PROS AND CONS OF σ-AROMATICITY*

Dieter Cremer
Institut für Organische Chemie, Universität Köln
Greinstr. 4, D-5000 Köln 41
West Germany

Abstract: A discussion of σ-aromaticity requires a dis-
tinction between σ-conjugation, σ-electron delocalization,
and σ-bond delocalization, all of which can be considered
as prerequisites of σ-aromatic character. All molecules with
three or more atoms encounter σ-conjugative interactions.
Also, all σ-electrons are delocalized if the term delocali-
zation is taken in its quantum theoretical meaning. Howev-
er, σ-conjugation and σ-electron delocalization do not ne-
cessarily imply σ-bond delocalization. - One can distinguish
between three different modes of σ-delocalization: *ribbon
delocalization* in acyclic molecules and larger rings, *sur-
face delocalization* in small rings, and *volume delocaliza-
tion* in cage compounds. Surface delocalization of σ-
electrons is found to lead to σ-bond delocalization. An ex-
ample is cyclopropane. Bonding in cyclopropane can only be
described in terms of nonclassical 2-electron 3-center and
4-electron 3-center bonds. Application of the criteria used
to define π-aromaticity reveals that the properties of cy-
clopropane are in line with these criteria and that the
term σ-aromaticity cannot be rejected on the grounds that
aromaticity is restricted to π-electrons. The pros and
cons of using the term σ-aromaticity in chemical discus-
sions are presented.

Introduction

Between 1979 and 1984, M.J.S. Dewar published several articles [1-3], in
which he described the possibility and the consequences of σ-conjugative
interactions in saturated compounds. The concept of σ-conjugation, origi-
nally put forward in papers by Dewar and Petit [4], Sandorfy [5], Pople and
Santry [6], and others [7], is based on the fact that resonance integrals
between different hybrid AOs of a given atom do not vanish even if the
AOs are orthogonal. This applies also to the resonance integrals between
geminal sp^n hybrid orbitals of a carbon atom, which are considerably

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* This paper is dedicated to Professor Michael J. S. Dewar on the occa-
sion of his seventieth birthday.

larger than that between adjacent 2pπ-AOs in the case of conjugated dou-
ble bonds. Hence, interactions between σ-bonds should be at least as
strong as interactions between π-bonds. Taking this into account Dewar
was able to rationalize a number of apparent anomalies in organic chem-
istry, which are difficult to explain in other ways. These examples in-
cluded the astonishing stability of three-membered rings, the pyramidal
structure of radicals and biradicals, the geometry of triplet carbene,
bond staggering in saturated molecules, the gauche and anomeric effects,
and the relationship between chelotropic and other cycloaddition reac-
tions. [1-3]

By drawing an analogy between the -HC-CH- groups of a conjugated polyene
or cyclopolyene and the -CH$_2$- groups of a cycloalkane and by applying
Hückel rules to σ-electrons, Dewar [1-3] explained the relative stabilities
of small ring molecules such as cyclopropane, cyclobutane, and cyclopen-
tane in terms of σ-aromatic and σ-antiaromatic electron interactions.
Aromaticity is normally associated with delocalization of π- rather than
σ-electrons and, therefore, Dewar's description of the electronic struc-
ture of cycloalkanes seemed to be rather unorthodox when it first ap-
peared. However, aromatic interactions of σ-electrons had been discussed
before by Cremer and co-workers who had investigated the energetic con-
sequences of σ-electron delocalization on the conformation of geminal me-
thyl rotors. [8]

Dewar's ideas have been met with both applause and skepticism. The ques-
tion has been raised whether it is necessary to invoke σ-aromaticity in
order to explain, e.g., the stability of cycloalkanes. [9] That is why,
in this work, the pros and cons of σ-delocalization and σ-aromaticity
are reviewed. In this connection the following questions will be dis-
cussed :

1. Do σ-electrons delocalize?
2. Are there examples of cyclic delocalization of σ-electrons?
3. What are the differences in σ- and π-electron delocalization?
4. Does σ-electron delocalization affect molecular properties?
5. Are there any energetic consequences of σ-electron delocalization that
justify the term "σ-aromaticity"?

Even if these questions can all be positively answered, it will be
still open to question whether a term such as "σ-aromaticity" means a
substantial improvement of model descriptions of chemical reality and
whether it facilitates or impedes day-to-day thinking of chemists. There-
fore, we will give special consideration to this point.

Conjugation and Delocalization - Do σ-Electrons Delocalize?

Before turning to the discussion of σ-aromaticity, it is useful to clar-
ify the meaning of the terms "delocalization" and "conjugation" and to
assess the chemical relevance of "σ-conjugation" and "σ-delocalization".

The electrons of an isolated atom are confined to the space of this atom, i.e. they are *localized* in this space. Upon formation of a bond between two isolated atoms their electrons *delocalize* over the whole space of the two atoms. [10] In this way the uncertainty in position of the electrons is increased which in turn leads to a decrease in the uncertainty of their momentum. The kinetic energy of the electrons is reduced. Delocalization of the electrons and a concomitant decrease of their kinetic energy is typical of the bond formation process. [11]

The bonding electrons of a molecule are always delocalized. Therefore, the question posed in the title of this section should actually be changed to: "Do σ-electrons localize?" Quantum theory says that this has to be clearly denied. All valence electrons of a molecule are delocalized. Even the inner shell electrons of an atom in a molecule delocalize to some extent over molecular space.

However, 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. This assumption is the basis of the concept of "bond localization", which reflects the fact that many properties of molecules, e.g. their heat of formation, dipole moment, diamagnetic susceptibility, etc. can be expressed in terms of bond contributions and that the properties of a given type of bond, e.g. its bond length, remains the same in very different molecules. Of course, neither "bond localization" nor "electron localization" refer to any observable molecular property and, therefore, these terms lack any physical justification. They simply suggest that most molecules behave as if the bonds in them were localized. [12] With the assumption of bond localization a large body of experimental

Scheme 1

Meaning of	Localization	Delocalization
	of electrons	
Quantum theoretical meaning	Electrons are confined to the space of an (isolated) atom.	Electrons are distributed over the total space of two or more bonded atoms.

Note: Terms are used to characterize the properties of *single* electrons.

of bonds (electrons)

| Heuristic meaning (within the concept of "bond localization") | The properties of molecules can be rationalized by assuming "bond localization" | |
| | Yes | No |

Note: Terms can only be used in connection with *collective* properties of molecules, but not with regard to one-electron properties such as ionization potentials, ESR properties, light absorption, etc.

Note: Conjugation not necessarily implies bond delocalization!

data on molecular properties can be rationalized, i.e. bond (electron) localization is a heuristic concept, the foundations of which were first outlined by G. N. Lewis.

Within the concept of bond localization, the meaning of the term elec-tron (de)localization is changed: *Electrons (or bonds) will now be con-sidered to be localized if the properties of the molecule can be ex-plained in terms of bond contributions. However, they will be considered to be delocalized if the properties of the molecule cannot be rational-ized on the basis of the concept of bond localization.* The different meanings of the terms localization and delocalization are compared in Scheme 1.

In general, the actual meaning of the terms localization and delocaliza-tion can be taken from the context in which they are used. Neverthe-less, confusion will arise if bond delocalization is identified with the term "conjugation" within the concept of bond localization. Originally, conjugation was used in a topological sense indicating that each pair of double (multiple) bonds in a conjugated system is separated by just one single bond. Such a bond arrangement leads to significant interactions between the π-MOs of the double (multiple) bonds thus yielding extended π-MOs. Nowadays, the term conjugation simply denotes interactions between single bonds (σ-conjugation) or between multiple bonds (π-conjugation). It implies alternation between stronger and weaker orbital interactions leading to a corresponding alternation of resonance integrals. [13] In Scheme 2, π- and σ-conjugation are described in terms of the relevant resonance integrals β^I and β^{II}. In the case of π-conjugation, both reso-nance integrals describe interatomic interactions, some stronger (β^I), some weaker (β^{II}), while in the case of σ-conjugation the stronger in-teractions are intraatomic (β^I) and the weaker are interatomic (β^{II}).

