crownlike geometry with pseudoaxial methyl is observed as the preferred local conformation of the minor epoxides (**19**, for example) obtained from *E*-disubstituted 3-methylcycloalkenes.

Transition-state geometries resembling any of these (*E*)-olefin conformers will encounter considerable transannular interactions as rehybridization proceeds. Thus, several factors complicate the correlation of favored ground-state and transition-state local conformation in reactions involving *E*-disubstituted cycloalkenes and bulky reagents. As noted earlier, our generalization is intended for use only with (*E*)-olefins having allylic *alkyl* substitution. Although there are examples in the literature where allylic OH directs epoxidations in the same stereochemical sense as in our system with allylic CH_3,[11b,c] the effect is smaller and not as reliable. This is evident from the nonselective epoxidation of **20**. Predictions in the (*E*)-olefin series must be made with caution.[13]

On the other hand, the behavior of medium-ring (*Z*)-alkenes having an allylic (C_3) branch point is easily predicted as long as olefin C_2 does not have additional substituents. In all such cases described in this paper or in earlier work,[3g,11b,c,14] the major product

can be rationalized by least hindered attack on a local conformer similar to **1**. Similar results have been observed for systems having either allylic hydroxyl or alkyl substitution, so the effect must be relatively large.

We believe that consistently high selectivity results from a good match between preferred local ground-state and transition-state geometry. Both CH_3 and R occupy innocuous locations near the olefin plane in conformers such as **1**, and there is sufficient flexibility to minimize transannular effects as rehybridization occurs. The selectivity is often large enough (>20:1 product ratios) to justify stereochemical predications based on the dominant local conformer even in more complex systems where other important conformational factors may not be known.

Supplementary Material Available: Table I, reduction of 2-methylcycloalkanones with $LiAlH_4$, Table II, formation of medium-ring cycloalkene by mesylate elimination, Table III, epoxidation of allylically substituted medium-ring olefins with mCPBA, Table IV, osmylation of allylically substituted *Z* medium-ring olefins, and Table V, osmylation of medium-ring allylically substituted (*Z*)-olefins, and complete experimental details and spectra data (44 pages). Ordering information is given on any current masthead page.

(13) We have described an example of osmylation of an *E*-trisubstituted alkene which occurs with high selectivity *opposite* to what is predicted using a local geometry as in **2**.[3g] A transannular electron-deficient π-system appears responsible for the anomaly.

(14) (a) Cope, A. C.; Wood, G. L. *J. Am. Chem. Soc.* **1963**, *85*, 3601 (allylic methyl). (b) Poulter, C. D.; Friedrich, E. C.; Winstein, S. *Ibid.* **1969**, *91*, 6892. (c) Friedrich, E. C.; Biresaw, G. *J. Org. Chem.* **1982**, *47*, 2426. (d) Kawabata, N.; Nakagawa, T.; Nakao, T.; Yamashita, S. *Ibid.* **1977**, *42*, 3031 (allylic OH).

(15) Brown, H. C.; Varma, V. *J. Org. Chem.* **1974**, *39*, 1631.

Description of Conjugation and Hyperconjugation in Terms of Electron Distributions

R. F. W. Bader,*[†] **T. S. Slee,**[†] **D. Cremer,**[‡] **and E. Kraka**[‡]

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and the Lehrstuhl für Theoretische Chemie, der Universität zu Köln, 5000 Köln 41, West Germany. Received January 10, 1983

