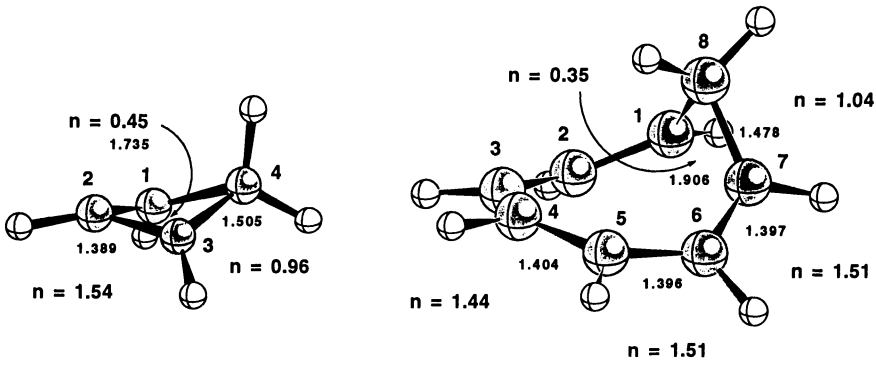
For planar π systems the major axis of ε is always perpendicular to the molecular plane, i.e. all major axes are parallel[27,80]. One can say that the bond ellipticities overlap completely. In the case of benzene the values of ε are all equal, indicating that the π electrons are fully delocalized (see Scheme 8). For conjugated systems such as *trans*-1,3-butadiene and cyclobutadiene, the bond ellipticities of the double bonds propagate to some extent into the formal single bonds, revealing that the latter possess partial π character. The degree of π conjugation can be quantitatively assessed by the calculated n and ε values[27,80,82]. In the same way, the extent of homoconjugation in a molecule is reflected by the calculated values of n and ε[27].



SCHEME 8. Schematic presentation of bond ellipticities in the cases of benzene, 1,3-butadiene and cyclobutadiene. Major axes of bond ellipticities are indicated by double-headed arrows

The Cremer–Kraka criteria for covalent bonding together with calculated bond orders and bond ellipticities have helped in many cases to distinguish covalent bonding from non-covalent, ionic or electrostatic interactions and to characterize covalent bonding in molecules with both classical and non-classical structures[27,84]. They have also been used to distinguish a homoconjugated bond from homoconjugative through-space interactions. In Figure 13, calculated MP2/6-31G(d) bond orders n are given for the homocyclopropenium cation, **44**[56], and the homotropenylium cation, **45**[49], at their equilibrium geometries.

Neither **44** nor **45** possesses a homoaromatic covalent bond between the interacting C atoms and, accordingly, these cations represent examples of no-bond homoconjugation



(**44**) (**45**)

FIGURE 13. Topological CC bond orders n of homocyclopropenium (**44**) and homotropenylium cation (**45**) calculated from the MP2 electron density distribution ρ(**r**) at the bond critical points. Note that n values for C1,C3 of **44** and C1,C7 of **45** correspond to interaction indices. MP2 bond lengths (in Å) are also given[49,56]

and no-bond homoaromaticity[49,56]. Utilizing the calculated electron density at the middle points between the interacting atoms C1, C3 (**44**) and C1, C7 (**45**) in connection with the bond-order equation 6, one obtains homoconjugative interaction indices of 0.45 and 0.35 at interaction distances of 1.74 and 1.91 Å. These values reflect a significant amount of electron delocalization thus leading to an equilibration of bond orders and bond lengths in the homoaromatic ring system, which is particularly nicely reflected by the bond orders of the homotropenylium cation[49]. They range between 1.44 and 1.51, i.e. they take values typical of an aromatic molecule such as benzene[27,80].

F. Description of Homoaromaticity in Terms of the Properties of the Electron Density Distribution

Cremer and coworkers have shown that the analysis of $\rho(\mathbf{r})$ provides a basis for a rigorous definition of homoaromaticity[27,44]. Utilizing the definitions of covalent bonding, bond order, π-character and π-delocalization (Section III.E), they translated Winstein's definition of homoaromaticity[14] (Section III.A) into density language[27,44]:

A cyclic system with $(4q+2)$ *π-electrons will be homoaromatic if*

1. *the system is closed by a 1,3-bond path with a bond critical point* **p** *(C1, C3) and* $H(\mathbf{p}) < 0$;
2. *the bond order n of the 1,3-bond is* $0 < n < 1$,
3. *the π-character of the 1,3-bond as measured by the bond ellipticity ε is larger than that of cyclopropane:* $\varepsilon(C1, C3) > \varepsilon$ *(cyclopropane) and*
4. *the major axis of ε (C1, C3) overlaps effectively with those of the neighbouring bonds.*

This is a quantitative definition of homoaromaticity that is generally applicable and helps to specify exactly the point R_b in Figure 3, at which cyclopropyl homoconjugation starts. However, this definition is much more stringent than Winstein's definition because it excludes all those systems with 1,3-interactions that do not lead to a bond path (no-bond homoaromaticity). Hence, it describes homoaromaticity only for the case of cyclopropyl homoconjugation. For example, Kraka and Cremer have used this approach to describe cyclopropyl homoconjugation in norcaradiene (**10**)[27,54].

Calculated bond orders and bond ellipticities of **10** (Figure 14a) reveal that about 6 π-electrons ($\Sigma n = 7.73$; number of π-electrons $= 2(7.73 - 5) = 5.5$; the C1C6 bond is excluded from the summation of σ-bonds because of the known π-character of cyclopropyl ring bonds, see Chapter 1 of this volume[2]) are delocalized in the six-membered ring. The C1C6 bond is relatively weak ($n = 0.85$) and possesses substantial π-character as indicated by a large ellipticity. π-Electron delocalization leads to a π-character of the formal CC single bonds, which possess ellipticities of 0.12 and 0.13. Hence, norcaradiene is described by the density analysis as a weakly homoaromatic system. This is in line with resonance energy calculations of Roth and coworkers[41,42] on annelated norcaradienes **33** and **34** (Table 2, see Sections II.C and III.G, and also the discussion in the following chapter[3]).

In a similar way, the electronic structure of potentially homoantiaromatic molecule can be investigated. Cremer and coworkers[44] have investigated the bicyclo[2.1.0]pent-2-ene **27** and the bicyclo[3.1.0]hexenyl cation **46** (Figure 14b and 14c), which have been described as being homoantiaromatic[73]. An interaction of the ene or allylic 2π system with the cyclopropane unit, as encountered similarly in norcaradiene, would entail destabilizing 4π electron interactions. However, both **27** and **46** avoid Hückel-homoantiaromatic 4π electron delocalization as is clearly revealed by calculated n and ε values (Figure 14b and 14c). In the case of ion **46**, the properties of the bond C1C3, including its length (1.501 Å[44]), are those of a CC bond in an isolated cyclopropane (see Chapter 1 of this Volume[2]). On the other hand, the two external bonds of the three-membered ring, C1C2 and C2C3, are

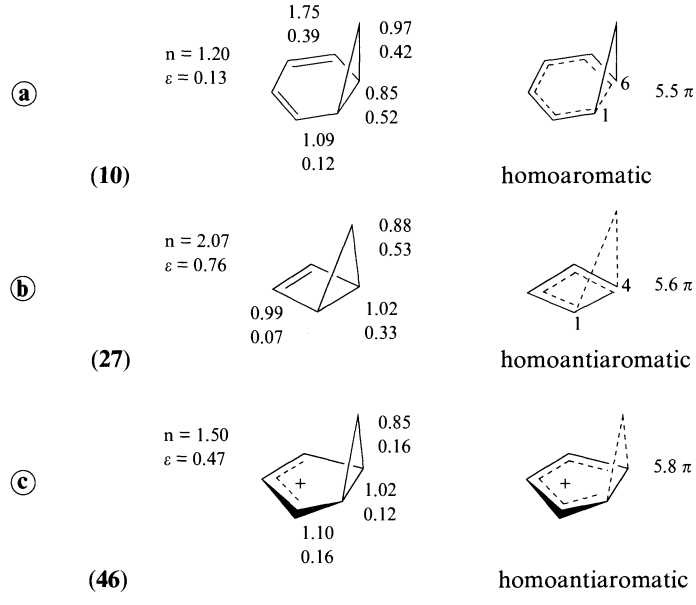


FIGURE 14. CC bond orders n and bond ellipticities ε of cyclopropyl homoconjugated molecules: (a) norcaradiene, (b) bicyclo[2.1.0]pentene, (c) bicyclo[3.1.0]hexenyl cation. On the right, the preferred mode of electron delocalization is indicated by dashed lines. Also given is the number of delocalized electrons as calculated from topological bond orders. See text

lengthened (1.535 Å); they are the weakest bonds in the cation with n being just 0.85. Their ellipticities substantially overlap the ellipticities of the neighbouring bonds in the five-membered ring[44].

The analysis of ρ (**r**) of cation **46** suggests that the ring of the six outer bonds forms a conjugated system. Their bond orders sum to 6.9, equivalent to four single bonds and a π-system of approximately six electrons. The labile character of bonds C1C2 and C2C3 accounts for the perambulatory properties of the cyclopropane ring (see following chapter[3]).

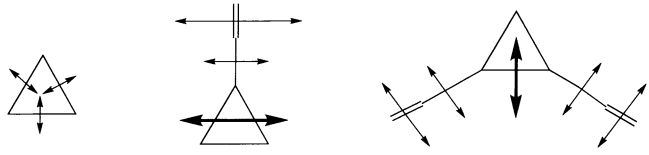
Similar observations can also be made for bicyclo[2.1.0]pent-2-ene (Figure 14b). Again, the external bonds rather than the bridging bond of the three-membered ring are labile as reflected by $n = 0.88$ and $\varepsilon = 0.53$. Approximately six electrons are delocalized on the perimeter of the five-membered ring. Electronic charge is delocalized over the entire surface of the three-membered ring and this surface is conjugated with the π-system of the adjoining ring. The direction of surface delocalization is parallel rather than perpendicular to the bond C1C3, indicating that the latter is excluded from conjugation[27].

Obviously, the density description suggests that homoantiaromatic molecules prefer Möbius $4q + 2$ electron systems rather than Hückel $4q$ systems. This is in line with the PMO analyses of Hehre[66,69] and Jörgensen[72,73] (see Section III.C).

From the electron density analysis it becomes clear that the cyclopropyl group is an electronic chameleon that can adjust to the different electron delocalization situations. Of course the real reason for this flexibility of the cyclopropyl group stems from the phenomenon of surface delocalisation (see Chapter 2 of this volume)[27,85]. The three CC bonds of

the cyclopropyl ring possess considerable π-character as revealed by the bond ellipticities. However, contrary to the ellipticity of an alkene double bond, the directions of the soft curvatures of the ring bonds are not perpendicular but lie in the plane of the carbon nuclei. This means that in the ring plane electron density extends both toward the ring centre and toward the outside of the ring. This is unique for three-membered rings since for cyclobutane and larger rings the bond ellipticities are vanishingly small[85]. The smearing out of electron density in the surface of the three-membered ring has been termed surface delocalization of electrons and stabilization of the cyclopropyl ring has been attributed to this phenomenon[85].

It has also been shown that surface delocalization can adopt a preferential direction if the cyclopropyl group interacts with a π-conjugated system. There are basically two directions of surface delocalization as indicated in Scheme 9 for vinylcyclopropane (**20**) and divinylcyclopropane **47**. In homoaromatic molecules, surface delocalization is perpendicular to the 1,3-bond while in homoantiaromatic molecules it is parallel to the 1,3-bond[27,85].