Scheme 2
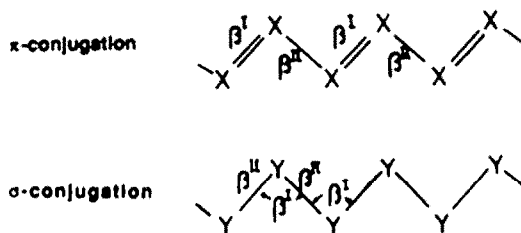
There always is σ-conjugation in a molecule with three or more atoms. This, however, does not imply that molecules with σ-conjugation cannot be described within the concept of localized bonds. On the contrary, conjugative effects between adjacent σ-bonds are approximately constant in most cases and, therefore, they can be absorbed in the empirical

values chosen for appropriate reference bonds.

In polyenes and cyclopolyenes, there is both σ- and π-conjugation. Accordingly, there are three possible explanations for the observed properties of a (cyclo)polyene, e.g. the CC bond lengths in benzene. They may be a result of

    a) π-conjugation or
    b) σ-conjugation or
    c) both π- and σ-conjugative effects.

A priori, it is difficult to say which of the three explanations is correct. The common view is that π-conjugation causes bond equalization in benzene. However, recent theoretical investigations suggest that σ-conjugation may be more important since the π-electrons of benzene tend to localize in double bonds. [14] Although the latter possibility seems to be unlikely in view of decades of research spent on π-conjugation and π-delocalization, unbiased consideration of the question reveals that it is very difficult to reject σ-conjugation as an important reason for bond equalization in benzene. [15]

Obviously, bond (orbital) conjugation is far more common than bond (electron) delocalization. Conjugation does not always lead to bond delocalization and, therefore, the identification of the first term with the latter is not correct within the concept of bond localization. An interchangeable use of these terms implies that the properties of conjugated molecules cannot be described with the model of localized bonds which, of course, is wrong in most cases. For example, Dewar has demonstrated that by using appropriate bond increments for double and single bonds the heats of formation and other properties of polyenes are well reproduced. [16]

It can also be misleading to consider electrons (bonds) to be delocalized if the corresponding MOs are delocalized. Canonical MOs are always delocalized and this is true for both σ- and π-MOs. However, by localizing canonical MOs one gains a basis to narrow down those cases where electron (bond) delocalization might occur. Localized π-MOs in conjugated systems possess long delocalized tails while the tails of the localized σ-MOs are much shorter. Therefore, it is common to consider electrons (bonds) to be localized if the corresponding localized MOs are essentially confined to the region of the bonds in question. Electron (bond) delocalization is expected if the localized MOs exhibit pronounced orbital tails. According to these definitions, a polyene should exhibit bond (electron) delocalization which, of course, is not true (see above). In other words: *The localized π-MOs of the polyene indicate (orbital) conjugation rather than bond (electron) delocalization.* This has to do with the fact that MOs refer to single electrons (although they depend on all of the other electrons) while bond (electron) delocalization reflects a collective effect of all electrons. The analysis of localized MOs, although useful in many respects, does not lead to an unique definition of delocalization.

In order to reduce confusion it is better to speak of *bond* (de)localization rather than *electron* (de)localization if these terms are used in their heuristic meaning. For that reason, the term bond is added in parenthesis when using the term "electron delocalization". Also, one should avoid an unjustified mixing of conjugation and electron (bond) delocalization. Conjugation is only a necessary prerequisite of electron (bond) delocalization but it does not necessarily imply delocalization in the heuristic sense of the word. Finally, one has to remember that (de)localization is first of all a technical, mathematically oriented term when it is applied to MOs. Canonical MOs are always delocalized as electrons are always delocalized in the quantum theoretical sense of the word. Localized MOs with long orbitals tails indicate π-conjugation but not necessarily bond delocalization.

Experimental observations of σ-delocalization. In view of the considerations presented above there is no question that σ-electrons delocalize in the molecule although their mobility may be lower than that of π-electrons. Delocalization of σ-electrons is nicely reflected, e.g., by ESR investigations on alkane cations by Iwasaki and co-workers. [17] These authors have provided conclusive evidence that the unpaired electron of a linear alkane cation is delocalized over the in-plane CH bonds (at the terminal C atoms) and all intermediate CC σ-bonds.

Delocalization of σ-electrons in alkane cations is also indicated by the measured ionization potentials (IP) of linear alkanes. [18] IPs decrease more strongly than can be expected in view of the stability of the alkanes themselves or in view of hyperconjugative effects acting in the cations. The observed trend in the IPs is in line with increasing delocalization of the σ-electrons as the chain length of the alkane grows. Delocalization causes a destabilization of the HOMO and, accordingly, a decrease of the IP.

Some ESR long range hyperfine spin coupling constants of bridgehead alkyl radicals also suggest that the unpaired electrons can delocalize through interacting σ-bonds. [19,20] Various "through-bond" mechanisms for spin delocalization have been discussed, although cooperative "through-space" and hyperconjugative interactions could not be excluded in these cases. Other examples of through-bond interactions involving σ-electrons and σ-bonds have been discussed in the literature. [21,22]

Experimental observations indicating σ-delocalization are not limited to hydrocarbons. For example, Bock and co-workers have found that the measured IPs of silanes suggest delocalization of the SiSi σ-electrons. [23,24] A similar conclusion was drawn by Pitt and co-workers [25] who investigated the IPs of peralkylated silanes, germanes, and stannanes. Theoretical orbital models that take σ-electron delocalization explicitly into account by using geminal resonance integrals β^I (Scheme 2) [5,26-28] reproduce measured IPs of saturated compounds very well.

All observations quoted so far are due to the **properties of single**

σ-electrons. They just confirm what is predicted by quantum theory. However, they do not reveal whether there is also σ-bond delocalization in these systems, i.e. whether σ-electrons delocalize in the heuristic meaning of the word. Clearly, known properties of alkane cations or alkane radicals that are **collective properties of all electrons** (e.g., heat of formation, geometry) are easily explained with the aid of the concept of localized bonds. Therefore, it is likely that these molecules do not exhibit σ-bond (electron) delocalization.

Dewar has mentioned in his articles on "σ-conjugation" various cases where σ-delocalization might be an important factor to rationalize the properties of acyclic molecules. [1-3] Since none of these cases is relevant to the question of σ-aromaticity, we will refrain from any further discussion of σ-conjugation and σ-delocalization in acyclic molecules. Instead we will focus on those cases in which σ-conjugation may lead to σ-delocalization in cyclic systems and, thereby, perhaps to σ-aromaticity.

## Possible Cases of σ-Electron Delocalization in Cyclic Systems

A first discussion of such a case was reported by Cremer and co-workers in 1974. [8] These authors investigated the conformational behavior of geminal methyl groups in $X(CH_3)_2$ with the aid of ab initio calculations. They found that for propane (X = CH_2), dimethylamine (X = NH) or dimethylether (X = O) a simultaneous rotation of the two methyl groups requires 7-8 kcal/mol. However, in the case of dimethyl carbene (X = C:) just 1.6 kcal/mol are needed for the same conformational process. Analysis of the ab initio results revealed that there is steric attraction between the methyl groups either in the staggered form **a** or the eclipsed form **b**, both shown in Figure 1. Steric attraction leads to an increase or decrease of the energy difference $\Delta = E_b - E_a$ that is due to bond eclipsing in form **b**. For X = O, NH, CH_2, the relatively large energy differences Δ result from π-electron delocalization in a cyclic orbital system involving the pseudo-π-orbitals of the methyl groups (Figure 1, middle). Form **a** is stabilized (π-aromaticity).