Abstract: This paper presents a description of CC bonds in hydrocarbons in terms of the properties of the charge density ρ at a bond critical point. This is the point (r_c), where ρ attains its minimum value along the path of maximum density (the bond path) linking the nuclei of neighboring atoms. A bond order is defined in terms of ρ_b, the value of ρ at r_c. A measure of the deviation of the charge distribution of a bond path from axial symmetry is provided by the bond ellipticity $\epsilon = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 ($|\lambda_1| > |\lambda_2|$) are the two negative curvatures of ρ at r_c. The value of ϵ is zero for the CC bond in ethane of order 1 and attains some maximum value for CC bonds of order 2. The ellipticity thus provides a quantitative measure of the π character of these bonds and the plane of the π distribution is uniquely specified by the direction of the axis associated with the curvature of smallest magnitude, λ_2. The values of ρ_b and ϵ enable one to translate the electronic effects predicted by orbital models into observable properties of ρ. Conjugative interactions between single and double bonds are reflected by $n > 1$ and $\epsilon > 0$ for the CC bonds of formal order 1. The major axes of the ellipticities induced in the single bonds are parallel to the corresponding axes of the double bonds. The largest effects are found for systems with an aromatic delocalization of π electrons. Antiaromaticity is reflected by a decrease in the value of n and ϵ for the intervening single bonds. Hyperconjugation is also reflected by a value of $n > 1$ and an $\epsilon > 0$ for the participating CC single bond. The CC bonds of a cyclopropyl fragment also exhibit substantial ellipticities as a consequence of the proximity of a ring critical point to the bond critical points in three-membered ring systems. The conjugative interaction of a three-membered ring with an unsaturated system as rationalized in terms of the Walsh orbitals for cyclopropane is here given a physical basis in terms of the topological properties of the charge density.

The topology of a molecular charge distribution yields a single unified theory of molecular structure, one that defines atoms, bonds, structure, and the mechanisms of structural change.[1,2] The same theory defines all average properties of an atom in a molecule.[3]

One may unambiguously assign a chemical structure to a molecule by determining the number and kind of critical points in its electronic charge distribution, points where $\nabla\rho = 0$. The

same information enables one to determine whether or not the structure is topologically stable with respect to the making and/or breaking of chemical bonds. If it is unstable, one may predict the possible ensuing structural changes. The determination of

[†] McMaster University.
[‡] Universität zu Köln.

(1) (a) Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389–1395. (b) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *J. Chem. Phys.* **1979**, *70*, 4316–4329.
(2) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893–948.
(3) (a) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871–2883. (b) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63–124.

the kind and number of critical points and thereby the structure of a molecule is computationally a straightforward procedure, being comparable in its simplicity of implementation and computer time requirements to a Mulliken population analysis. It is shown that chemical information about a molecular system is usefully summarized and economically extracted from its charge distribution in terms of the properties of ρ at its critical points.

In this paper a bond order and a bond ellipticity for carbon–carbon bonds are defined in terms of the value of the charge density ρ and its principal curvatures at a bond critical point. The ellipticity measures the deviation of the charge distribution of a bond path from axial symmetry. In terms of the orbital model of electronic structure, the ellipticity provides a quantitative measure of the π character of a bond and the direction of its major axis. Predictions of partial π character based upon conjugation and hyperconjugation models of orbital theory may thus be tested in terms of a property of the total charge distribution.

Also, the π character of cyclopropane bonds, first suggested in a molecular orbital study by Walsh,[4] is revealed by the significant ellipticities of these bonds which occur as a consequence of the topological properties of a molecular charge distribution in three-membered ring structures. It will be shown that the value of the ellipticity provides a sensitive measure of the susceptibility of a system to a change in structure. Predictions of structural change in non-classical carbocations containing three-membered rings are presented in the following paper[5] on the basis of the properties bond order, bond ellipticity, and the curvature of the bond path, all defined in terms of a system's charge distribution.

Molecular Structure

The definitions of structure and structural stability have been previously illustrated in a study of hydrocarbon molecules.[6] As mentioned above, an important general observation of the present paper is the presence of substantial ellipticities in the CC bonds of three-membered rings. Since the following paper deals specifically with the chemical consequences of this observation with regard to structural stability, the cyclopropane system is used here to illustrate how the properties of ρ at its critical points serve to characterize structure and its change. The first derivatives of ρ vanish at a critical point. The position of such a point is denoted by the vector $\mathbf{r}_c$. One can easily calculate the second derivatives of ρ at a critical point and from them determine the three principal curvatures of ρ at $\mathbf{r}_c$ (denoted by λ_i) and their associated (mutually orthogonal) axes of curvature.[7] A critical point is then characterized by its *rank*, the number of nonvanishing curvatures of ρ, and its *signature*, the algebraic sum of the signs of the curvatures. A negative (positive) curvature means that ρ is a maximum (minimum) at $\mathbf{r}_c$ along the associated axis of curvature.