(**17**) (**20**) (**47**)

SCHEME 9. Schematic presentation of surface delocalization in cyclopropane (**17**), vinylcyclopropane (**20**) and 1,2-divinylcyclopropane (**47**). Major axes of bond ellipticities are indicated by arrows; the direction of surface delocalization in **20** and **47** is given by a bold arrow

An extension of the density description to through-space interactions is in principle possible as shown in Section III.E. For example, for the homocyclotropenylium cation (**45**) a 1,7 homoconjugative interaction index n of 0.35 is calculated. But this does not indicate at what n value homoconjugative interactions cease to play a role, i.e. for which n the point R_a in Figure 3 is reached. For example, planar **45**, for which homoconjugative interactions should be marginally small, still possesses an interaction index $n = 0.21$ ($R = 2.675$ Å)[49] suggesting that homoconjugative interactions become small for n values between 0.2 and 0.3. This example shows that no bond homoconjugation can only be described with the help of the electron density analysis if for each compound investigated a suitable reference molecule is found and a comparison of bond orders and interaction indices is carried out.

Alternatively, one could investigate the Laplace concentration of the electron density, $-\nabla^2\rho$ (**r**), rather than ρ (**r**) itself. The Laplace concentration indicates regions in the molecule in which negative charge concentrates and is depleted[27,82,83,86]. Therefore, it is the correct quantity to reveal changes in the electronic structure due to through-space interactions leading to homoaromaticity.

Figure 15 presents a schematic view of how the atomic subspaces C1, C6 and C11 of 1,6-methano[10]annulene (**35**) change upon an approach of C1 to C6. Bond paths (solid lines between atoms), bond critical points (dots) and the traces of the zero-flux surfaces S(A, B) (perpendicular to bond paths) that separate the atomic subspaces are shown in Figure 15a. Clearly, the subspace C11 extends less and less into the region between C1 and C6 until the surfaces of C1 and C6 coincide and a bond path between C1 and C6 is formed. At the same time, the Laplace concentration between C1 and C6 gradually increases and coverges to the one found for a three-membered ring. As shown in Figure 15b, this change corresponds to the valence tautomerism of the 1,6-methano[10]annulene to bisnorcaradiene[27,54].

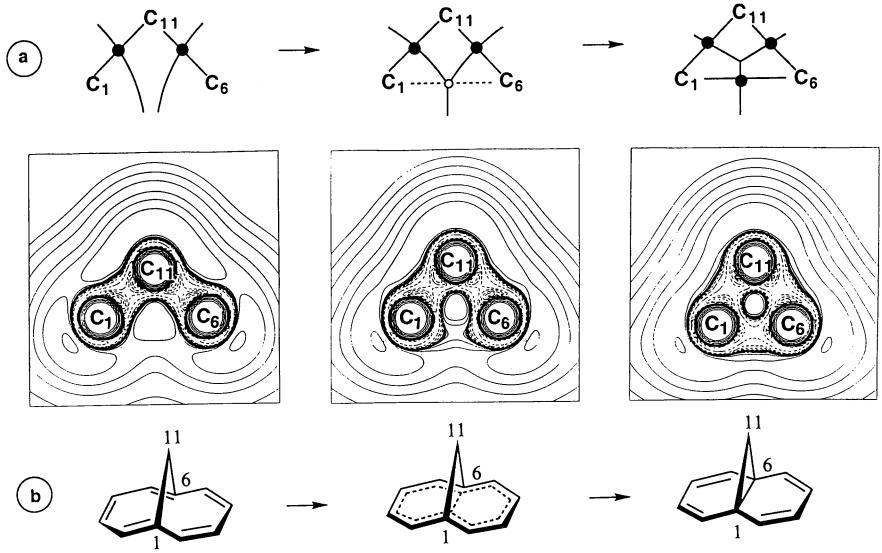


FIGURE 15. Valence tautomerization of 1,6-methano[10]annulene (**35**) to bisnorcaradiene (tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene). (a) Schematic representation of atomic subspaces of C1, C6 and C11 for the three molecular forms shown at the bottom. Solid lines between atoms denote bond paths, dots denote bond critical points and a circle denotes the creation of a bond critical point in the moment of a structural catastrophe[27]. The traces of the zero-flux surfaces that separate the atomic basins of C1, C6 and C11 are given as light solid lines. (b) Contour line diagrams of the Laplace concentration $-\nabla^2\rho(\mathbf{r})$ of the molecular forms shown at the bottom of the figure given for the plane of the nuclei C1, C6 and C11. Dashed contour lines denote concentration of negative charge [$\nabla^2\rho(\mathbf{r}) < 0$] and solid contour lines denote depletion of negative charge [$\nabla^2\rho(\mathbf{r}) > 0$]. HF/6-31G(d,p) calculations[27].

An analysis of the Laplace concentration, $-\nabla^2\rho$ (**r**), yields information about the extent of through-space interactions and the concomitant changes in the molecular properties. Hence, a clear distinction between the various modes of intermolecular interactions should be possible. However, a quantification of these changes again needs an appropriate reference, something which in most cases is not present. Therefore, a description of homoconjugative interactions in terms of the Laplace concentrations has only been applied in selected cases[49–58] but has not been worked out to a more general description of no-bond homoaromaticity.

G. Energy-based Definitions of Homoaromaticity

Energy is certainly the most important property of a molecule. Thus, homoconjugative effects leading to changes in the electronic structure of a molecule should be first assessed by investigating changes in the molecular energy. As with conjugation and aromaticity, determination of a homoconjugative delocalization energy or resonance energy leads to a direct measure and description of homoconjugation. If the homoconjugative delocalization (resonance) energy is negative (< -2 kcal mol^{-1}), one can speak of a homoaromatic stabilization (resonance, delocalization) energy; if it is positive (> 2 kcal mol^{-1}) one can speak of a homoantiaromatic destabilization (resonance, delocalization energy). In this

connection, ± 2 kcal mol^{-1} are used as threshold values above or below which (de) stabilization energies become significant.

Resonance energies can be directly calculated by semi-empirical methods via appropriate energy partitioning provided that the conjugated π-system is planar and all π-bonds are well defined. However, in the case of a non-planar homoconjugative molecule with non-classical atom, atom interactions (through-space or through-bond), this approach is no longer possible and, as a result, early attempts to estimate resonance energies by assuming arbitrary resonance integrals are of no or just qualitative value. Although *ab initio* theory should provide a better basis for a direct calculation of homoconjugative resonance energies, basic problems also exist with this approach, which are discussed in Section III. G. 1. There have been some interesting attempts to determine homoconjugative resonance energies from calculations with model Hamiltonians (Section III.G.2), but again their application has been limited to semi-empirical methods.

As an alternative to the direct calculation of homoaromatic stabilization energies, there is the possibility of describing the stability of homoconjugated compounds by the calculated energies of formal reactions. Two classes of reactions have been used in this connection, namely isodesmic and homodesmotic reactions, both of which involve the use of suitable reference molecules to obtain meaningful stabilization energies. In Section III.G.3 and III.G.4, we will discuss the use of formal reactions in connection with homoconjugated molecules. Finally, in Section III.G.5, we will report on one approach to determining homoconjugative resonance energies that, although based on force-field rather than quantum-chemical calculations, has been quite successful and seems to provide the most reliable resonance energies at this moment, at least for neutral homoconjugated compounds.

1. Direct calculation of homoaromatic stabilization energies

The stabilization of an aromatic molecule is given by its resonance energy RE, which is the energy (or enthalpy) difference between the aromatic system and the corresponding reference system containing localized non-resonating double bonds[4–10]. Since the latter energy is not a measurable quantity, various ways have been suggested to deduce its value from additivity relationships of bond increments taken from suitable reference compounds. The most successful definition of a resonance energy in this connection is the Dewar resonance energy, which is based on the atomization energies of (linear) polyenes as appropriate reference states, i.e. the resonance energies of polyenes are taken to be zero within this approach[39,65]. The advantage of the Dewar resonance energy as a stability measure for aromatic molecules results from the fact that comparison is made with a real conjugated compound with similar bonding features rather than with a hypothetical model compound with non-resonating multiple bonds. In this way, the number of molecules with significant resonance energies is considerably reduced and chemical research focuses on those few cases with really unusual bonding features.

Since the Dewar resonance energy differs from REs derived for a hypothetical reference system with regard to the bond energy ascribed to a C—C single bond, RE values can be normalized by using the RE value of 1,3-butadiene (or appropriate butadiene derivatives) according to equation 9[87]:

$$\mathrm{RE(normalized)} = \mathrm{RE} - k\,\mathrm{RE(1,3\text{-}butadiene)} \tag{9}$$

where k is the number of C—C single bonds in the reference state.

A direct calculation of RE for planar conjugated compounds using *ab initio* theory is possible, as has been demonstrated by Kollmar[87]. Calculations comprise the following steps:

(a) A model wave function, in which the SCF π-MOs are replaced by strictly localized π-MOs representing non-resonating multiple bonds, has to be determined.

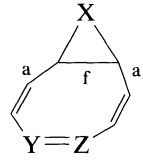
(b) Since the geometry of the non-resonating π-system is not the same as that for the resonating π–system, the geometry of the reference state with the model wave function has to be optimized.

(c) Energy comparison between the model reference state and original π-system leads to the determination of vertical (geometry frozen at equilibrium values of the original π-system) and adiabatic (optimized geometries used in both cases) RE values.

(d) RE values are normalized according to equation 9[87].

Using this procedure and correlation-corrected *ab initio* methods, reasonable resonance energies can be obtained for planar aromatic (or antiaromatic) compounds[87]. However, there are basic problems in extending this approach to homoaromatic molecules. As a result of the non-planarity of most homoaromatic compounds there is considerable σ–π mixing. The determination of a model wave function with non-resonating double bonds is not trivial. It will require extensive re-optimization of the σ-MOs because localization of the π-MOs leads to different σ–π mixing. The optimal geometry of the reference state will differ much more from that of the target system as in the case of planar aromatic systems. In view of these difficulties, it is not surprising that a direct calculation of RE of an homoaromatic molecule by *ab initio* methods has not so far been reported.

In addition, there is also the question of how to use suitable reference molecules to obtain normalized RE values which correspond to Dewar resonance energies. In the case of cyclopropyl homoconjugation, butadiene is clearly the wrong reference molecule to consider the two C—C single bonds *a* adjacent to the fusion bond *f* (see Scheme 10). The



SCHEME 10. Description of fusion bond *f* and single bonds *a*

appropriate reference molecule would be vinylcyclopropane, and therefore normalization can only be achieved by determining and using the RE value of vinylcyclopropane according to equation 10:

$$\text{RE(normalized)} = \text{RE} - (k\text{-}2)\,\text{RE(butadiene)} - 2\,\text{RE(vinylcyclopropane)} \qquad (10)$$

in the case of a monohomoaromatic compound. (For bis-, tris- or multihomoaromatic systems, methylcyclopropylcarbinyl cation, bicyclopropyl and other reference molecules can become important to set up appropriate normalization equations.) Apart from this, one has to consider a problem that is already inherent in the calculation of RE(normalized) for aromatic compounds, but does not become obvious immediately. The appropriate butadiene conformation to be used in the normalization process should be the *cis* form rather than the *trans* form (see discussion in Section II.C). For homoaromatic molecules, one has to use the RE values of distorted butadiene and vinylcyclopropane forms in order to mimic exactly the conformation of the target compound. Although this problem could be solved, it is not clear to which extent steric interactions, e.g. in the *cis* forms, might spoil results since they will be different for target and reference molecules. Much more research is needed in this direction to find out whether RE values can also be obtained for homoconjugated molecules with aromatic or antiaromatic electron ensembles.

2. Homoaromatic stabilization energies from calculations with a model Hamiltonian

An elegant alternative to the direct calculation of RE values is based on the following consideration. If an impenetrable wall is built between the interacting centres of a homoconjugated molecule, a model system will be obtained that should be identical to the original molecule with regard to strain, hyperconjugative, inductive, etc. effects, but should differ in energy because of the absence of homoconjugation. Hence, the difference in molecular energies should be a direct measure of the homoaromatic or homoantiaromatic resonance energy.