For X = C:, steric attraction is dominated by σ-electron interactions in form **b** (Figure 1, middle), which reduce Δ. σ-Electron interactions can be explained by considering the AOs involved in the in-plane CH bonds and the σ-type lone pair of the carbene carbon to constitute a ring of five AOs closed by H,H interactions. If the two electrons of the lone pair and the electrons of the in-plane CH bonds are assigned to the corresponding MOs, *a σ-aromatic six electron system* results. Since the electron lone pair of carbene is easy ionizable, there is σ-donation from the lone pair MO into the in-phase combination of the CH σ-bond orbitals via vicinal interactions. This leads to bonding overlap populations between the in-plane hydrogens and, hence, an over-all stabilization of conformation **b** (*σ-aromaticity*).

a   b
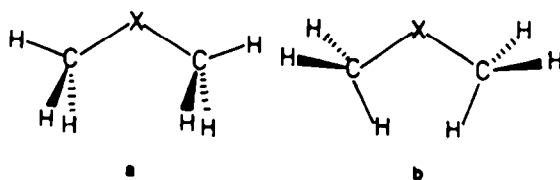
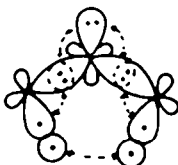X = O, NH, CH$_2$ X = C:
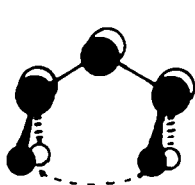
π-aromatic   σ-aromatic

system with 6 electrons

system with 10 electrons

Figure 1: Staggered (a) and eclipsed (b) conformations of geminal double rotors X(CH$_3$)$_2$. (top) - Relevant orbital interactions leading to π-aromatic or σ-aromatic stabilization. (middle) - σ-Conjugation in the case of the eclipsed conformation of dimethyl carbene. (bottom)

One might argue that anomeric rather than σ-conjugative interactions are responsible for the stabilization of form b in the case of dimethyl carbene. However, Dewar has shown [3] that anomeric interactions are accompanied by σ-conjugation. Also, anomeric interactions between the lone pair orbital of the carbene carbon and the (antibonding) CH bond orbitals would not lead to bonding H,H overlap populations. A better understanding of the interactions in dimethyl carbene will be obtained if the CC bond orbitals are also included (see Figure 1, bottom) and a Hückel-aromatic ten electron system is considered. Then, it becomes obvious that the carbene carbon takes the same role as for example the nitrogen atom in pyrrole, i.e. both donate electrons to a conjugated system.

Another example, that seems to be relevant in connection with the question of σ-electron delocalization in cyclic systems, stems from kinetic studies on the formation of N-membered cycloalkanes. [29,30] In general, the activation energy for ring formation should increase with decreasing N since ring strain increases in that order. At the same time, the activation entropy decreases since entropy favors ring closure of small rings (Ruzicka hypothesis [31]). However, in the case of the formation of small cycloalkanes with N = 3, 4, and 5, it is found that closure of a four-membered ring is exceptionally slow compared to closure of a N-membered ring with N = 3 or 5. [29,30] A careful analysis of the kinetic data has revealed [29] that this is due to irregularities in the activation enthalpies rather than the activation entropies, i.e. anomalies in the kinetics of the ring formation are due to electronic reasons. This becomes obvious when utilizing the Dewar-Zimmermann rules for transition states of pericyclic reactions [32]: A thermal pericyclic reaction is allowed (forbidden) for an aromatic (antiaromatic) transition state. Aromatic character requires the involvement of 4q+2 electrons for a Hückel system and 4q electrons for a Möbius system.

6 electrons
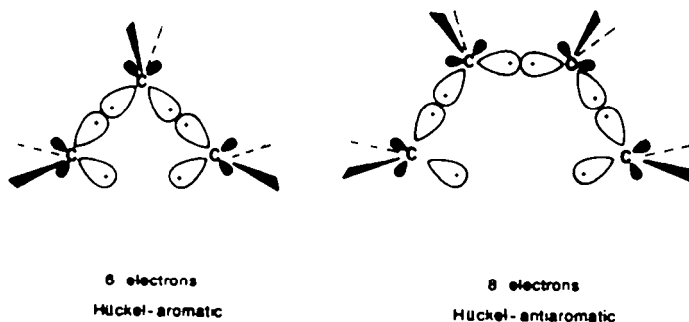Hückel-aromatic

8 electrons
Hückel-antiaromatic

Figure 2: Hückel-aromatic and Hückel-antiaromatic transition state encountered in the formation of cyclopropane and cyclobutane, respectively.

In Figure 2 it is shown that during the formation of a three-membered ring a Hückel-aromatic transition state is encountered that is energetically favorable and that leads to a relatively large reaction rate. To some extent this should also be true in the case of the transition state leading to a five-membered ring. However, in the case of the formation of a four-membered ring, a Hückel antiaromatic transition state with eight electrons is traversed (Figure 2). As a consequence, the activation energy (enthalpy) is relatively high and the reaction rate relatively small. One can conclude that σ-electron delocalization in cyclic transition states leading to cycloalkane formation is a rate determining

factor. [33]

In the early stages of CC bond formation in trimethylene (Figure 2), the singly occupied orbitals overlap in a way that is closer to π-type rather than σ-type overlap. Therefore, it is not clear whether one should speak of σ-orbitals and σ-electrons. Both this and the first example in this section reveal that guidance is needed when classifying orbitals and orbital interactions in cyclic systems.

Modes of σ-Electron Delocalization

Electrons can delocalize in various ways. They can stay predominantly in the region between bonded atoms or they can also move into regions between the bonds. The various modes of electron delocalization become obvious when analyzing the electron density distribution $\rho(\mathbf{r})$ and its associated Laplace field $\nabla^2 \rho(\mathbf{r})$, which indicates where electrons are concentrated ($\nabla^2 \rho(\mathbf{r}) < 0$) or depleted ($\nabla^2 \rho(\mathbf{r}) > 0$) in an atom or molecule.[40-43] The Laplace concentration $-\nabla^2 \rho(\mathbf{r})$ of a molecule with a classical structure adopts a pattern that is reminiscent of the electron pair model of bonding. Thus, the Laplace distribution of the electrons in a molecule contains concentration lumps that can be associated with inner shell, bonding, and lone electron pairs, i.e. a concentration lump in the bonding region can be considered as an image of the localized bond. In this way, the localized bond model is related to a property of a molecuar observable, namely the electron density $\rho(\mathbf{r})$, which actually is a consequence of electron delocalization. This, however, is not a contradiction in itself since the assignement of concentration lumps to electron pairs establishes a new ad hoc model that is no longer within the realm of quantum theory and electron delocalization. The Laplace concentration $-\nabla^2 \rho(\mathbf{r})$ of the electrons is simply used within this new model to lead a way from quantum theory with its complicated and difficult to interpret probabilities on the locations of electrons in the molecule, to the heuristic chemical concepts that are needed to explain the manifold of experimental observations. The association of concentration lumps with electron pairs does not "proof" that electron pairs and bonds are localized. It simply helps to describe the electronic structure of a molecule on the basis of the electron pair model.