The nuclear-electron attractive force is the dominant force in a molecule and the form of a charge distribution is the result of the balance achieved in the competition of the nuclei in the system for its charge density. The major consequence of the dominance of this force is that ρ is a local maximum only at the position of a nucleus (see Figure 1).[2,6] All three curvatures of ρ at such a critical point are negative and it is a $(3,-3)$ critical point.[8] To determine the region of space dominated by a particular nucleus, one appeals to the global properties of the gradient vector field
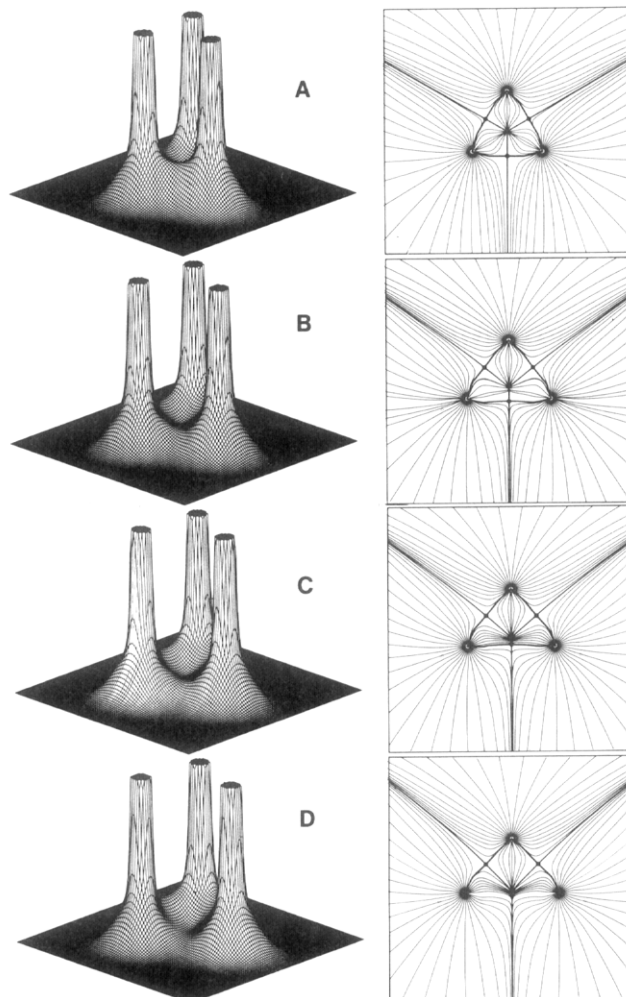

Figure 1. Displays of ρ and its associated gradient vector field in the plane of the carbon nuclei of cyclopropane at the STO-3G level of approximation. (A) The equilibrium geometry,[21] $R(CC) = 1.50$ Å. All trajectories terminate at one of the three carbon nuclei with the exception of the three pairs of trajectories that terminate at each bond critical point and mark the intersections of the interatomic surfaces with this plane. These trajectories, and those which originate at each bond critical point and define the bond paths, are indicated by heavy lines. (B) A CC separation has been lengthened by 0.30 Å reducing the symmetry to C_{2v}. The ring critical point, which serves as the origin of all the trajectories in the ring surface, has approached the critical point of the extended bond. A profile of ρ along the C_2 symmetry axis exhibits a shallow minimum at the ring critical point followed closely by a low maximum at the critical point of the extended bond. (C) A further extension of the CC bond to 1.88 Å. The ring and bond critical points have merged to yield a singularity in ρ. Their corresponding minima and maxima in the profile of ρ along the C_2 axis have been replaced by a single point of inflexion. At this geometry the CC bond is broken. (D) A still further increase in the CC separation. The singularity has vanished and ρ decreases monotonically along the C_2 axis from its maximum value at the uppermost carbon nucleus.

(4) (a) Walsh, A. D. *Nature* (London) **1947**, *159*, 712–713. (b) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179–190.

(5) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C.; Nguyen-Dang, T. T.; MacDougall, P. J. *J. Am. Chem. Soc.*, following paper in this issue.

(6) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 940–945.