This approach is quite suitable for semi-empirical NDO methods. The impenetrable wall can be simulated by defining a model Hamiltonian which does not contain any interactions between atoms separated by the wall. Within NDO theory, this goal is simply achieved by setting all resonance integrals of the Fock matrix that would lead to interactions through the wall equal to zero[88]. The difference between original energy and the energy obtained for the impenetrable wall model leads to the interaction energy in question, e.g. a homoaromatic stabilization energy. In this way, conjugative and hyperconjugative effects can be studied. Schweig and coworkers[89,90] have used this approach to describe conjugation in a number of cyclopolyenes with heteroatoms. Wirth and Bauld[91] have used the same approach to study homoaromaticity in the case of the cyclobutenyl cation and related ions. However, a systematic extension of this approach to homoaromatic systems in general has never been carried out. This may be due to the fact that at the NDO level of theory confusing results were obtained. For example, homoaromatic stabilization energies were predicted to be larger in planar (30 kcal mol^{-1}) than puckered cyclobutenyl cation (6.5 kcal mol^{-1}). The larger stability of the latter form could only be explained by invoking nonclassical σ-delocalization effects[91].

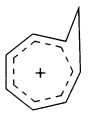
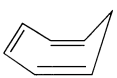
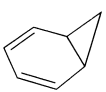
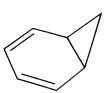
Apart from these confusing predictions, a verification of semi-empirical results by *ab initio* calculations is not possible because the dropping of certain Fock matrix elements should be accompanied by the dropping of the corresponding overlap matrix elements which leads to singularities in the overlap matrix. Weinhold and coworkers[78] have suggested an alternative approach based on localized MOs, but this approach can only be applied for the investigation of hyperconjugative effects.

3. Evaluation of homoaromatic stabilization energies by using isodesmic reactions

An isodesmic reaction[92] is a formal reaction, in which the number of electron pairs as well as formal chemical bond types are conserved while the relationships among the bonds are altered. A subclass of the isodesmic reactions is the class of bond separation energies, in which all formal bonds of a molecule are separated into two-heavy-atom molecules containing the same type of bonds. Stoichiometric balance is achieved for the bond separation energies by adding an appropriate number of one-heavy-atom hydrides to the left side of the reaction[92].

In Scheme 11, isodesmic bond separation reactions for homotropenylium cation (**45**), cycloheptatriene (**30**) and norcaradiene (**10**) are given together with calculated HF/3-21G reaction energies[93]. The latter comprise ring strain, inductive and hyperconjugative effects beside homoconjugative effects. Barzaghi and Gatti[93] have compared the isodesmic bond separation energies with those of suitable reference compounds to estimate homoconjugative stabilization effects (see Scheme 11). From the comparison of **45** with **47** (reactions 12 and 11) and **30** with **48** (reactions 14 and 13), they concluded that **45** and **30** retain 68% and 43%, respectively, of the resonance energy of the parent compounds i.e. tropylium cation and benzene while **10** is already slightly destabilized showing no homoaromaticity[93].

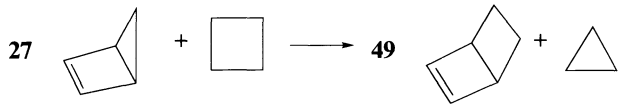
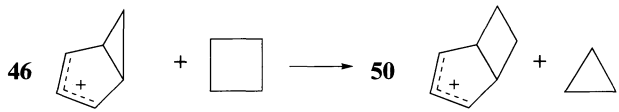
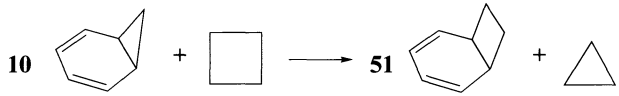
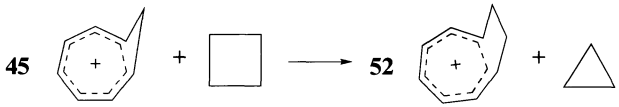
These results are contrary to all other observations and calculations. They reflect the danger of a careless use of bond separation reactions in connection with homoconjugated

Isodesmic bond separation reaction			Calculated ΔE	Reaction
47		$+ 6\,CH_4 + CH_3^+ \longrightarrow 2\,CH_3CH_3 + 2\,CH_3CH_2^+ + 3\,CH_2{=}CH_2$	80	(11)
45		$+ 7\,CH_4 + CH_3^+ \longrightarrow 3\,CH_3CH_3 + 2\,CH_3CH_2^+ + 3\,CH_2{=}CH_2$	55	(12)
48		$+ 6\,CH_4 \longrightarrow 3\,CH_3CH_3 + 3\,CH_2{=}CH_2$	60	(13)
30		$+ 7\,CH_4 \longrightarrow 4\,CH_3CH_3 + 3\,CH_2{=}CH_2$	26	(14)
10		$+ 9\,CH_4 \longrightarrow 6\,CH_3CH_3 + 2\,CH_2{=}CH_2$	−5	(15)
10		$+ CH_2{=}CH_2 + 2\,CH_4 \longrightarrow$  $+ 2\,CH_3CH_3$	−31	(16)

SCHEME 11. Isodesmic bond separation energies (kcal mol^{-1}) calculated at the HF/3-21G level[93]

molecules. Clearly, the molecules compared in Scheme 11 differ with regard to both strain, inductive and hyperconjugative effects and therefore are far from being suited for a comparison of (homo)conjugative resonance energies. For example, the large difference in the bond separation energies of **30** and **10** simply results from the fact that the conversion of ethene + 2 CH_4 into two ethane molecules (see reaction 16) is exothermic by 21 kcal mol^{-1}. Since the actual energy difference between **30** and **10** is wrongly predicted by HF/3-21 G to be 10 kcal mol^{-1} [93], a misleading reaction energy of −31 kcal mol^{-1} is obtained for the formal reaction 16 in Scheme 11, thus suggesting a large destabilization of norcaradiene **10**.

The stabilization energies obtained from isodesmic reaction energies become only useful if differences in strain, inductive, hyperconjugative or other effects are known. A possible solution to this problem has been suggested by Jörgensen[73], who investigated the cyclobutyl analogues to cyclopropyl homoconjugated molecules. He found that the cyclobutyl group does not participate in homoconjugation. Since the strain energies of cyclobutane and cyclopropane are similar[94], it is likely that strain energies in cyclopropyl homoconjugated molecules and in their cyclobutyl analogues are also similar. Therefore, the latter are the ideal reference compounds to determine homoaromatic resonance energies in cyclopropyl homoconjugated systems.

Isodesmic reaction	Calculated ΔE	Reaction
	−5.5; −14.1	(17)
	1.4; −5.5	(18)
	6.8; 4.2	(19)
	14.4; 16.3	(20)

SCHEME 12. Isodesmic reactions based on cyclobutyl derivatives **49**–**52**. Reaction energies from MINDO/3 (first entry) and EHT calculations (second entry) in kcal mol^{-1} [73]

Energies for reactions 17 to 20 have been calculated by Jörgensen at the MINDO/3 and EHT level of theory[73]. They suggest that the potentially homoantiaromatic electron systems **27** and **46** are destabilized leading to exothermic reaction energies (the positive MINDO/3 value of **46** is probably a consequence of neglect of differential overlap[73]) while the potentially homoaromatic molecules **10** and **45** are stabilized leading to endothermic reaction energies. However, a caveat is also necessary in this case. A slight variation of the reactions in Scheme 12 by using also the saturated analogues of **10**, **27**, **45**, **46** and **49**–**52** as suitable reference compounds led to conflicting results as for the homo(anti)aromatic character of the target compounds. Jörgensen[73] attributed this to deficiencies of the

semi-empirical methods used, but also possible are significant differences in the strain energies of the bicyclic molecules used as references.

4. Evaluation of homoaromatic stabilization energies by using homodesmotic reactions

A homodesmotic reaction is a formal reaction, for which extraneous energy contributions arising from changes in hybridization and A—H bonding are minimized by keeping equal numbers of each type of A(sp^m) B(sp^n) bond and each type of A(sp^m) H_k group in reactants and products. The concept of homodesmotic reactions was developed by George and coworkers[95] and used to calculate resonance energies of π-systems and strain energies of cyclic compounds with considerable success[95,96]. In selected cases, it has also been used to calculate homoaromatic stabilization energies.

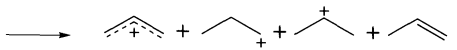
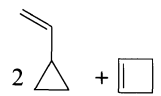
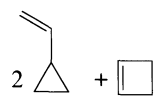
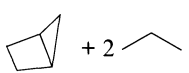
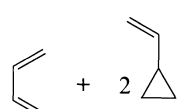
In Scheme 13, homodesmotic reaction energies are given for compounds **27**, **10** and **44**. Reaction 21 indicates that the homocyclopropenium cation is actually destabilized by 42 kcal mol^{-1} according to MP4 (SDTQ)/6–311G(d,p) calculations of Sieber and coworkers[56]. The major part of this destabilization energy is due to ring strain diminished by homoconjugative and hyperconjugative stabilization energies. Since the latter may be small [the CH_2 group is located in the nodal plane of the π(LUMO) of the allyl system] and the former are reduced in planar cyclobutenyl cation, the ring strain energy can be estimated by using planar **44** in equation 21 rather than the more stable puckered form. This leads to a ring strain energy of 50 kcal mol^{-1} and, accordingly, to an estimate of the homoaromatic delocalization energy of 8 kcal mol^{-1}, which is identical with the barrier of ring inversion[56].

Homodesmotic reactions have to be based on appropriate reference compounds to be suitable for the calculation of homoconjugative resonance energies. They may also be extended to balance strain and other effects on both sides of the formal reaction as is demonstrated in equations 22–24 of Scheme 13. Suitable reference molecules for homoconjugative compounds **27** and **10** are vinylcyclopropane and 1,3-butadiene. However, relating **27** to vinylcyclopropane (equation 22, Scheme 13) leads to a homoconjugative destabilization energy of 44 kcal mol^{-1}, which is contaminated by the strain energy of the cyclobutene ring of **27** (29.2 kcal mol^{-1}). When correcting for ring strain by extending equation 22 to 23, a homoconjugative destabilization energy of 14.8 kcal mol^{-1} results. This value still contains the strain energy caused by annelation of a cyclobutene ring to a cyclopropane ring which can be estimated by the homodesmotic reaction splitting bicyclo[2.1.0]pentane into cyclobutane and cyclopropane. In this way, the corrected homodesmotic reaction 24 is obtained, which provides an improved balance of ring strain energies. According to equation 24, the homoconjugative destabilization energy (resonance energy) of **27** is 11.7 kcal mol^{-1}.

A final correction is needed because the vinylcyclopropane units in **27** or **10** do not adopt the stable *trans* forms but less stable *gauche* forms. This leads to a reduction of the homoconjugative resonance energy by another 2 kcal mol^{-1}. The final resonance energy is 9.7 kcal mol^{-1}, clearly indicating the homoantiaromatic character of **27**.

In the case of **10**, the strain of the six-membered ring is small, as is the strain energy due to ring annelation. Utilizing heats of formations for *cis*-1,3-butadiene, *gauche*-vinylcyclopropane[41,97] and norcaradiene[54], a homoaromatic stabilization energy of 4 kcal mol^{-1} is calculated in line with a description of **10** as a cyclopropyl homoaromatic 6π electron system.

The derivation of the resonance energies for **27** and **10** reveals that (a) homodesmotic reactions are well suited to compensate for the different electronic effects that hinder the calculation of pure homoconjugated resonance energies, (b) use of a homodesmotic reaction such as 24 requires the inclusion of many reference compounds, which of course can lead to considerable error progression in the calculated reaction energy, and (c) the

Homodesmotic reaction	Calculated ΔE Reaction	
44  $+ C_2H_6 + 2C_2H_5^+ + C_2H_4$ 	–42	(21)
27  +  $+ C_2H_4$ 	–44.0	(22)
27  +  + 2  + 2   $+ 3C_2H_6$	–14.8	(23)
27  +  + 2 + 2  + 2  		
 $+ 2C_2H_6$	–11.7	(24)
corrected:	–9.7	
10  $+ 2C_2H_4$ 	3.8	(25)

SCHEME 13. Homodesmotic reaction energies according to *ab initio* data for **44**[56] and **10**[54] and experimental heats of formation for **27**[97] in kcal mol^{-1}

calculation is necessarily based on assumptions. For example, if annelation of a cyclobutene ring with a cyclopropane ring leads to a considerably larger strain increase than that calculated for the annelation of a cyclobutane ring with cyclopropane in the case of bicyclo[2.1.0]pentane, then the value of the resonance energy will be overestimated severely.