In view of the model bound interpretation of the Laplacian of the electron density distribution, the following can be said. If the concentration lumps of the bonding electrons are confined to the framework of the bonds, then the only way of electron delocalization will be along the ribbon of bonded atoms. The degree of ribbon delocalization of electrons can be assessed from a quantitative analysis of $\rho(\mathbf{r})$ and $\nabla^2 \rho(\mathbf{r})$.

If concentration of electrons is also found in the region between the actual bonds, e.g., in the space inside a ring or cage, we will speak of surface or volume delocalization of electrons. This will occur if a classical description of bonding in a molecule is no longer valid and

bond delocalization has to be expected. Of course, surface and volume delocalization of electrons are model bound terms, which emerge from a $\nabla^2 \rho(r)$ based electron pair model of bonding. Within this model, there is no possibility to distinguish between σ- and π-electrons since the σ-π-concept is based on orbital theory. However, by relating typical patterns of the Laplace concentration to certain orbitals it is possible to speak of the delocalization of either σ- or π-electrons. For this purpose, we discuss in the following the Walsh-MOs of a ring, which are better suited than hybrid orbitals to interpret the various modes of electron delocalization.

While for acyclic molecules it is not difficult to distinguish between σ- and π-MOs, this becomes problematic in cyclic compounds. Therefore,
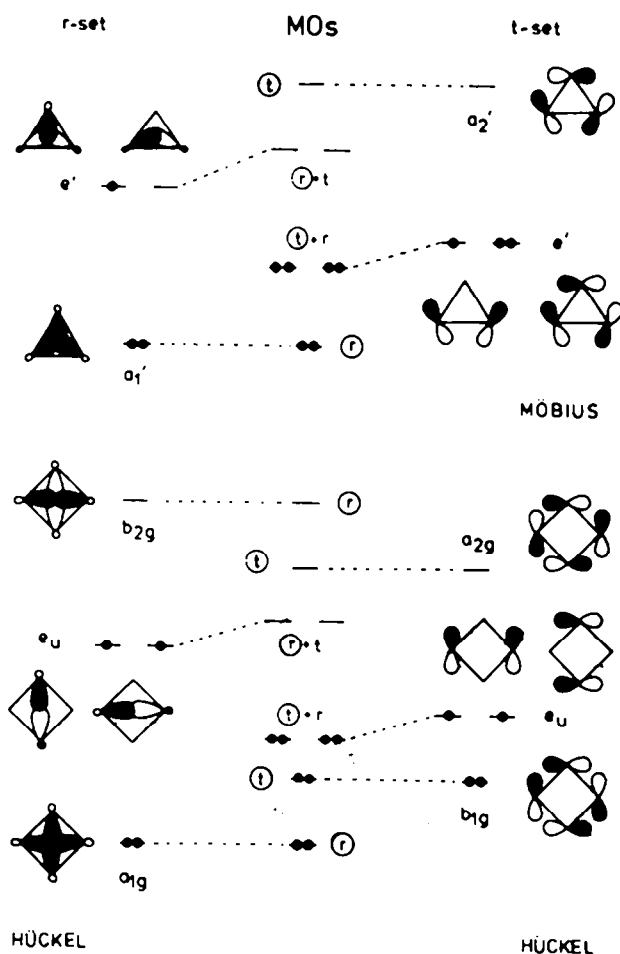

Figure 3: Radially oriented (r-set) and tangentially oriented (t-set) orbitals of cyclopropane (top) and cyclobutane (bottom). The predominat nature of the final MOs is indicated by a circle.

it is useful to introduce some definitions, which help to classify orbi-
tals in cyclic systems and which allow a distinction between various
modes of electron delocalization. For reasons of simplicity, we will
consider in the following only hydrocarbons, but a generalization to
other cylic systems is straightforward.

1. If a cycloalkane is considered to be made up of CH_2 entities each
possessing two singly occupied orbitals, two sets of orbitals can be
distinguished: a) the r-set that consists of radially (toward the ring
center) oriented sp^2 hybrid orbitals and b) the t-set that consists of
tangentially (with regard to the ring perimeter) oriented p-orbitals.

The two orbital sets are shown in Figure 3 for the three- and the
four-membered ring. The r-orbitals always lead to a Hückel system while
the t-orbitals form a Möbius system for odd N but a Hückel system for
even N. The actual framework MOs of the ring are formed by linear com-
binations of r- and t-orbitals, respectively. The ring MOs with dominant
r- or t-character (for even N) are occupied by 4q+2 electrons while
ring MOs with dominant t-character (for odd N) are occupied by 4q elec-
trons. In this way Hückel- or Möbius-aromatic subshells are formed.

2. If r-(t-)orbitals enclose angles $90° \geq \tau > 45°$ with the internuclear
connection lines of a ring (see Figure 4), then the orbitals are clas-
sified as π-orbitals. For $45° > \tau \geq 0°$, they are classified as σ-
orbitals. Accordingly, the r-orbitals are σ-MOs for N = 3 while they
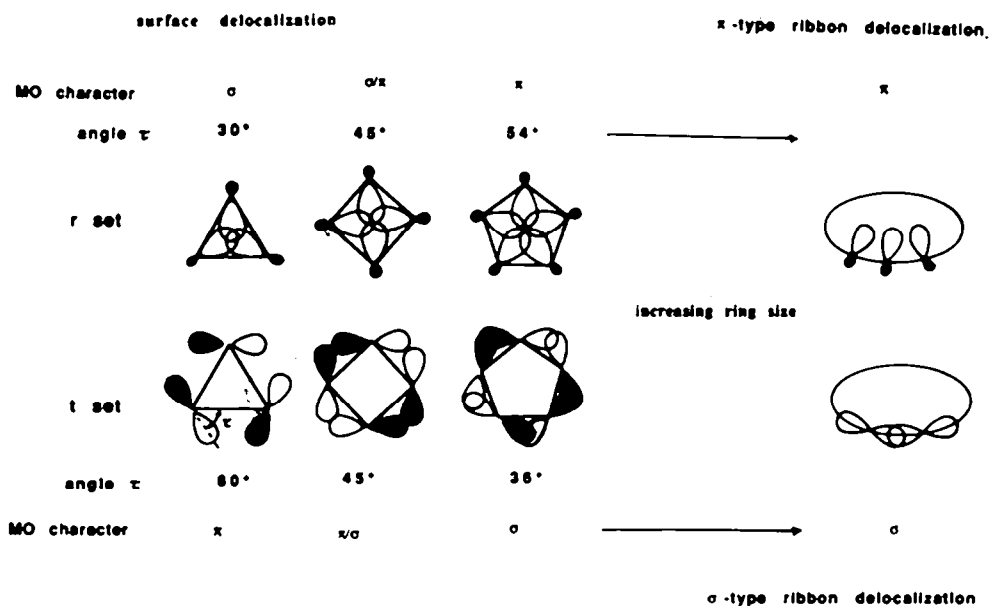

Figure 4: Characterization of ring orbitals (σ or π) with the aid
of the angle τ.

are π-MOs for N > 4. For large N, the rπ-MOs are topologically equival-
ent to the pπ-MOs of a π-conjugated system such as a cyclopolyene (see
Figure 4).

The t-orbitals correspond to π-MOs for N = 3. This is in line with the
well-known π-character of the ring bonds of three-membered rings such as
cyclopropane. [34] For N > 4 the t-orbitals form σ-MOs (Figure 4). These
definitions collapse in the case of the four-membered ring since both r-
and t-orbitals enclose angles of 45° with the interatomic connection
lines (Figure 4).