(7) The collection of the nine second derivatives of ρ at $\mathbf{r}_c$ define a real symmetric matrix. This matrix can be diagonalized to yield three eigenvalues λ_i, the principal curvatures of ρ at $\mathbf{r}_c$, and three associated eigenvectors, $\mathbf{u}_i$, the principal axes of curvature. The term curvature is used in place of eigenvalue to emphasize the physical significance of the latter term in the present context.

(8) The maximum in ρ at a nuclear position is not a true critical point as $\nabla\rho$ is discontinuous there as a consequence of the cusp condition on ψ. However, there always exists a function homeomorphic to ρ that coincides with ρ almost everywhere, and for which the nuclei are $(3,-3)$ critical points.

of ρ. The gradient vector $\nabla\rho(\mathbf{r})$ points in the direction of maximum increase in ρ. Thus each such vector is directed toward some neighboring point. By calculating $\nabla\rho(\mathbf{r})$ at a continuous succession of points where each point is determined by the direction of $\nabla\rho$ at the preceding one, a trajectory of $\nabla\rho(\mathbf{r})$ is obtained—the path traced out by the gradient vector of ρ. In general this trajectory will terminate at a nucleus. All points on the path "belong" to that nucleus as they lie on a line along which ρ increases continuously to some maximum value at the nucleus (Figure 1). The nucleus is an attractor and the basin of the attractor is the space traversed by all the trajectories which terminate at the attractor. *The atom is the union of an attractor and its basin.* Since a nucleus is a three-dimensional attractor (all three curvatures of ρ are negative at a nucleus) its associated

basin is a region of three-dimensional space.

When the basins of two atoms are neighboring there must necessarily exist a surface of demarkation between them. Points on this surface, the interatomic surface, cannot belong to either nucleus and instead each one lies on a trajectory that terminates at an interjacent critical point rather than at either of the neighboring nuclei. This is a (3,–1) critical point. Its two negative curvatures denote the existence of a surface in which $\rho(\mathbf{r})$ is a maximum at the critical point. An interatomic surface is therefore defined by all the trajectories $\nabla\rho(\mathbf{r})$ which terminate at this critical point—one which acts as an attractor in two dimensions. The positive curvature of such a critical point is associated with the axis perpendicular to the interatomic surface along which ρ is a minimum at $\mathbf{r}_c$. This axis defines the initial directions of two trajectories of $\nabla\rho$ that originate at the critical point and each of which terminates at a neighboring nucleus. They define a line linking the two nuclei along which ρ is a maximum with respect to any neighboring line. They define the bond path.

Thus the interaction of two three-dimensional attractors results in the formation of a two-dimensional attractor. The distribution of charge in the basin of the two-dimensional attractor, the interatomic surface, is determined by and serves to characterize the state of balance achieved between two competing centers of force. The total force acting on the charge density of the atom (the Ehrenfest force), for example, is determined by an integration of the stresses operative in its atomic surface.[3] The properties of ρ at a (3,–1) critical point determine the interatomic surface and the bond path and they therefore serve to summarize the nature of the interaction between the two atoms that create it. These properties, as previously shown, readily distinguish different types of bonding[9] and they play the crucial role in the theory of structural change presented here.

A molecular graph is the network of bond paths linking pairs of neighboring nuclei. The molecular graph for a molecule in an equilibrium geometry is identified with the corresponding network of chemical bonds.[2,6] In addition to yielding the anticipated ring structure for cyclopropane (Figure 1), the molecular graph indicates that the CC bonds are curved, in that the bond paths lie outside of the geometrical perimeter of the ring. For a curved bond, *the bond path length*, R_b, exceeds the equilibrium value R_e of the internuclear separation.[10]

This same molecular graph for cyclopropane is obtained for any and all displacements from its equilibrium geometry within some neighborhood of this geometry (see Figure 1B for a neighboring geometry of cyclopropane). A molecular graph with these generic properties denotes a *stable molecular structure*.[2,6]

The presence of a bonded ring of atoms as found in cyclopropane necessitates the existence of a (3,+1) or ring critical point in the interior of the ring. The axes associated with the two positive curvatures define a ring surface and ρ is a minimum in the ring surface at $\mathbf{r}_c$ (Figure 1A). The single negative curvature of ρ at a ring critical point, directed along an axis perpendicular to the ring surface, is the intersection of the interatomic surfaces of the atoms forming the ring.