5. *Homoconjugative resonance energies from force field calculations*

Roth and coworkers[41,42] have chosen carefully recalibrated force fields to predict reliable heats of formation with errors intended by the authors to be as small as ± 0.5 kcal mol^{-1}. They started with the MM2 force field of Allinger[98] and added to this parameters for the C(sp^2)—C(sp^2) and the C(cyclopropyl)—C(sp^2) single bonds of reference compounds such as substituted 1,3-butadienes and vinylcyclopropanes[41]. Particular care was given to the correct description of the torsion potential of the reference compounds. The modified MM2 force field (MM2ERW) developed by Roth and coworkers describes polyenes and cyclopolyenes in terms of localized bond structures without any reference to quantum chemical methods such as the Pariser–Parr–Pople (PPP) approach (see Section II.C)[41].

Because of the additional calibration, the MM2ERW force field leads to heats of formation of conjugated polyenes or conjugated systems containing the cyclopropyl group in close agreement with experimental heats of formation (see Table 1 in Section II.C). With 1,3-butadiene and vinylcyclopropane as reference compounds, none of these molecules possesses any extra stabilization. This, however, is different for the potentially homoconjugated molecules listed in Table 2 of Section II.C.

MM2ERW force field calculations lead to heats of formations for cycloheptatriene (**30**), the bridged cycloheptatrienes **31** and **32** and the norcaradienes **33** and **34** which are 3–6 kcal mol^{-1} larger than the experimental values, thus suggesting a homoaromatic resonance (electron delocalization) energy (RE) of this magnitude. Although calculated RE values are rather small, they reflect the expected trends depending on the magnitude of overlap between the interacting centres. Thus, planar cycloheptatriene **29** does not benefit from any homoaromatic electron delocalization because of the negligible overlap between parallel pπ orbitals at C1 and C6. Similarly, the large interaction distances in cyclononatriene **38** (R = 2.45 Å) reduces the stabilization energy to a negligible amount. Molecules **27** and **28** with the unfavourable Möbius 6-electron ensembles are destabilized by 9.9 and 6.6 kcal mol^{-1} [41,42] in line with PMO predictions (Section III.C) and RE values based on homodesmotic reaction energies (Section III.G.4).

The homoaromatic RE values in Table 2 cannot directly be related to aromatic REs normally cited in the literature. This becomes obvious when considering MM2ERW REs of aromatic compounds: they are all larger than REs derived from experimental heats of formation with the help of homodesmotic reaction energies. For example, the RE value of benzene is calculated to be 25.9 kcal mol^{-1} [41] while the accepted homodesmotic RE value is 21.6 ± 1.5 kcal mol^{-1} (relative to 1,3-butadiene)[96]. Deviations of up to 20 kcal mol^{-1} and more are obtained for aromatic compounds such as naphthalene (MM2ERW: 40.1; accepted: 30.3 ± 2.6 kcal mol^{-1}), anthracene (MM2ERW: 51.5; accepted: 36.6 ± 5 kcal mol^{-1}), pyrene (MM2ERW: 68.6; accepted: 53.6 ± 5.9 kcal mol^{-1}), phenanthrene (MM2ERW: 58.6; accepted: 43 ± 5 kcal mol^{-1}) or tetracene (MM2ERW: 67.5; accepted: 47.4 ± 6.6 kcal mol^{-1}), where the difference compared to the corresponding homodesmotic REs increases with the number of annelated benzene rings[41,96].

These deviations are the result of the fact that the MM2ERW force field makes explicit use of the rotational potential of 1,3-butadiene. Thus, *cis*-1,3-butadiene is used as the appropriate reference conformation of butadiene for benzene and other aromatic molecules. The *cis* form of butadiene is about 3.5 kcal mol^{-1} higher in energy than the *trans* form,

of which about 2 kcal mol^{-1} may be due to steric interactions and about 1.4 kcal mol^{-1} to a decrease in electron delocalization (as a result of approaching the unfavourable cyclobutadiene form)[41]. Since *cis*-butadiene is contained three times in benzene, the resonance energy of benzene taken relative to *cis*-butadiene is 4.2 kcal mol^{-1} higher than the value normally given relative to *trans*-butadiene. Similar considerations apply to naphthalene, anthracene, etc. for which, in addition to *cis*- and *trans*-butadiene, various methylated butadienes have been used as a reference. While it is easy to renormalize the REs of Roth and coworkers to *trans*-butadienes, the REs of Roth are reasonable since they are based on reference systems that agree better with the actual target molecules than the reference systems normally used in the literature.

In the case of homoconjugated molecules, similar considerations have to be made when comparing MM2ERW REs with RE values based on different reference molecules or reference conformations. Since the MM2ERW values correspond to the actual conformation taken by vinylcyclopropane or 1,3-butadiene in the homoconjugative molecule, their magnitude is 3–4 kcal mol^{-1} larger in the case of a potential 6π electron system. Inspection of Table 2 (Section II.C) reveals that this is about the magnitude of the MM2ERW RE values of potentially homoaromatic molecules such as cycloheptatrienes **30**, **31**, **32** and norcaradienes **33**, **34**. Accordingly, descriptions based on the calculation of homodesmotic reaction energies, that use *trans*-vinylcyclopropane and *trans*-butadiene as references, get in these cases no or vanishingly small homoaromatic REs. *This explains some of the confusion, which has accompanied the discussion as to whether molecules such as cycloheptatriene or norcaradiene are homoaromatic*[4–10,27].

It remains to be questioned whether one should not use in general Roth's approach of picking both the right reference molecule and the right reference conformation[41,42]. In principle, this should be possible since, for molecules such as butadiene or vinylcyclopropane, the full rotational potentials have been carefully investigated by both experimental means and *ab initio* methods. On the other hand, using *cis* forms as appropriate reference conformations leads to an artificial increase of homoaromatic REs. The destabilization of a *cis* form results not only from unfavourable π-electron interactions (e.g. by through-space formation of an antiaromatic 4π-system) but also from destabilizing steric interactions not present in the target compound. Because of σ–π mixing in non-planar conformers, it is difficult to separate steric and delocalization effects for any arbitrary conformation of the reference system. However, if one disregards steric effects, calculated homoaromatic stabilization energies will contain, beside the electron delocalization effect, a small but significant steric stabilization energy, which has nothing to do with the concept of homoconjugation.

IV. *AB INITIO* EXAMINATIONS OF HOMOCONJUGATION

The *ab initio* investigation of homoconjugated molecules in general and cyclopropyl homoconjugated molecules in particular is not trivial, and requires a careful choice of method, basis set and level of geometry optimization. In addition methods for calculating other molecular properties such as charge distribution, NMR chemical shifts, magnetic susceptibility and susceptibility exaltations, vibrational spectra, etc. have to be carefully selected, which is beyond the level of routine work in quantum chemistry. Therefore, we will discuss in Section IV.A the basic requirements for a reliable *ab initio* description of homoconjugated molecules. In Section IV.B, we will describe the *ab initio* investigation of the homotropenylium cation to demonstrate practical aspects of *ab initio* calculations on homoaromatic compounds and to show how *ab initio* theory can lead to a more complete picture of homoconjugation and homoaromaticity. Finally, in Section IV.C, we will take steps toward a more general definition of homoaromaticity based on the results of *ab initio* calculations.

A. Basic Requirements

In the seventies and eighties, *ab initio* calculations on potentially homoaromatic molecules were preferentially carried out with the Hartree–Fock (HF) method using minimal or double-zeta (DZ) basis sets. However, neither HF nor small basis sets are appropriate to describe a homoaromatic system. In the case of cyclopropyl homoconjugation, the use of a DZ + P basis set is mandatory since polarization (P) functions are needed to describe the bond arrangements of a three-membered ring.

If one wants to scan the whole region of bond and no-bond homoconjugative structures, even a DZ + P basis set may not be sufficient. Through-space interactions at distances of 2–3 Å are mediated by diffuse density distributions in the tail region of the wave function. Accordingly, the valence region and the tail region of the wave function have to be described in a balanced way. This is not possible by using one of the energy-optimized standard basis sets. The basis set has to include diffuse functions that lead to a correct account of diffuse density distributions. Various recipes are nowadays available to add diffuse functions to standard DZ + P basis sets[99].

The problem of selecting the correct basis set becomes simpler when cationic molecules have to be investigated. The positive charge leads to a contraction of orbitals and wave function, and therefore a correct description of the tail region is no longer that important. In this case, a standard DZ + P basis set may already lead to reasonable results for positively charged homoaromatic molecules. However, such a basis will definitely be too small if no-bond homoaromatic anions are investigated. This has to be considered when evaluating the reliability of the many HF/small basis set calculations from the seventies and eighties.

A major calculational problem is the correct description of bond equalization and bond alternation in conjugated systems. HF theory exaggerated bond alternation by making formal double bonds too short and formal single bonds too long. This trend is enhanced by the use of larger basis sets, which indicates that only a correlation-corrected method can compensate for these deficiencies. Promising results have been obtained with second-order Møller–Plesset (MP2) perturbation theory, which may be considered as one of the simplest correlation-corrected *ab initio* methods nowadays available[100].

If a molecule with no-bond homoaromaticity is investigated, the system in question possesses a non-classical structure with an interaction distance typical of a transition state rather than a closed-shell equilibrium structure. One can consider no-bond homoconjugative interactions as a result of extreme bond stretching and the formation of a singlet biradical, i.e. a low-spin open-shell system. Normally such a situation can only be handled by a multi-determinant description, but in the case of a homoaromatic compound the two single electrons interact with adjacent π-electrons and form together a delocalized electron system, which can be described by a single determinant *ab initio* method provided sufficient dynamic electron correlation is covered by the method.

MP2 theory, which includes all doubly excited configurations (pair correlation effects) but neglects any coupling between these excitations, is the right method to describe non-classical structures and stretched bond situations[101,102]. But it also exaggerates their stability and therefore leads to an imbalance between classical bicyclic structures and non-classical homoaromatic structures. It is a typical experience with HF and MP2 calculations of potentially homoaromatic molecules that the former method predicts the classical bicyclic or open structure while the latter method predicts the non-classical homoaromatic structure to be more stable (see Sections II.D and IV.B). In general, one can say that MP2 results should be closer to reality than HF results, in particular with regard to calculated geometries and the assessment of bond equalization in conjugated molecules. However, to get reliable stabilization energies one certainly has to go beyond MP2 calculations. This is particularly true when the energy difference between bicyclic and a potential no-bond homoaromatic form is relatively small, which is quite often the case[49–58].

Extension to third-order MP (MP3) theory[103] normally leads to a decrease of homoaromatic stabilization energies because at the MP3 level the coupling between double excitations is included and, accordingly, an overestimation of dynamic pair correlation effects is partially reduced. Although MP3 is more accurate than MP2, it is quite unattractive for *ab initio* investigations since it just corrects the correlation effects introduced at the MP2 level without including any new correlation effects. These are introduced at the fourth-order MP (MP4) level[104] in the form of single (S), double (D), triple (T) and quadruple (Q) excitation effects. MP4(SDQ) already provides an important correction with regard to MP2 homoaromatic stabilization energies. S excitations lead to orbital relaxation effects and Q excitations cover pair, pair correlation effects. The overestimation of the stability of structures with stretched bonds is largely corrected by a coupling of D with Q excitations[101,102]. Hence, MP4(SDQ) represents a relatively inexpensive correlation method for homoaromatic systems that may not be described correctly by MP2.