3. Electrons occupying r-type orbitals can delocalize in the surface of
the ring for small N (*surface delocalization* [35]) or along the chain
(ribbon) of ring atoms if N is large (*ribbon delocalization*, see Figure
4). Electrons occupying t-type orbitals for N = 3 delocalize on a cir-
cle enveloping the three-membered ring. For large N, they delocalize
along the ribbon of atoms.

If N is small, overlap should be better for r-orbitals than t-orbitals
while the reverse should be true for large N (see Figure 4). This sug-
gests that surface delocalization can only be found for small rings.

4. For a cage compound of the type $(CH)_N$ (N = 4: tetrahedrane), r-
orbitals are oriented toward the center of the cage. At each C atom
there are two tangentially oriented, mutually orthogonal p-orbitals. Both
r- and t-orbitals can be classified using the rules given for monocyclic
systems. For example, the r-MOs (t-MOs) of tetrahedrane correspond to σ-
MOs (π-MOs).

The actual cage MOs are formed as linear combinations of r- and t-
orbitals. Cage MOs with dominant r-(t-)character are occupied in such a
way that "aromatic" subshells are formed similar as in the case of cy-
cloalkanes. Electrons occupying MOs with dominant r-character can delo-
calize inside the cage provided N is small and there is strong overlap
between the r-orbitals (*volume delocalization of electrons* [36]).

One has to distinguish between three different modes of electron delo-
calization, namely
        i) ribbon delocalization of either σ- or π-electrons,
        ii) surface delocalization of σ-electrons or
        iii) volume delocalization of σ-electrons.
The three modes of σ-electron delocalization are shown in Figure 5.

The extent of surface delocalization depends on the overlap of the r-
orbitals, i.e. it depends on the topology and the geometry of the ring.
Inspection of the overlap in cycloalkanes reveals that significant ef-
fects resulting from surface delocalization can only be expected for
three-membered rings. *Due to their topology, three-membered rings are ex-
ceptional since they possess σ-electrons delocalized over the ring sur-
face and π-electrons delocalized in peripheral bent bonds.*

Modes of Electron Delocalization

Ribbon delocalization :

σ-electrons   π-electrons

Surface delocalization :

Cyclopropane   σ-electrons

Volume delocalization :

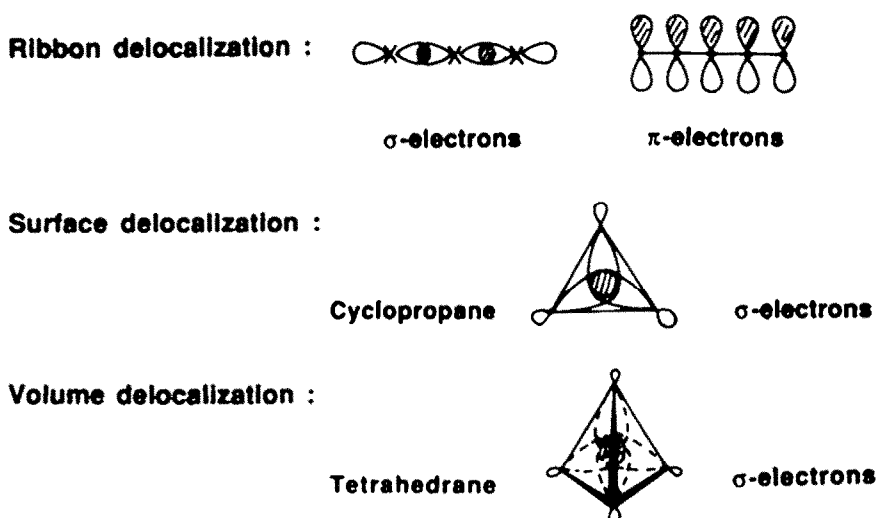Tetrahedrane   σ-electrons

Figure 5: Possible modes of electron delocalization.

Similar considerations apply to volume delocalization. If a cage consist-
ing of three-membered rings is formed (e.g. tetrahedrane), *volume delo-
calization* of σ-electrons will be possible. [36]

Surface Delocalization of σ-Electrons: Cyclopropane

The examples we have considered so far, although clearly supportive of
σ-delocalization, do not provide enough evidence to support σ-
aromaticity. This, however, is different in the case of cyclopropane.
There has been evidence indicating that the properties of cyclopropane
are exceptional. Dewar [1-3] was the first to discuss this evidence in
view of σ-electron delocalization, which may cause or, at least, may in-
fluence a number of properties of cyclopropane. Dewar's work has been
extended by Cremer and co-workers. [35-37] According to these investiga-
tions, cyclopropane differs from other cycloalkanes by

1. its relatively low strain energy (SE) that is almost identical to that of
    cyclobutane (28 and 27 kcal/mol, respectively) [3,36,37],
2. its relatively high electron density in the center of the ring [35,36],
3. its relatively short CC distances [3],
4. its relatively high CC bond strength [3,36]
5. the upfield shifts of its proton and ^{13}C NMR signals [3],
6. its electronic interactions with substituents [35],
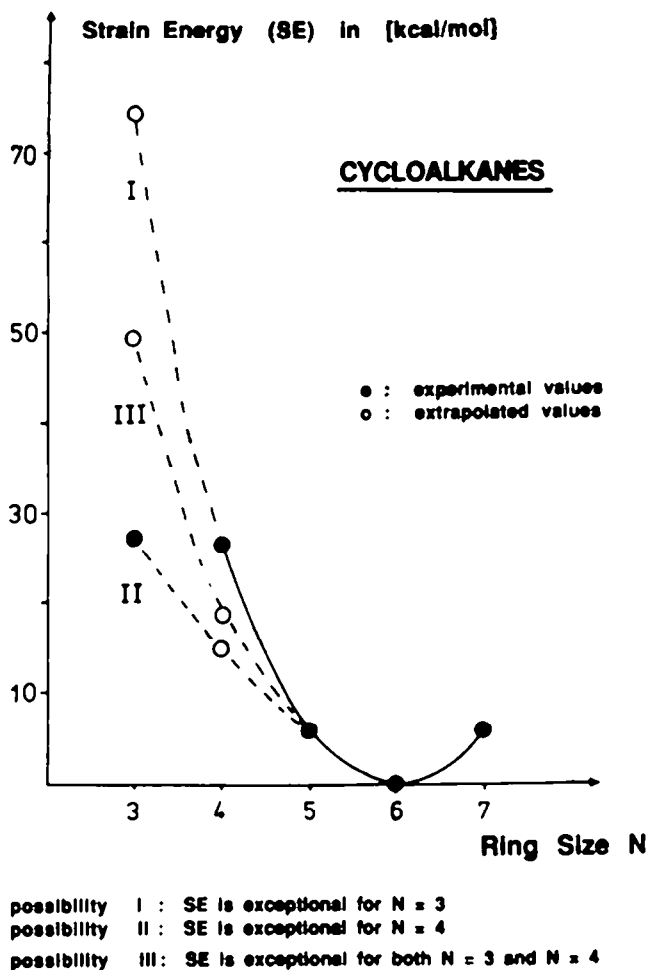7. its ability to enhance conjugation in homoaromatic systems. [35,38]

Figure 6: Dependence of the conventional strain energy (SE) on the ring size N of an N-membered cycloalkane. For an explanation of curves I, II, and III see text.

In Figure 6, the SEs of cycloalkanes with N > 8 are shown as a function of the ring size N. If the values for N = 7, 6, 5, and 4 are extrapolated to N = 3, a SE more than 40 kcal/mol larger than the experimental SE value of 28 kcal/mol will result (possibility I). If, however, SE values for N = 3, 5, and 6 are connected, the SE of cyclobutane is found about 10 kcal/mol smaller than the actual SE value of 27 kcal/mol (possibility II in Figure 6). Hence, the striking similarity of the SEs of cyclopropane and cyclobutane suggests that either cyclopropane is abnormally stabilized (I) or cyclobutane is strongly destabilized (II). Of course, there is also the possibility that both SE values are the result of special electronic effects influencing the stability of both cyclopropane and cyclobutane (possibility III in Figure 6).