Changes in Structure

The succession of diagrams in Figure 1 illustrates the important topological changes in ρ that are associated with the opening of a ring structure by the lengthening of a ring bond. Since these changes are universal it is unnecessary to follow any minimum-energy reaction path. Instead, as one CC separation $R(CC)$ is increased, the remaining bond lengths and angles are relaxed to standard values. The value of ρ at the corresponding bond critical

point decreases as $R(CC)$ is increased and, corresponding to this lessening of charge density in the interatomic surface as the two atoms separate, the positive curvature at the critical point, λ_3, becomes more pronounced. The distribution of charge between this bond critical point and the ring critical point becomes increasingly flatter. The magnitude of the negative curvature of the bond critical point that is associated with the axis directed at the ring critical point λ_2 decreases and, simultaneously, the positive curvature of the ring surface along this same axis is also decreased (Figure 1B). The ring critical point approaches the bond critical point in position and in value. All these effects are enhanced as $R(CC)$ is increased until at some particular value, the two critical points coalesce to form a new critical point (Figure 1C). For the bond and ring critical points to so merge, the negative curvature λ_2 of the bond critical point and one of the positive curvatures of the ring critical point must simultaneously approach zero and vanish upon coalescence. Thus the newly created critical point is of rank two, the curvature along the axis of approach of the two critical points having vanished. The charge density exhibits a singularity at this point—both its first and second derivatives along one axis vanish. This critical point is unstable, as is the new molecular structure it defines. They exist for this single geometry along the chosen reaction path. For a further infinitesimal increase in $R(CC)$, this critical point vanishes and the two carbon nuclei are no longer linked by a line of maximum charge density. The resulting open molecular structure is again structurally stable (in the sense defined above) as its molecular graph persists over a region of nuclear geometries. Thus a change from one stable structure to another is accomplished by the passage of the system through a nuclear configuration whose associated structure is topologically unstable and transitional in form between that of the initial and final structures.[2]

Figure 2 summarizes the changes in the values of ρ and in its curvatures at the bond and ring critical points for the opening of the cyclopropane ring. Figure 2a shows the approach of and ultimate simultaneous vanishing of the negative and positive curvatures of the two critical points that lie on their axis of approach. In addition to one curvature at each critical point approaching zero as d, the distance between them, decreases, the remaining pairs of positive and negative curvatures at the two critical points approach each other in value and become equal when the singularity is formed (Figure 2b). The onset of the formation of the singularity is signalled by the sudden increase in the ratio of the two negative curvatures of ρ perpendicular to the bond path at the bond critical point. This is illustrated in Figure 2c which shows the behavior of the quantity $\epsilon = \lambda_1/\lambda_2 - 1$. As is apparent from Figure 2c and as discussed more fully in the following paper,[5] the value for ϵ is a measure of the susceptibility of a bond in a ring structure to rupture.

What is important about the above description of the changes in the charge density is the new perspective that it gives regarding a change in structure; the change in the charge distribution for motion along the reaction coordinate must result in the coalescence of a bond and a ring critical point if a ring structure is to be opened.[11] Clearly, if in a given equilibrium geometry two such critical points are found to be in close proximity and have nearly identical values of ρ, the associated structure is potentially unstable. The distribution of charge between the two critical points is then relatively flat with little curvature and is altered with little change in energy.

The development and application of this theory of structural change is facilitated through the definitions of a bond order and a bond ellipticity (the quantity ϵ) in terms of the properties of ρ at a bond critical point. It is shown that within this classification scheme, labile CC bonds are characterized by bond orders less than one and substantial ellipticities.[5]

Bond Order

For carbon–carbon bonds, ρ_b, the value of ρ at a bond critical point, increases as the equilibrium internuclear separation R_e

(9) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952.