T excitation effects have turned out to be essential for an accurate description of non–classical systems. Although the contribution of a single T excitation to the correlation energy is rather small, the large number of T excitations leads to sizeable effects, which must not be neglected if very accurate homoaromatic stabilization energies are desired. However, with MP4, there is the danger that T effects are overestimated since TT as well as ST, DT and QT coupling effects enter perturbation theory not before fifth-order MP (MP5)[105,106]. In general, it is a disadvantage of any MPn description that calculated molecular properties oscillate between even-order and odd-order results, since the former introduce new correlation effects while the latter just install the coupling between the new correlation effects[101,102,106]. This means that at one order of perturbation theory one fuels the 'perturbation engine', while in the next order one pushes the 'break' thus causing an oscillatory approach to the true value of the property calculated. Relative energies and geometries oscillate very often between MP1 (= HF) and MP2 values and, in critical cases, it is difficult to predict at what level oscillations are dampened out[106].

One can avoid these problems by using Coupled Cluster (CC) theory[107], which contains infinite-order effects and therefore does not lead to the oscillatory behaviour of properties calculated with MPn[108]. Homoaromatic stabilization energies have been calculated for smaller molecules with CCSD(T) or QCISD(T)[54,56]. These are CC methods, which cover S and D excitations and, in addition, include T effects in a perturbational way[109,110]. They represent some of the most accurate single determinant *ab initio* methods available today that can be applied in a routine way.

There have been just a few investigations of homoaromatic molcules with other than HF, MP or CC methods. Therefore, it is justified to concentrate on the latter and refrain from a lengthy discussion as to how GVB, MCSCF, Cl, MRD-Cl, etc. might lead to a reasonable account of homoconjugative interactions.

Apart from the choice of method and basis set, the geometry optimization of a homoaromatic compound is an essential factor. The optimization of all geometrical parameters is a must for all state-of-the-art *ab initio* calculations. Use of experimental, semiempirical or standard geometries will lead to relatively large errors in the calculated energies. Similarly, one has to warn against the use of *ab initio* results based on partial geometry optimizations or HF/small basis set optimized geometries. Reliable are geometries obtained at the HF/DZ + P, MP2/DZ + P or any higher level of theory[49–58].

Another criterion for the reliability of *ab initio* data is the testing of the character of calculated stationary points by vibrational frequencies. These reveal whether the calculated geometry corresponds to a minimum point on the PES (all eigen values of the Hessian matrix of second derivatives are positive), a first-order saddle point (one eigen value is negative, i.e. one gets one imaginary frequency) or any higher-order saddle point with two, three, etc. negative eigen values. In addition, calculated frequencies are needed for

calculating zero-point energy and other vibrational corrections to relative energies, which can be quite important.

Apart from energy and geometry, calculation of the charge distribution in a potentially homoaromatic molecule is very informative. This can be done by the Mulliken population or the NBO/NLMO analysis[78]. In this way, gross atomic charges are obtained, which reflect localization or delocalization of electrons in the molecule. Similar information is obtained from bond orders and bond ellipticities, which are results of the topological analysis of the electron density distribution[80–84]. The latter is based on the virial partitioning of the total electron density distribution[81]. Virial partitioning leads to the most complete and certainly most reliable analysis of electron density features. As described in Section III.E and III.F, one obtains bond orders, π-character, etc. at very low computational cost. In addition, atomic charges and other atomic properties can be determined, although this requires expensive numerical integration.

In the last ten years, NMR chemical shift calculations have become a most valuable asset to *ab initio* descriptions of molecules. This development was triggered by the work of Kutzelnigg and Schindler on the IGLO (Individual Gauge for Localized Orbitals) method[111], which made it possible to calculate reliable relative chemical shifts for rather large molecules in an efficient way. Beside the IGLO method, several other *ab initio* methods are available today for routine calculations of magnetic properties of molecules: (1) The LORG (localized orbital/local origin) method by Hansen and Bouman[112]; (2) GIAO-HF in the version of Pulay and coworkers[113]; (3) GIAO-MP2, GIAO-MP3 and GIAO-MP4 (SDQ) by Gauss to calculate correlation-corrected NMR chemical shifts with second-, third- and fourth-order many-body perturbation theory[114]; (4) MC-IGLO by Kutzelnigg and coworkers for problems that require a MCSCF wave function[115].

The use of *ab initio* methods for the calculation of NMR chemical shifts was pushed forward by Schleyer and his coworkers in collaboration with the Kutzelnigg group or other groups[116]. The success of this research tremendously increased the acceptance of *ab initio* results in general and *ab initio* NMR results in particular among experimentally working chemists.

Calculations with IGLO, LORG or GIAO have led to a wealth of NMR chemical shift data and to a new dimension in the cooperation between quantum chemists and experimentalists as is amply documented in the literature[111–116]. Beside energies and geometries, quantum chemists can nowadays offer experimentalists detailed NMR chemical shift data which provide a direct link between theory and experiment, so that calculated energies and geometries become more meaningful for the experimentalist. NMR chemical shift calculations have not only been used to describe the magnetic properties of molecules but also to identify unknown compounds by comparison of experimental and theoretical shift values, to determine equilibrium geometries, to investigate conformational changes, to elucidate the mechanism of molecular rearrangements, to determine solvent effects on NMR data, to identify complexation or coordination of solute molecules by solvent molecules, to detect electronic structure changes caused by the medium and to describe chemical bonding, to mention just some of the many possibilities that have opened to quantum chemists[111–116].

This is the background for using NMR chemical shifts in *ab initio* studies on potentially homoaromatic compounds. Very often these compounds have been generated as labile intermediates in solutions of super acids and therefore no other molecular properties than NMR data are available. In this situation, the calculation of NMR chemical shifts provides the only bridge from theory to experiment. It leads to a determination of relative energy, geometry and other properties of the molecule as will be described in Section IV.B. Reliable values in the case of relative ^{13}C chemical shifts can already be obtained with a DZ + P basis at the IGLO level although more accurate values require basis sets of TZ + P quality[111].

With the available *ab initio* methods, one can also calculate infrared, Raman and ultraviolet spectra as well as many other molecular properties. However, none of these properties has been used extensively in investigations of homoaromatic compounds and therefore we refrain from discussing basic requirements in calculating them by *ab initio* methods.

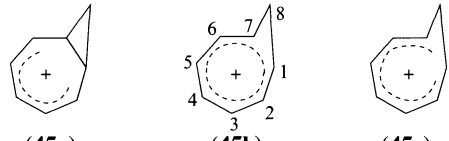
B. Investigation of the Homotropenylium Cation

In the following, we will discuss *ab initio* descriptions of the prototype of homoaromatic molecules, namely the homotropenylium cation (**45**). Theoretical work on this cation reflects all the problems involved in an *ab initio* investigation of homoaromatic compounds[44,49,53,56,64,69,73,79,93,117–119].

1. *Ab initio calculations of geometry and energy*

Experimental measurements of the geometry of cation **45** have not been possible so far. There is just indirect information on the molecular geometry coming from NMR data, UV measurements or other sources[120]. Direct information on the geometry of **45** is only provided by quantum chemical calculations (see also the discussion in the following chapter[3]).

In line with the discussion given in Section II.E, three different structures are possible (Scheme 14), namely a classical bicyclic structure **45a** that can benefit from cyclopropyl homoconjugation, then a classical monocyclic open structure **45c**, that should possess normal conjugation of a cyclopolyene, and finally a non-classical no-bond homoaromatic structure **45b** with a cyclic 6π electron system formed by 1,7 through-space interactions.



(45a) **(45b)** **(45c)**

SCHEME 14. Possible structures of the homotropenylium cation

HF/STO-3G as well as semi-empirical calculations predict for **45** the bicyclic structure **45a** while HF/6–31 G(d) calculations suggest the open structure **45c**[44,49,64,68,69,93,117]. X-ray structure determinations of substituted homotropenylium cations make the situation even more confusing for deciding the correct geometry for the parent cation[121,122]. For example, 2-hydroxy-**45** was found to possess a relatively short 1,7 distance in line with the bicyclic structure **45a**[121] while 1-ethoxy-**45** has a 1,7 distance of 2.4 Å in line with the open structure **45c** (see also the discussion in the following chapter[3])[122].

To clarify the structural problem of **45**, it is of advantage to calculate the PES in the direction of the 1,7 interaction. This is done by selecting fixed values of R(1,7) between 1.5 and 2.5 Å and optimizing the molecular geometry for each chosen R(1,7) value. Normally, HF/DZ + P or MP2/DZ + P provide a reasonable description of geometrical parameters depending on the interaction distance, although the latter itself may not be described well because of reasons discussed in Section IV.A. As soon as a number of trial geometries is generated, their relative energies can be tested by various methods to find the true shape of the PES in the direction of the interaction distance. This procedure has been used by Cremer and coworkers to investigate homoconjugative interactions in a number of potentially homoaromatic molecules[49–58]. In the following section it is described for cation **45**.

The HF/6–31 G(d) PES in the direction of the 1,7 interaction distance is shown in Figure 16 which, because of the deficiencies of the HF approach, predicts the global minimum of

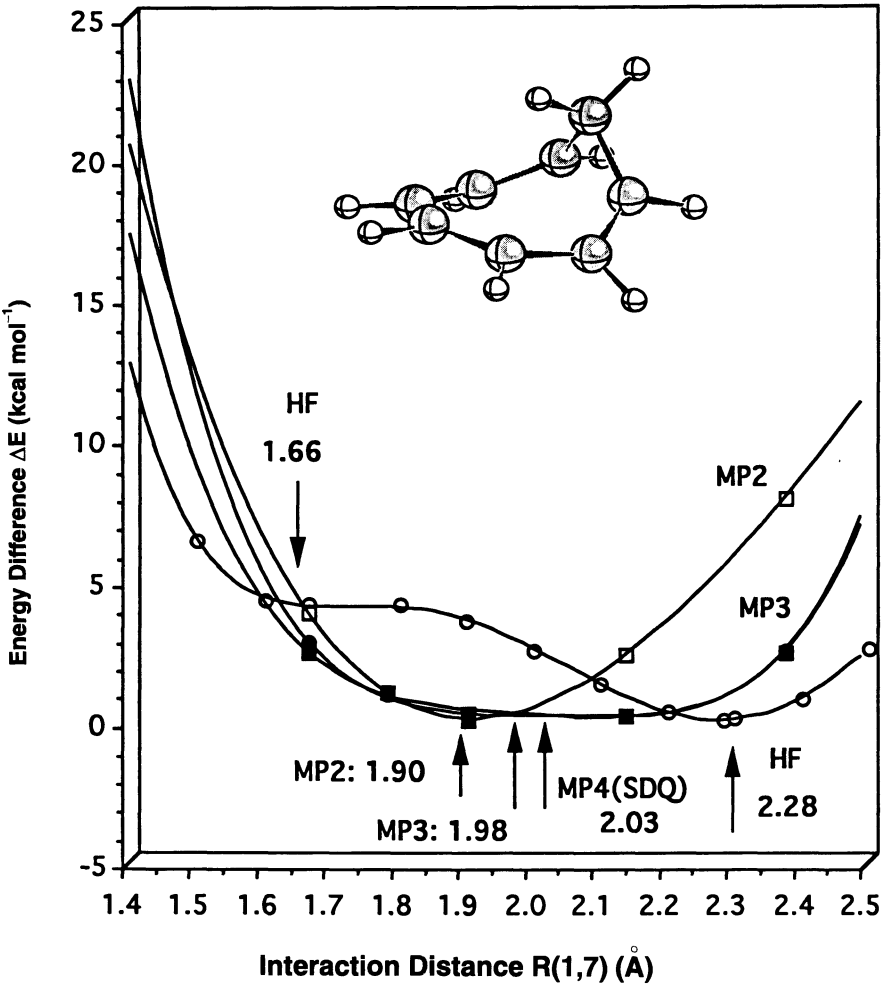


FIGURE 16. Potential energy surface of the homotropenylium cation (**45**) as a function of the C1,C7 interaction distance according to HF, MP2, MP3 and MP4(SDQ) calculations with the 6-31G(d) basis set. Positions of the energy minima are indicated by arrows

45 to be located at $R(1,7) = 2.285$ Å and a local minimum at $R(1,7) = 1.664$ Å[49]. The energy difference between the two minima is 4.1 kcal mol^{-1}, in agreement with similar calculations of Haddon[64].