The fact that the SEs of cyclopropane and cyclobutane are the same within one kcal/mol has been disguised for a long time by discussing SE values per CH_2 group ("normalized SEs" [39]) rather than total SE values themselves. If, however, normalized SE values are plotted as a function of N (see Figure 7), the same conclusions can be drawn.
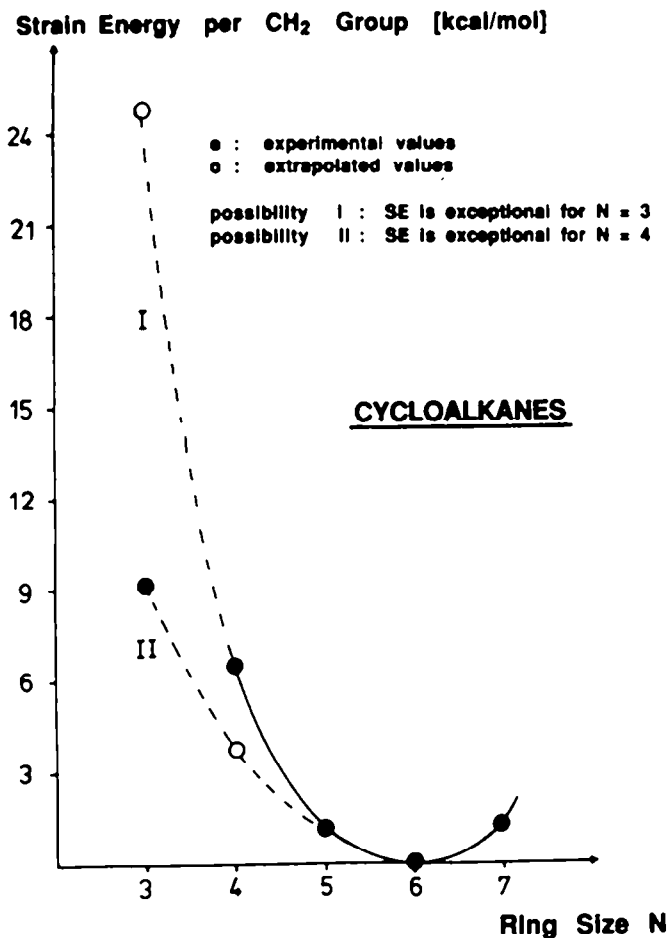

Figure 7: Dependence of the strain energy per CH_2 group on the ring size N of an N-membered cycloalkane. For an explanation of curves I and II, see text.

Dewar has analyzed the SEs of cyclopropane and cyclobutane in terms of Baeyer strain (bond angle strain) and Pitzer strain (bond eclipsing strain). [1,3] On the basis of this analysis he concluded that the three-membered ring has to be stabilized by σ-aromaticity in order to explain the discrepancy between the actual SE and the SE to be expected for a ring with CCC angles almost 50° smaller than the tetrahedral angle. This

has been criticized by Schleyer [9] who claimed that the SE of cycloprop-
ane can be understood without invoking σ-aromaticity.

Cremer and Gauss [36] reconsidered the possibility of σ-aromatic stabiliza-
tion of cyclopropane by quantitatively determining the various energy
contributions that play a role with regard to the stability of the
three-membered ring. They used methane, ethane, and propane as suitable
reference molecules and evaluated with the aid of ab initio calculations
the energetic consequences of Pitzer strain, Baeyer strain, Dunitz-
Schomaker strain (nonbonded interactions, in particular 1,3 repulsive CC
interactions), and strengthening of external bonds both for cyclopropane
and cyclobutane. For this purpose, definitions of bond length and bond
angle had to be established that are not based on sometimes misleading
geometrical features. The bond length was set equal to the length of
the path of maximum electron density ("bond path") between bonded (ring)
atoms since the bond paths in the electron density distribution can be
considered as images of the chemical bonds of a molecule. [40-43] For the
same reason, the bond angle was defined as the interpath angle. Due to
the bend of the ring bonds, the CC bond paths are 0.01 Å longer than
the internuclear distances. The interpath angles of cyclopropane (79°)
and cyclobutane (96°) turn out to be substantially larger than the geo-
metrical angles (60 and 90°, respectively). [35,36]

The use of the bond paths as images of the bonds also provided a basis
to calculate bond energies for individual bonds. It was found [36] that
the CH bonds of cyclopropane are strengthened by about 1 kcal/mol each,
in line with the increased s-character in these bonds. [44] Finally, a
bending force constant was determined that is valid for CCC bending in
the absence of 1,3 CC-interactions. [36] In this way it was possible to
separate energetic contributions resulting from Baeyer strain from those
resulting from Dunitz-Schomaker strain.

Table 1 gives the various SEs for cyclopropane and cyclobutane calculat-
ed in Ref. 36. As expected Baeyer strain is the dominant energetic fac-
tor for cyclopropane. The Baeyer SE is more than three times larger
than in cyclobutane. For the latter molecule, both Baeyer strain and Du-
nitz-Schomaker strain lead to comparable destabilization of the ring. The
energetic effects of Pitzer strain are much smaller and of the same
magnitude (4 kcal/mol) for both molecules. If CH bond strengthening is
taken into account, then the various SE contributions will add up to
the thermochemically obtained SE of cyclobutane (Table 1). This, however,
is not true for cyclopropane. A difference of -16 kcal/mol remains be-
tween the theoretically derived and the thermochemical SE. This energy
difference was associated with the stabilizing effect of σ-electron delo-
calization in the surface of the cyclopropane ring.

Surface delocalization of σ-electrons in cyclopropane is nicely reflected
by the Laplace concentration of the electrons in the plane of the cy-
clopropane ring. In Figure 8 both a perspective drawing and a contour
line diagram of the theoretically determined Laplace concentration is

Table 1.   Ab initio Strain Energies and Stabilization Energies
                 of Cyclopropane and Cyclobutane[a]

Strain	Strain Energy	
	Cyclopropane	Cyclobutane
	Destabilization Energies	
Stretching	0.5	1.0
Baeyer[b]	46.3	13.0
Pitzer	4.0	3.9
Dunitz-Schomaker	0	12.0
Total	50.8	29.9
	Stabilization Energies	
CH Strengthening	6.4	2.8
σ - Delocalization	x = 16.4	0
Strain energy	28.0 = 44.4 + x	27.1