(10) Chipman et al. (Chipman, D. M.; Palke, W. E.; Kirtman, B. *J. Am. Chem. Soc.* **1980**, *102*, 3377–3383) have recently discussed bent bonds and orbital following in hydrides in terms of self-consistent valence bond orbitals. Their conclusion, that in general orbitals lag behind a nuclear bending motion, is, in such molecules, in agreement with an increase in curvature of the bond path found in the bending of H_2O, NH_3, and BH_3 (Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040–3045) and of the HCH angle in ethylene.[9]
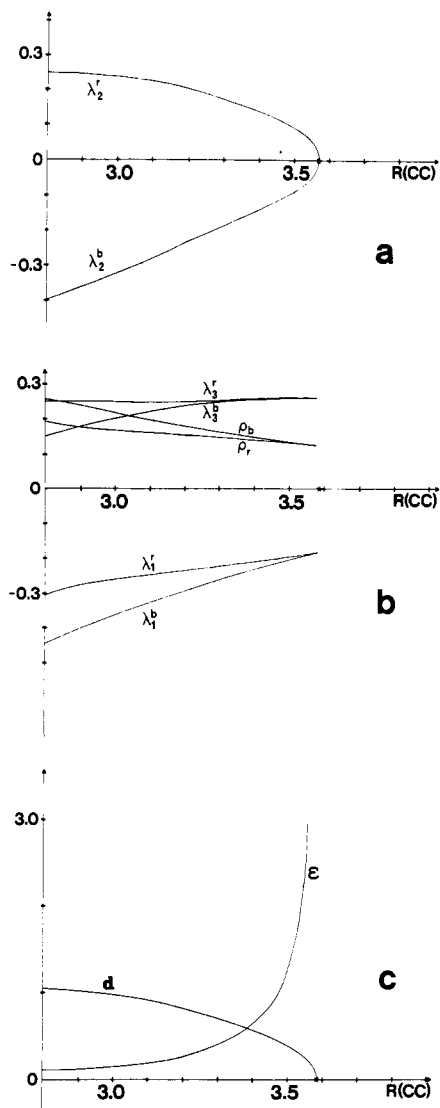
(11) Collard, K.; Hall, G. G. *Int. J. Quantum Chem.* **1977**, *12*, 623–637.

Figure 2. Plots of the curvatures of ρ at the bond and ring critical points vs. the extension of a CC internuclear separation in cyclopropane. All quantities are in au. (a) The curvatures of the bond (λ_2^b) and ring (λ_2^r) critical points that vanish upon the coalescence of the two critical points to form the singularity in ρ. At the STO-3G level this occurs when $R(CC) = 3.55$ au = 1.88 Å. The singularity exists for this one value of $R(CC)$. If $R(CC)$ is decreased from this value the singularity bifurcates into a bond and a ring critical point and the ring structure (Figure 1B) is obtained. An increase in $R(CC)$ causes the singularity to vanish and the open structure (Figure 1D) is obtained. (b) The approach to common values of the remaining pairs of curvatures of ρ at the bond and ring critical points in the opening of the cyclopropane ring. The approach to a common value by the charge density at the bond and ring critical points is also shown. (c) The distance d between the bond and ring critical point and the ellipticity ϵ of the extended bond as a function of $R(CC)$. Both d and ϵ have the same scale. Note the sudden increase in $\epsilon = (\lambda_1^b/\lambda_2^b - 1)$ as the geometry of the system approaches that at which the singularity in ρ is formed and the CC bond is broken.

decreases. A plot of ρ_b vs. R_e (calculated) for ethane, benzene, ethylene, and acetylene[12] is best described by a linear relation.[9] CC bonds for which $R_b = R_e$ in neutral hydrocarbons obey this relationship well. Bonds with curved bond paths are observed to have shorter R_e values than bonds with the same value of ρ_b. For example, ethane and cyclopropane have the same ρ_b values, but

Table I. Constants for Bond Order Relation

basis set	$n = \exp\{A(\rho_b - B)\}$		
	A	B	σ^a
STO-3G	1.23	1.63	2.9×10^{-2}
4-31G	0.904	1.52	2.7×10^{-3}
6-31G	0.939	1.52	3.1×10^{-3}
6-31G*	0.957	1.70	1.8×10^{-2}

^{a} Root-mean-square deviation of the ln n values. σ is determined for the fit of the standard bond orders, 1.0, 2.0, and 3.0.