However, the shape of the PES changes completely when correlation-corrected calculations are carried out (Figure 16)[49]. The MPn/6–31 G(d) (n = 2, 3, 4) PES for **45** possesses only one minimum in the direction of the 1,7 coordinate. This is located between 1.9 and 2.1 Å {1.901 (MP2), 1.985 (MP3) and 2.031 Å [MP4 (SDQ)][49]}, i.e. in a region typical of a non-classical structure **45b**. A 1,7 distance of *ca* 2 Å is accompanied by almost complete bond equalization in the seven-membered ring. The CC bond lengths vary between 1.396 and 1.404 Å with an average CC bond length (without C1—C7) of 1.399 Å (Figure 17).

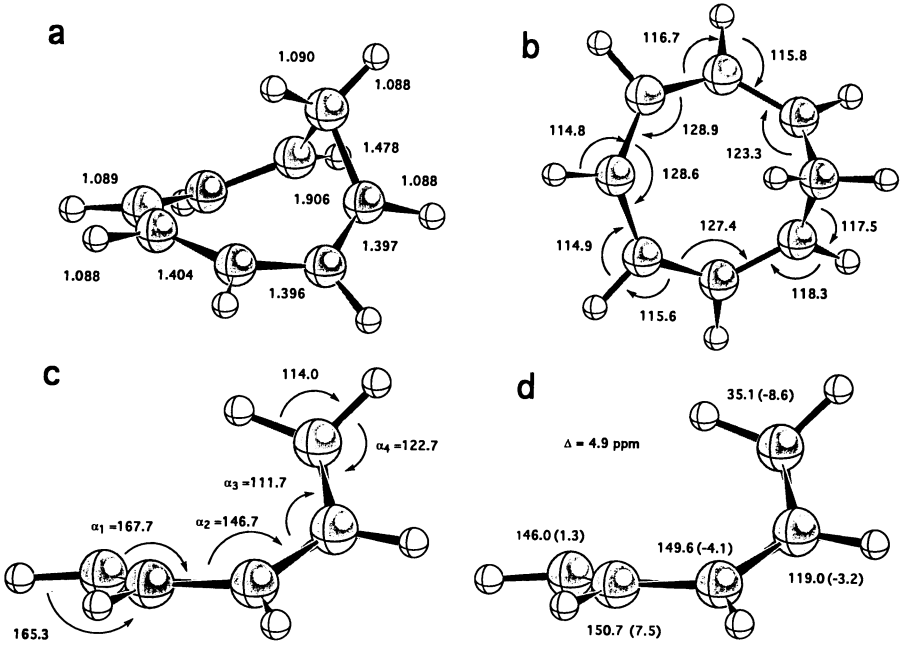


FIGURE 17. MP2/6-31G(d) equilibrium geometry and IGLO/6-31G(d,p) ^{13}C NMR chemical shifts of the homotropenylium cation (**45**). (a) Bond lengths in Å. (b) Bond angles in deg. (c) Folding angles in deg. (d) ^{13}C NMR chemical shifts in ppm relative to TMS calculated at the MP2 geometry with the distance C1,C7 determined at the MP4(SDQ) level of theory. Numbers in parentheses give the deviation of calculated shift values from experimental ^{13}C shifts. The mean deviation between calculated and experimental shifts is denoted by Δ[49]

Noteworthy is the fact that the CH_2 bridge is bent inward by 12° (see Figure 17c). In this way, the *endo* H atom takes a position about 2.2 Å above the centre of the seven-membered ring. The H atoms at the periphery of the ring are slightly bent downward away from the bridge (see Figure 17).

A feature, which becomes apparent from Figure 16, is the flatness of the PES in the region between 1.5 and 2.5 Å[49]. At MP4 (SDQ)/6–31 G(d), a change in the equilibrium value of $R(1,7)$ by $\pm$ 0.4 Å leads to an energy change of just 3.5 kcal mol^{-1} corresponding to a (harmonic) force constant of just 0.2 mdyn Å^{-1}[49].

2. Determination of the equilibrium geometry by the ab initio/ chemical shift/NMR method

An alternative approach to test the homoaromatic character of a molecule is based on the calculation and analysis of NMR chemical shift values[49–58]. The determination of NMR chemical shifts by *ab initio* methods such as IGLO, LORG or GIAO turns out to be very sensitive with regard to the geometry used[49,111–116]. *Ab initio* geometries provide a consistent description of molecules that does not suffer from the ambiguities of experimental geometries. Many calculations have shown that reasonable NMR chemical shifts are obtained for HF/DZ + P or MP2/DZ + P optimized geometries[49,111–116,118]. Since the calculated NMR

chemical shifts clearly depend on the geometry, *an agreement between experimental and theoretical shifts not only means a clear identification but also a geometry determination of the molecule in question*. On the other hand, if theoretical and experimental shifts differ considerably, other possible geometries or structures have to be tested.

Schleyer was the first to fully realize the sensitivity of calculated NMR chemical shifts with regard to molecular geometry and use this for *ab initio*/IGLO/NMR-based structural determinations in many cases[116]. Cremer and coworkers realized the usefulness of this approach for the determination of geometries of potentially homoaromatic compounds not amenable to experiment[49–58].

In Figure 18 experimental and IGLO/6–31G(d) ^{13}C chemical shifts of **45** are compared[47]. Experimental ^{13}C chemical shifts[120] do not agree with chemical shifts calculated for the two HF/6–31G(d) minima structures or any structure close to **45a** or **45c**. Mean deviations Δ between calculated and experimental ^{13}C shifts are as large as 40 ppm, thus exceeding normal IGLO/6–31G(d,p) errors by a factor of 6 and more. Clearly, IGLO ^{13}C

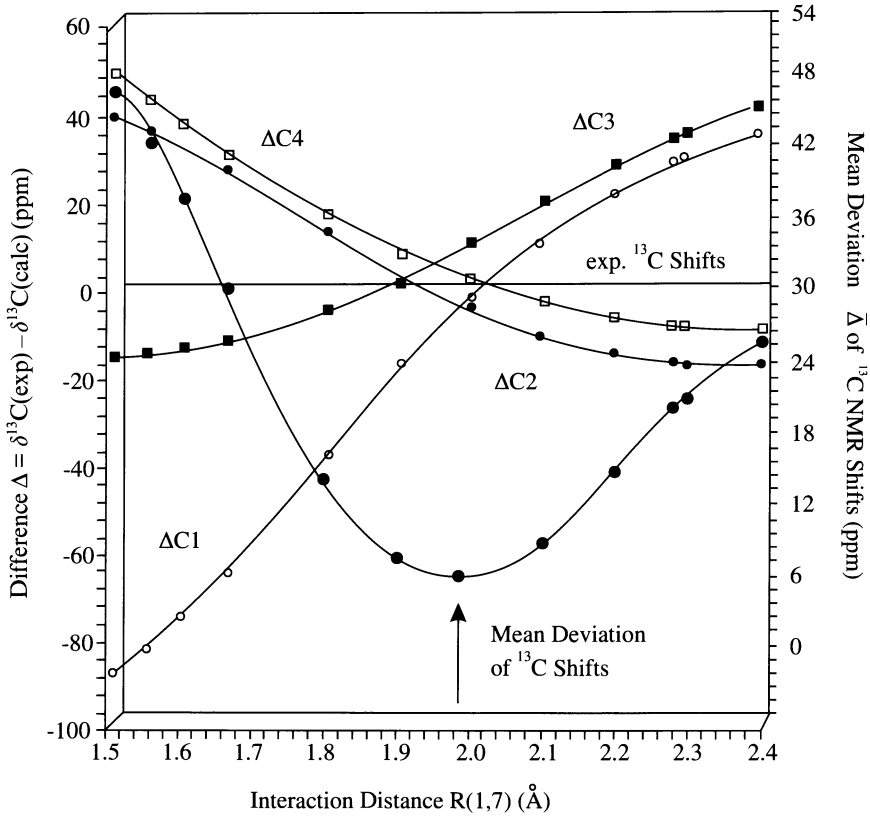


FIGURE 18. Differences between IGLO/6-31G(d,p) ^{13}C NMR chemical shifts and experimental shift values of the homotropenylium cation (**45**) given as a function of the interaction distance C1,C7. The zero line corresponds to the experimental shifts. Also given is the mean deviation $\bar{\Delta}$ of calculated chemical shifts. The minimum of $\bar{\Delta}$ (indicated by an arrow) defines the equilibrium value of the interaction distance C1,C7. All shift values in ppm

chemical shifts suggest that neither **45a** nor **45b** represents the true equilibrium structure of **45**.

If differences Δ for atoms C1–C7 are plotted as a function of the distance $R(1,7)$, all the curves are found to intersect the zero line corresponding to the experimental ^{13}C values at a C1,C7 distance between 1.9 and 2.0 Å (Figure 18). In this region of $R(1,7)$, the best agreement between IGLO and experimental ^{13}C chemical shifts for **45** is found as reflected by a mean deviation $\bar{\Delta}$ of 6 ppm [Figure 18, $R(1,7) = 1.97$ Å][49]. This implies that the PES of **45** in the direction of the $R(1,7)$ coordinate possesses a single minimum rather than the double minimum calculated at the HF level of theory (Figure 16).

In Figure 19, IGLO/6–31G(d) differences $\delta H_a - \delta H_b$ and magnetic susceptibilities $-\chi$ are also plotted as a function of the interaction distance $R(1,7)$. The difference between the shifts of *endo* (H_a) and *exo* proton (H_b) at C8 as well as the magnetic susceptibility are sensitive to electronic delocalization in the potential ring C1—C7. If, for a particular $R(1,7)$ value between 1.5 and 2.5 Å, homoaromatic 6π delocalization becomes a maximum, then this will lead to a large exaltation of $|-\chi|$ as well as large diamagnetic shielding of the *endo* proton H_a and, therefore, to a large difference $\delta H_a - \delta H_b$[49].

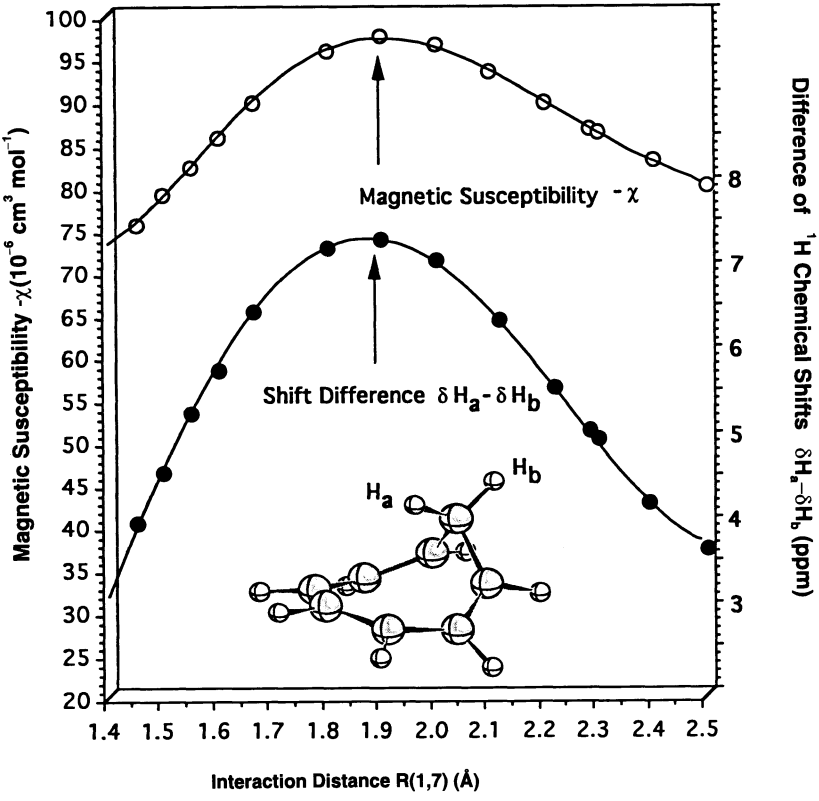


FIGURE 19. IGLO/6-31G(d,p) magnetic susceptibility $|-\chi|$ and shift difference $\delta H_a - \delta H_b$ of the homotropenylium cation (**45**) as a function of the interaction distance C1,C7. In each case, the position of the maximum is given by an arrow

Both $\delta H_a - \delta H_b$ and magnetic susceptibility $|-\chi|$ adopt maximal values at $R(1,7)$ distances close to 1.9 Å, suggesting that for this 1,7 distance (homoaromatic) 6π delocalization is strong. Since 6π delocalization will add to the stability of **45**, the location of the maximum of both the difference $\delta H_a - \delta H_b$ and $|-\chi|$ provides further support for the prediction that the equilibrium structure of **45** is characterized by the homoconjugated structure **45b** and a 1,7 distance close to 1.9 Å[49].