[a]   From Ref. 36. All energies in kcal/mol.
[b]   Baeyer strain energy of cyclopropane calculated with Hooke's law
(41.3 kcal/mol) plus energy increase from anharmonicity effects calculat-
ed form a bending function with and without a cubic term for an inter-
path angle β = 79° (5 kcal/mol). Note that the strain energy of propane
(Ref. 36, Table IX) has been set erronously to 5.1 kcal/mol. This ener-
gy, however, is compensated by the increase in the CC bond energy rela-
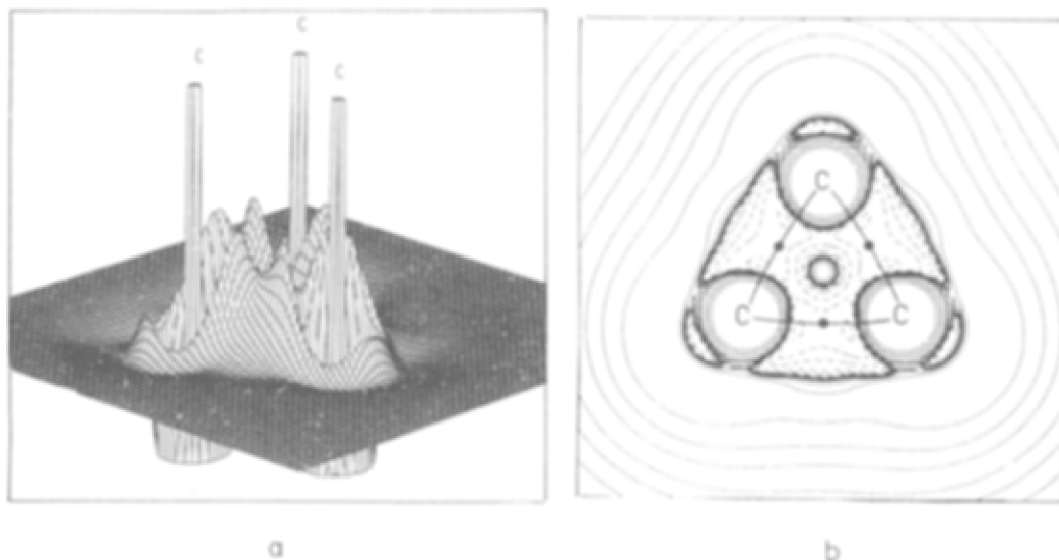tive to that of ethane, Table V, Ref. 36.

a   b

Figure 8: (a) Perspective drawing of the calculated [HF/6-31G(d,p)] La-
place concentration $-\nabla^2\rho(\mathbf{r})$ of cyclopropane, depicted in the ring plane.

Inner shell concentrations are indicated by the atomic symbol C. For a
better presentation values above and below a threshold are cut off. -
(b) Contour line diagram of the calculated [HF/6-31G(d,p)] Laplace con-
centration $-\nabla^2\rho(r)$ of cyclopropane. Dashed lines are in regions where el-
ectronic charge is concentrated and solid lines in regions where charge
is depleted. Bond paths are indicated by heavy solid lines, bond criti-
cal points by dots. Inner shell concentrations are not shown. [36]

shown. [35,36] Electrons are concentrated (dashed contour lines) along the
CC bond paths (heavy solid lines) as well as inside the ring. At the
ring center, the electron density itself possesses a value that is still
82% of the value found in the CC bond region (at the dots). For other
cycloalkanes such as cyclobutane there is depletion rather than concen-
tration of negative charge inside the ring. [35-37]

Various other authors have made similar observations when investigating
the electron density distribution of cyclopropane. Coulson and Mofitt [44]
were the first to note that there is a plateau of relatively high nega-
tive charge inside the C_3 ring. In a more recent investigation, Schwarz
and co-workers [45] found that the total electron density is increased by
0.16 e/$Å^3$ in the center of cyclopropane as compared to the electron den-
sity of the promolecule formed by three spherical free carbon atoms.
Delocalization of σ—electrons occupying the surface orbital leads to a
strong reduction of their kinetic energy which in turn triggers enhanced
AO contraction at the C atoms. This restores the virial relation, lowers
the total energy, and leads to CC bond shortening. [45] Hence, σ—electron
delocalization directly influences the length of the ring bonds.

Ahlrichs and Ehrhardt [46] have calculated shared electron numbers for al-
kanes. While bonding is reflected in these compounds by two center con-
tributions and negligible contributions from three and four center terms,
a CCC shared electron number of 0.3 is calculated for cyclopropane,
which is indicative of three-center bonding.

Putting all facts together, the following conclusions can be drawn:

Bonding in cyclopropane is exceptional since the C atoms are linked by
(see Figure 9)
        a) *a central 2-electron 3-center bond ("super-σ-bond")*
and
        b) *two peripheral 4-electron 3-center bonds ("π-bonds")*.
The classical structure of cyclopropane is misleading. It does not re-
flect the high degree of σ—electron delocalization which influences sta-
bility, geometry, magnetic properties, etc. of cyclopropane.

Pros and Cons of σ-Aromaticity

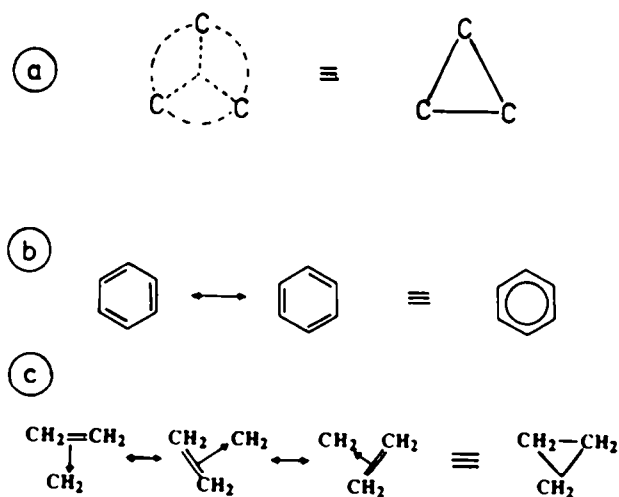The description of cyclopropane as a system with six delocalized σ—

Figure 9: (a) Nonclassical 2-electron 3-center bond and 4-electron 3-center bonds in cyclopropane. - (b) Resonance structures of benzene and shorthand notation. - (c) "Resonance structures"of cyclopropane and shorthand notation.

electrons dates back to the sixties. For example, Brown and Krishna [47] carried out PPP calculations on the excited electronic states of C_3H_6 by treating its σ-electrons in the same way as the π-electrons of benzene. These authors explicitly pointed out that there is a striking similarity between the CC σ-electrons of cyclopropane and the π-electrons of benzene. [47]

The peculiar properties of cyclopropane, in particular its relatively large stability, are causally coupled with the unusual bonding features of the three-membered ring. The question is only whether such a situation should be described with a term (aromaticity) that is heavily loaded with what has been found for cyclopolyenes with 4q+2 π-electrons. Aromaticity is expected for those systems that can only be represented in form of two or more resonance structures. For example, the electronic structure of benzene has to be described as a resonance hybrid of two classical cyclohexatriene structures (Figure 9). It is impossible to anticipate π-delocalization and π-aromaticity of benzene by just looking at one cyclohexatriene structure. It seems that there is a considerable difference between benzene and cyclopropane in so far as the latter molecule is normally represented by just one classical structure. However, does this structure provide a realistic image of bonding and electron delocalization in cyclopropane?

Dewar was the first to point out the close electronic relationship between three-membered rings and π-complexes. [48-50] According to this relationship, cyclopropane can be written as a resonance hybrid of three

equivalent methylene,ethylene π-complexes as shown in Figure 9. [51] Of course, a methylene,ethylene π-complex does not exist but the same is also true for cyclohexatriene. One might argue that resonance structures used to describe π-aromatic compounds are all "classical" in the sense that they possess just single and double bonds. However, this argument can easily be refuted. Cremer and Kraka have demonstrated that the bond paths, i.e. the paths of maximum electron density between bonded atoms, nicely describe the bonds of three-membered rings and π-complexes. [35] For π-complexes a bond path is found where chemists draw the arrow between basal group, e.g. ethylene, and the apical group, e.g. a halogen cation. Hence, the π-complex notation is as realistic as any other representation of molecular structure and, accordingly, it can be placed at the same level with the "classical" structures.

Actually, the π-complex description of cyclopropane is better suited to reflect its properties than the notation normally used in chemistry. It indicates that
a) there are different types of CC bonds in cyclopropane,
b) the π-character of the CC bonds,
c) the possibility of resonance stabilization
d) a possible shortening of the CC bonds,
e) increased s-character in the CH bonds and a corresponding CH bond strengthening, etc.
In conclusion, one can consider cyclopropane in the same way as a resonance hybrid as this is done for benzene. In this respect, the classical structure of cyclopropane is the shorthand notation for the three equivalent resonance structures shown in Figure 9.

This discussion clearly shows that a rejection of the term σ-aromaticity on the grounds that this is inconsistent with common understanding of the term aromaticity is not justified. It needs a basic assessment of the concept of aromaticity in order to decide on the usefulness of the term σ-aromaticity. We will do this by recalling how π-aromaticity is defined. [16,52]

π-Aromaticity describes a ground state property of the molecule. It is given when
a) $4q+2$ π-electrons are delocalized in a cyclic system (Hückel rule),
b) the Dewar resonance energy of the π-system, i.e. the difference between the delocalization energy of the aromatic system and that of an acyclic system with the same number of π-electrons in a localized form, possesses a significant value (e.g. > 3 kcal/mol),
c) partial or complete bond equalization is observed, and
d) its magnetic properties lead to a diatropic ^{1}H-NMR spectrum.

If these criteria are applied to cyclopropane, the following picture will develop.
    a) There are six delocalized σ-electrons that form the ring
    bonds of cyclopropane. Two of them establish a Hückel-aromatic,
    the remaining four a Möbius-aromatic system (Figure 3). In what-

ever way the electron count is carried out, an aromatic ensemble
of electrons is obtained.

b) Calculation of the Dewar resonance energy implies a comparison
with a suitable acyclic reference compound that contains the same
number of CC σ-bonds. In addition it requires the separation of
energetic effects resulting from ring strain on the one hand and
σ-aromaticity on the other hand. This has been done for cyclo-
propane and a delocalization energy of 16 kcal/mol has been ob-
tained. [36]

c) The CC bonds in cyclopropane are all equivalent. In addition,
they are considerably shorter (0.03-0.05 Å) than those of other
(cyclo)alkanes.

d) Due to the high s character of the CH bonds, one would ex-
pect the ^{1}H-NMR signal for cyclopropane to appear downfield from
the signals of the CH_2 protons of alkanes. However, it appears
upfield by 1 ppm (δ - 0.22 ppm). [53] Also, the ^{13}C-NMR signal is
shifted by 20 ppm upfield from other aliphatic ^{13}C-NMR signals.
[54] It was found that the isotropic shift of -3.8 ppm from Me_4Si
is the consequence of that component of the chemical shift ten-
sor for CH_2 that is perpendicular to the ring plane. The value
of this component (-36 ppm from Me_4Si) is indicative of strong
circulation of electrons in the ring plane. [54] Both the [1]H- and
the ^{13}C-NMR shifts of cyclopropane suggest σ-electron delocaliza-
tion in the ring.

Seeing points a) to d) in one context, it seems to be appropriate to
consider cyclopropane as being σ-aromatic. Nevertheless a number of ca-
veats have to be raised before accepting this classification.

1. Argument a) applies in some way to all cycloalkanes since all pos-
sess aromatic subshells. Only if the total number of σ-electrons, inde-
pendent of the MOs they occupy, is considered, can a distinction between
odd- and even-membered rings, e.g. between cyclopropane and cyclobutane,
be made.

2. Clearly, the definition of the σ-aromatic character of cyclopropane
heavily depends on the notion of ring strain which is only vaguely de-
fined. [37] Cremer and Gauss [36] have chosen the classical definition of
ring strain that considers bonds as elastic springs which can be de-
scribed by Hooke's law. In the future this way of describing strain may
be replaced by more sophisticated ones that may account for surface del-
ocalization in three-membered rings differently.

3. The CC bonds in cyclobutane are also equal and the same is true for
many other cycloalkanes. Therefore, the criterion of bond equalization is
not a valid criterion in the case of σ-conjugation. Also, bond shorten-
ing may be the result of bond bending rather than σ-aromatic interac-
tions.

4. The anisotropy effect of a bent bond is not known. It could be pos-
sible that the observed NMR shifts are a result of anisotropy effects
of the CC bonds rather than σ-aromatic character of cyclopropane.

Comparing the pros (a to d) and the cons (1 to 4) one is left with the impression that with the acceptance of σ-aromaticity all properties of cyclopropane are easily rationalized while the rejection of this concept entails the unpleasant task to look for additional explanations. Certainly, this is a reason to lean to an acceptance of the notion of σ-aromaticity. However, before accepting σ-aromaticity one should ask for the predictive power and the applicability of the concept of σ-aromaticity. What can be gained by expecting aromatic (antiaromatic) electron interactions not only in the case of cyclic π-conjugation but also in the case of cyclic σ-conjugation?

The concept of π-aromaticity can be applied to cyclopolyenes of different size and different composition. [52] This is not true for the concept of σ-aromaticity. From the discussion given above it is clear that the latter applies only to three-membered rings. In a five-membered ring, effects should be already too small to lead to any significant changes in the molecular properties. [55] Among the three-membered rings, only cyclopropane can be discussed. For rings with hetero atoms, e.g. oxirane or aziridine, a separation of strain effects from σ-delocalization effects is not possible at the moment. Therefore, the concept of σ-aromaticity seems to be only applicable to cyclopropane and multicyclic systems containing one or more cyclopropane units. Even in the latter case not much is known at the moment and future research has to establish the predictive value of the concept.

One might reject the term σ-aromaticity since it applies essentially to one compound, namely cyclopropane. Yet this view is also not completely valid. The concept of σ-aromaticity could be very useful to rationalize the properties of substituted cyclopropanes [35], those of the Si, Ge, etc. analogues of cyclopropane [36,56], those of homoaromatic compounds [38], etc. Hence, the criterion of applicability does not lead to a clear answer whether to exclude or to support the term σ-aromaticity.

One way out of this dilemma is to explain the peculiar properties of three-membered rings by referring to surface delocalization of σ-electrons rather than using the term σ-aromaticity. Surface delocalization
a) is easily verified by analyzing electron density distribution and associated Laplace field of a molecule (compare with Figure 8),
b) is in line with the Walsh-MO description of three-membered rings,
c) indicates a stabilization of the system,
d) helps to rationalize observed bond lengths, magnetic properties, etc.,
e) leads to predictions with regard to substituent effects [35],
f) can be used to describe three-membered rings with hetero atoms. [56]

In addition, surface delocalization is a term that denotes a certain pattern of the Laplacian of an *observable* quantity, namely the electron density distribution $\rho(r)$. This particular pattern can also be found in other cases, for example, for nonclassical hydrocarbons or boranes. Hence, surface delocalization is more general and does not necessarily

imply σ-aromaticity. The same holds for volume delocalization of σ-
electrons. It helps to rationalize the properties of molecules such as
tetrahedrane [57], capped annulenes or other cage compounds. However, it
does not necessarily indicate three-dimensional σ-aromaticity.

There is, however, one general argument in favor of the use of the term
σ-aromaticity despite its inherent imponderabilities. This has to do with
the pedagogical value of using this term. The model bound idea that σ-
bonds and σ-electrons are localized has found such wide acceptance, that
it is now generally regarded as physical (chemical) reality. Certainly,
by using the terms σ-delocalization and σ-aromaticity this fallacious be-
lief is shaken and, hopefully, it will quickly be abandoned. In view of
M.J.S. Dewar's distinct propensity to change petrified models and mis-
leading simplifications it is quite possible that he chose these terms
in order to put a spotlight on some long overlooked chemical facts that
clearly evidence σ-conjugation and σ-delocalization.

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