In conclusion, the calculated magnetic properties of cation **45** suggest that:

(a) the homotropenylium cation possesses a single minimum PES along the 1,7 coordinate (Figures 16 and 18);

(b) the preferred 1,7 distance is close to 2 Å;

(c) 6π electron delocalization at this $R(1,7)$ value increases the difference $\delta H_a - \delta H_b$ and the magnetic susceptibility $|-\chi|$ to maximum values.

Magnetic susceptibility and chemical shifts are sensitive antenna by which changes in the electronic structure due to geometrical and conformational changes can be measured and analysed. Therefore, they can be used to detect homoaromatic electron delocalization in a compound such as cation **45**. Their sensitivity may be illustrated by the data in Figure 17. If the MP2 equilibrium geometry of **45** is used, the mean deviation between experimental and calculated shift values is 6.2 ppm. However, utilizing the optimal MP4 (SDQ) 1,7 distance (see Figure 16) for the shift calculations, the mean deviation drops to 4.9 ppm caused by an improvement in the ^{13}C shift for atoms C1 and C7[49]. Since this shift value is probably most sensitive to a correct description of 1,7 interactions at the true C1,C7 distance, the improvement of the mean deviation $\bar{\Delta}$ indicates that MP4 (SDQ) provides the best account of homoconjugative interactions and the resulting equilibrium geometry **45b**.

C. Toward a General Definition of Homoaromaticity

Ab initio theory provides exact data on many molecular properties not amenable to experiment. In this way, it leads to a largely complete description of homoconjugated molecules and helps to identify and characterize homoconjugative systems with bond or no-bond homo(anti)aromaticity. A reliable description will be obtained if the PES is systematically scanned in the direction of the interaction distance using correlation-corrected methods with sufficiently large basis sets as described in the case of the homotropenylium cation (Section IV.B). Mere inspection of the PES reveals whether situation 1, 2, 3 or 4 of Figure 6 (see Section II.D) is given. Use of the Cremer–Kraka criteria of covalent bonding[27,82,83] will show whether calculated equilibrium structures belong to the class of bond or no-bond homoaromatic compounds, i.e. the position of point R_b (see Figure 3) can be clearly determined. However, it is not possible to decide by a single criterion whether the compound in question benefits from homoconjugative interactions or exhibits just normal cyclopropyl conjugation or weak through-space interactions, i.e. where points R_a and R_c (see Figure 3) are located. To answer this question a whole series of checks has to be carried out as is listed in the following for the two basic possibilities of bond and no-bond homoconjugation.

1. Bond homo(anti)aromaticity caused by cyclopropyl homoconjugation

Bond homoaromaticity is literally identical with cyclopropyl homoaromaticity since no examples involving cyclobutyl or other rings are reported in the literature. Nevertheless, it is advisable to define bond homoaromaticity in a general way that leaves open the question whether there is any bond homoaromaticity beyond cyclopropyl homoaromaticity.

A homoaromatic system is characterized by the following properties:

(1) The interacting centres are connected by a bond path with a bond critical point **p**, at which the energy density distribution $H(\mathbf{r})$ is stabilizing [$H(\mathbf{p}) < 0$].

(2) The bond order n of the closing bond is between 0 and 1, thus indicating a partial bond.

(3) The π-character of the closing bond as measured by the bond ellipticity ε is larger than that of cyclopropane.

(4) Electron delocalization in the cyclic system is characterized by:

(a) a relatively large degree of bond equalization with bond lengths differing from those of normal single or double bonds,

(b) calculated bond orders and bond ellipticities that are approaching those of an aromatic π system,

(c) the major axes of the bond ellipticities of the cyclic system formed by the homoconjugative bond overlap effectively,

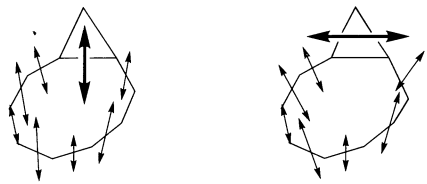
(d) in case of charged molecules, positive or negative charge is delocalized throughout the cyclic system.

(5) The number N of π-electrons participating in electron delocalization, $N = 2\Sigma_i n_i - 2N_\sigma$ (where N_σ is the number of formal σ-bonds), is close or identical to $4q + 2$ ($q = 0,1,2,\cdots$).

In a similar way, a homoantiaromatic system formed by bond (cyclopropyl) homoconjugation can be described. There is, however, one major difference between homoaromatic and homoantiaromatic systems (observed in the case of cyclopropyl homoconjugation) that separates homoaromaticity from aromaticity. While aromaticity and antiaromaticity involve different numbers of electrons ($4q + 2$ or $4q$), homoaromaticity and homoantiaromaticity both involve $4q + 2$ electrons but differ with regard to the delocalization modes of these electrons, which are best described by the direction of surface delocalization in a three-membered ring (Scheme 15):

(6) For a homoaromatic system, surface delocalization in the cyclopropyl ring is perpendicular to the bridging bond, thus forming a Hückel aromatic electron ensemble which is delocalized in just one part of the bi(poly)cyclic system.

(7) For a homoantiaromatic system, surface delocalization in the cyclopropyl ring is parallel to the bridging bond, thus forming a Möbius antiaromatic electron ensemble delocalized along the periphery of the bi(poly)cyclic ring system.



SCHEME 15. Surface delocalization in homoaromatic and homoantiaromatic molecules. Major axes of bond ellipticities are indicated by arrows; the direction of surface delocalization in the three-membered ring is given by a bold arrow

Homoconjugative electron delocalization leads to stabilization or destabilization of the molecule, which can be determined provided correct reference compounds with appropriate reference conformations are chosen. In the case of cyclopropyl homoconjugation, these should be vinylcyclopropane, 1,3-butadiene and their methyl derivatives. The discussion in Section III.G clearly shows that by the use of either correctly chosen homodesmotic

reactions or appropriately parametrized force fields, reliable resonance energies for homoconjugated molecules can be calculated.

(8) The resonance energy of a homoaromatic molecule is ≤ -2 kcal mol^{-1} and that of a homoantiaromatic molecule ≥ 2 kcal mol^{-1}. Typical values are between |2| and |10| kcal mol^{-1} indicating that homoconjugative stabilization or destabilization is normally just a matter of a few kcal mol^{-1}.

The many homoaromatic stabilization energies or homoantiaromatic destabilization energies published in the literature very often are contaminated by energies resulting from strain, hyperconjugative or inductive effects, and therefore care must be taken if those values are used to decide the homo(anti)aromatic character of a molecule. Also, one has to warn against comparing homoconjugative resonance energies with resonance energies of aromatic or antiaromatic compounds published in the literature. In most cases, the latter are defined with regard to the *trans* rather than the *cis* form of 1,3-butadiene and therefore they are too low. The argument that norcaradiene (RE = 4 kcal mol^{-1}, Section III.G.4) possesses about 19% of the resonance energy of benzene (21 kcal mol^{-1}, Section III.G.5) is wrong, since the latter value has been obtained using *trans*-1,3-butadiene as a reference. The resonance energy of benzene relative to *cis*-1,3-butadiene is 25.9 kcal mol^{-1} (Section III.G.5) and accordingly norcaradiene covers just 15% of this value.

There are no systematic investigations that clarify how the magnetic properties of a molecule change if cyclopropyl homoconjugation leads to cyclopropyl homoaromaticity. However, in view of the sensitivity of magnetic properties with regard to homoconjugation in the case of no-bond homoaromaticity (see Section IV.B and the following section), it is likely that further research will unravel the dependence of magnetic properties on the extent of cyclopropyl homoconjugation. Such relationships will definitely add to the list of criteria that characterizes cyclopropyl homo(anti)aromaticity.

2. *No-bond homoaromaticity*

All investigations carried out so far suggest that no-bond homoaromaticity in the case of hydrocarbons manifests itself in the following way:

(1) A cyclic system is formed by strong though-space interactions via interaction distances between 1.8 and 2.2 Å with an optimal value at about 2 Å.

(2) There is no path of maximum electron density between the interacting atoms which, according to Cremer–Kraka[27,82,83], is a necessary condition for covalent bonding. However, interaction indices derived from the electron density distribution are as large as 30% of the bond order of a normal single bond.

(3) Through-space interactions are confirmed by the Laplace concentration $-\nabla^2\rho(\mathbf{r})$ that reveals polarization of the electron density at the interacting atoms.

(4) Electron delocalization in the cyclic system is characterized by:

(a) a relatively large degree of bond equalization with bond lengths differing from those of normal single or double bonds (averaged bond length close to 1.40 ± 0.01 Å),

(b) calculated bond orders and bond ellipticities that are approaching those of an aromatic π system,

(c) the major axes of the bond ellipticities of the cyclic system formed overlap effectively,

(d) in case of charged molecules, positive or negative charge is delocalized throughout the cyclic system.

(5) The number N of π-electrons participating in electron delocalization, $N = 2\Sigma_i n_i - 2N_\sigma$ (where N_σ is the number of formal σ-bonds), is close or identical to $4q + 2$ ($q = 0, 1, 2, \cdots$).

Contrary to bond homoantiaromaticity, very little is known about no-bond homoantiaromaticity[123]. In a potentially no-bond homoantiaromatic molecule, there is often the

possibility of avoiding strong destabilizing through-space interactions either by valence tautomeric rearrangements of by conformational changes that lead to larger interaction distances and, accordingly, reduced through-space interactions. Therefore, the energetic consequences of no-bond homoconjugation are considered just for homoaromatic molecules.

(6) The resonance energy of a homoaromatic molecule is ≤ -2 kcal mol^{-1}. Typical values are between -2 and -10 kcal mol^{-1} indicating that homoconjugative stabilization is normally just a matter of a few kcal mol^{-1}.

For the magnetic properties of a no-bond homoaromatic molecule, one can expect typical values.

(7) Because of electron delocalization, there should be a significant equalization of ^{13}C chemical shifts in the cyclic system.

(8) For the magnetic susceptibility $|-\chi|$ determined as a function of the interaction distance, a maximum value should be calculated for the homoaromatic system, i.e. the exaltation of the magnetic susceptibility should indicate homoaromatic electron delocalization.

(9) If the system in question possesses a CH_2 group located above the ring in a similar way to the case of the homotropenylium cation, the shift difference between *endo*- and *exo*-oriented proton should also adopt a maximum value for the homoaromatic system.

3. General remarks

According to the definition given above, both bond (cyclopropyl) and no-bond homoaromaticity can occur for cationic (many examples), neutral (several examples) and anionic systems (few examples) with a frequency that can be explained on the basis of PMO theory (Section III.C). Apart from a few exceptions[124], homoaromaticity has just been observed for hydrocarbons, but recent calculations indicate that homoconjugative interactions can also be expected for Si-containing analogues of homoaromatic systems[35]. In principle, there is no reason to exclude homoaromaticity for heteroatom-containing systems. The only question is how to detect homoconjugative interactions in the presence of strong inductive, anomeric, hyperconjugative or steric effects. Too little work has been done in this direction to clarify whether homoconjugation is an important factor in heteroatomic molecules.

As stressed in Section II.D, homoaromaticity plays an important role in the transition states of certain pericyclic reactions. The valence tautomeric rearrangement of cycloheptatriene to norcaradiene is an example par excellence, as has been demonstrated by calculations of Kraka and Cremer[54]. Other examples have been described by Grimme and coworkers[125]. There seems to be a special relationship between transition states and systems with no-bond homoaromaticity. The latter possess geometries and other properties typical of transition states. By proper substituiton, they can be pushed into the classical bicyclic form **42a** or the classical monocyclic form **42c** as has been demonstrated elegantly by Childs and coworkers[121,122] in the case of the homotropenylium cation. Therefore, *it is appropriate to consider no-bond homoaromatic systems as frozen transition states* (Section II.D), i.e. transition states that by homoconjugative electron delocalization have been energetically lowered below the energies of the two classic forms **42a** and **42c** of a valence tautomeric rearrangement **42a** to **42c**. *No-bond homoaromatic molecules, such as the homotropenylium or the 1,4-bishomotropenylium cation, are the first frozen transition states discovered so far*[49–55].

The description of no-bond homoaromatic systems as frozen transition states is in line with the observation that their PES is rather flat in the direction of the interaction distance. This means that (a) homoaromatic stabilization energies are small (see Table 2 and the discussion presented above) and (b) relatively small energy increases lead to relatively large

changes in geometry as well as other properties. Homoaromaticity is mostly accompanied by a delicate balance between (destabilizing) strain and (stabilizing) through-space or through-bond interactions, and therefore *small perturbations due to substituent, counter ion or media effects may disrupt no-bond homoaromatic delocalization.* This has to be kept in mind when trying to confirm homoaromatic character by investigating substituted derivatives of the target molecule.

The possibilities of experiment are often very limited when it comes to the detection, verification and description of homo(anti)aromatic character. These limitations, however, can be compensated by combining experimental with theoretical tools. This holds in particular with regard to the measurement and calculation of the magnetic properties of potentially homoaromatic molecules. Using the NMR/chemical shifts/*ab initio* approach of Cremer and coworkers[49–58] which combines experimental and calculated shift values, it is possible to determine geometry (in particular with regard to the interaction distance), relative energy, electron delocalization and many other properties of the compound in question. *The shift values themselves as well as the magnetic susceptibility exaltation provide sensitive detectors for homoconjugative electron delocalization.* Since one has just started to use these tools to investigate homoconjugated molecules, one can foresee for the future many surprising insights into an electronic phenomenon that, although generally known and accepted for a long time, was only very vaguely described and defined in the textbooks and review articles of the past.

V. CONCLUSIONS AND OUTLOOK

Research on (cyclopropyl) homoconjugation and homoaromaticity has inspired generations of chemists to develop new strategies and techniques for exploring the possibilities of homoaromatic electron delocalization. Quantum Chemistry has accompanied experiment through 40 years of homoaromaticity research and has resulted in many useful descriptions and explanations. Nevertheless, it took until the nineties before theory was able to provide the exact data on molecular properties that are needed in research on homoaromatic molecules. In this respect one must mention the availability of Coupled Cluster methods for high accuracy calculations of energies and geometries as well as the availability of *ab initio* methods for calculating magnetic properties of a molecule (see Section IV.A).

Ab initio research on homoconjugation and homoaromaticity has to fulfil several requirements and tasks to lead to a reliable account of the homoaromatic character of homoconjugated molecules.

(1) *Calculation of reliable energies and accurate geometries.* State-of-the-art *ab initio* methods can fulfil this requirment, if necessary even for medium-sized molecules. It is doubtful whether such a statement can also be made without any reservation for semiempirical methods. Although improved descriptions of energy and geometry are obtained with methods such as MNDO-Cl or AM1-Cl in selected cases, one cannot rely on this in general. Since investigations with these methods always included configuration interaction in a limited way, one had to decide from case to case how many MOs are considered in the Cl treatment to get reliable results. Thus in the case of investigations based on MNDO or AM1 in connection with limited Cl one cannot speak of a predictive approach, more of an ad hoc adjustment of theory to reproduce experimental facts already known.

(2) *Potential energy surface (PES) scans. Ab initio* research on homoaromatic compounds always requires some exploration of the PES rather than just the investigation of equilibrium geometries. As discussed in Sections II.D and IV.B, it is essential to determine the shape of the PES as a function of homoconjugative interaction distances. The number and location of all stationary points have to be determined so that one can distinguish

between (homoconjugated) classical structures, (homoaromatic) non-classical structures or the existence of valence tautomeric equilibria (Figure 6, Section II.D).

(3) *Calculation of magnetic properties.* A most valuable tool in *ab initio* studies on homoconjugated molecules is the calculation of magnetic properties. NMR chemical shifts or shift differences are very sensitive with regard to geometric changes and charge delocalization. In addition, the magnetic susceptibility represents a useful antenna for electron delocalization. Theory has just begun to use the calculation of magnetic properties as a descriptive tool, and therefore one can expect that future *ab initio* investigations will lead to new and probably unexpected insights into the electronic nature of potentially homoaromatic molecules.

(4) *Electron density analysis.* Another important part of *ab initio* research on homoaromatic molecules is the electron density analysis along the lines worked out by Cremer and coworkers[27,82–84] and based on Bader's virial partitioning method[81]. Applying the Cremer–Kraka criterion of covalent bonding[82,83], a differentiation between bond and no-bond homoconjugation (homoaromaticity) (determination of point R_b in Figure 3) becomes possible. In addition, the electron density analysis provides useful molecular parameters (bond orders, interaction indices and π-character indices) that provide an assessment of the degree of electron delocalization. Analysis of the Laplace concentration gives insight into the degree of through-space interactions, although this has not been put on a quantitative basis so far.

(5) *Calculation of homoaromatic resonance energies.* A new element of future *ab initio* work on homoconjugated molecules must be the calculation of homoaromatic resonance energies. In this respect, the analysis of homodesmotic reaction energies can provide a reasonable basis for getting reliable resonance energies (Section III.G). The only method currently available to obtain accurate resonance energies is the molecular mechanics approach of Roth. This approach demonstrates how resonance energies have to be calculated, although it suffers from all the limitations normally encountered by molecular mechanics methods. For example, it depends strongly on the availability of exact structural, conformational and thermochemical data. Since the latter are only available for certain classes of neutral homoaromatic molecules, Roth's method is applicable only to neutral compounds, not to the many interesting cationic and anionic homoconjugated molecules. The future will show whether extension of the force field parametrization can be based on accurate *ab initio* rather than experimental data.

(6) *Investigation of environmental effects.* As has been stressed in this chapter, homoaromaticity is just a matter of a few kcal mol^{-1} stabilization energy in most cases, and therefore environmental effects may have a large impact on structure, stability and other properties of a homoaromatic compound. Future work in theory (as well as in experiment) has to clarify how environmental effects can influence electron delocalization, through-space interactions and bonding in homoaromatic molecules. The theoretical methods are now available to calculate solvent and counter ion effects (for homoaromatic ions in solution) or to study intermolecular and crystal packing forces in the solid state.

By complying with these guidelines, *ab initio* theory should be able to answer some of the pending questions in research on homoconjugation and homoaromaticity.

Although the structural elements supporting cyclopropyl homoaromaticity and no-bond homoaromaticity are now generally understood, it is not clear under what conditions a homoconjugated molecule will prefer to occupy a single minimum or to adopt classical forms connected by a valence tautomeric equilibrium. Of course, one can explain that the norcaradiene/cycloheptatriene system is characterized by a valence tautomeric equilibrium while the homotropenylium cation possesses a single minimum PES. This has simply

to do with the fact that in the cyclopropyl carbinyl cation (embedded in the homotropenylium cation) the vicinal bonds are much more labile than the corresponding bonds in vinylcyclopropane (embedded in norcaradiene) (see Chapter 2 in this volume[2]). But this qualitative explanation is not sufficient if one wants to predict on a quantitative basis under which structural and electronic conditions a valence tautomeric equilibrium degenerates to a single minimum situation.

Actually, this question focuses on the generation of a frozen transition state situation. Can each valence tautomeric equilibrium between an unconstrained cyclopropyl homoconjugated compound and its open monocyclic counterpart be manipulated in such a way that a frozen transition state is obtained? There are results pointing in this direction (see the following chapter[3]), however at the moment one is far from being able to generalize any of these observations.

The investigation of homoaromatic moleclues with frozen transition state character is certainly one of the most fascinating goals in chemistry. Transition states are transient points on the PES where the reacting molecule does not stay any longer than at any other non-equilibrium point. Accordingly, there are only a few experimental ways of getting indirect evidence on the nature of transition states. On the other hand, chemists need exact knowledge about transition states in order to steer and manipulate chemical reactions. The freezing of a transition state provides a very attractive way of getting direct evidence on its properties. For example, the investigation of the homotropenylium cation reveals that stabilizing electron delocalization is very effective at distances of 2 Å. This can also be assumed for the transition state of a pericyclic reaction characterized by an aromatic ensemble of electrons. As a consequence, the transition state energy is relatively small compared to the dissociation energies of normal CC bonds. CC bond formation or bond rupture in pericyclic reactions can be manipulated using rather mild steering and regulating devices (temperature, solvents, etc.) compared to the brute forces needed for dissociation of a molecule into its atoms.

Another interesting, but only little investigated aspect concerns electron delocalization and homoaromaticity in three dimensions (homoradial aromaticity, homo-3D aromaticity, homospherical aromaticity (Figure 2, Section I). An increasing number of examples are becoming available suggesting that electron delocalization is not just a one-dimensional phenomenon (along the acyclic or cyclic chain of atoms in the form of ribbon delocalization; Figure 2 and Reference 13) but can also be two- or three-dimensional, i.e. in the form of surface or volume delocalization[13]. Examples of three-dimensional homoaromaticity will be discussed in the following chapter by Childs, Cremer and Elia[3]. From this discussion it will become evident that much more research is needed to fully understand the electronic structure of compounds with 'three-dimensional' homoaromaticity.

Homoconjugation influences the reactivity and internal rearrangements of polycyclic unsaturated hydrocarbons such as semibullvalene, bullvalene, barbaralyl cation, etc. The facile rearrangements of these compounds become possible because of stabilization of their transition states by homoconjugative (homoaromatic) interactions. As described in the case of the barbaralyl cation[57], electron delocalization involves all parts of the molecule and makes all carbon–carbon bonds prone to dissociation and reformation. The rapid rearrangements of the barbaralyl cation (all barriers ≤ 5 kcal mol^{-1} [57]) lead to a complete exchange of all nine carbon positions at temperatures above –150 °C and an equilibration of their properties. Again, a cyclopropylcarbinyl cation group, now in the form of a divinylcyclopropylcarbinyl cation, is responsible for the labile character of the barbaralyl cation. *Ab initio* calculations show that the transition states of the degenerate rearrangements of the barbaralyl cation benefit from no-bond homoaromaticity.

It should be possible to further reduce the energy barriers to internal rearrangements of the barbaralyl cation or related polycyclic compounds by relatively small changes in the structure or by appropriate substitution. In this way, a situation should be reached in which

rearrangements are so fast that the molecule in question no longer possesses a fixed structure. Then, the molecule will be best described by a ball or spherical surface of electron density in which the nuclei swim just obeying Coulomb's law but otherwise taking all possible positions on the surface. For such a molecule, the evolutionary path from chaos to the ordered structure of an assembly of nuclei in a molecule would be reversed and a new field of elementary investigations would become possible.

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