their R_e values differ by 0.036 Å at STO-3G. Thus the points for curved CC bonds fall below the line representing the linear relationship between ρ_b and R_e. As illustrated previously, if ρ_b is plotted vs. the bond path length (R_b) rather than R_e, curved bonds are brought into better agreement with a linear relationship.[13]

Previous assignments of bond order[14] or bond valence[15] have been used to obtain a bond order-bond length relationship. In using ρ_b rather than R_e in such a relationship one obtains a different measure of bond order, since ρ_b is in general linearly related to R_b and not R_e. The ρ_b values yield a classification on the basis of the nature of the interaction between the bonded atoms, one which is directly related to the distribution of electronic charge that results in electrostatic equilibrium, rather than to the value of R_e at which this equilibrium is attained. Thus bonds with similar chemical characteristics are grouped together by their ρ_b values in spite of differences in their R_e values.[9] For example, in the molecules C_6H_6, $C_3H_3^+$, $C_7H_7^+$, and $C_5H_5^-$ which satisfy the Hückel $4n + 2$ rule of aromaticity, all the CC bonds have ρ_b values of 1.98 ± 0.02 Å^{-3} and bond path lengths within 0.01 Å of 1.39 Å.

If CC bonds in ethane, ethylene, and acetylene are assigned (Lewis) bond orders $n = 1, 2, 3$, respectively, then the simplest relationship between n and ρ_b that yields a good fit is of the form

$$n = \exp\{A(\rho_b - B)\} \qquad (1)$$

The values of A and B for various basis sets are listed in Table I. For convenience, a value of $n = 1$ is obtained for ethane by setting $B = \rho_b(\text{ethane})$ for each basis set. This does not cause any significant change in the line or its fit. For example, the least-squares value for B and the value of $\rho_b(\text{ethane})$ are respectively 1.636 and 1.628 Å^{-3} for the STO-3G basis and 1.514 and 1.518 Å^{-3} for the 4-31G basis. For all the basis sets the CC bond in benzene is assigned an order of 1.6 by eq 1. This value is intermediate between the Lewis value of 1.50 and the Hückel molecular orbital value of 1.67.

There is a notion of simple molecular orbital theory that may be a cause of concern in employing ρ_b as a measure of bond order. One may be led to conclude that since a bond critical point can lie in the nodal surface of a π orbital, the value of ρ_b may not be dependent upon the π orbital occupancy. As stressed by Mulliken,

(12) The STO-3G and 6-31G*, but not the 4-31G or 6-31G, basis sets predict a spurious maximum in ρ at the midpoint of the CC bond in acetylene. The values of ρ at these exceptional maxima exceed those of neighboring minima on the same axis by only 0.020 Å^{-3}, or approximately 1% of the value of $\rho(r_c)$. In better approximations to the charge distribution of acetylene these off-nucleus maxima are not found (see Table III for details).

(13) Some time ago Copley (Copley, G. N. *Chem. Ind. (London)* **1941**, *60*, 663–665) noted that the length of a bent (strained) CC bond (or of CC double and triple bonds), as measured along the axes of overlapping sp³ hybrid orbitals directed from neighboring carbon nuclei, equalled the length of a normal CC single bond. The idea that some effective length of a bent bond should equal the normal bond length is not quite fulfilled by definition of the bond path length in cyclopropane for which $R_b = 1.53$ Å compared to 1.54 Å for R_e in ethane. Along these lines it is interesting to note that the notion of a bond path and its length were qualitatively introduced 30 years ago by Dunitz and Schomaker: "It appears that this argument might be expressed in terms of the significant existence of a bond line to be distinguished from the internuclear (straight) line which more or less follows a line of maximum density of the bonding electron distribution and which in the bent bond tends to retain a fixed length thereby possibly causing the internuclear distance to be shortened in spite of the resulting increased internuclear repulsion." (Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703–1707).

(14) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press, Ithaca, N.Y., 1960, Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1951**, *207*, 91–100. Coulson, C. A.; Daudel, R.; Robertson, J. M. *Ibid.* **1951**, *A207*, 306–320.

(15) Brown, A. D. *Struct. Bonding Cryst.* **1981**, *2*, 1–29.

Table II. Change in ρ at the Bond Critical Point for Vertical Electron Ionization and Addition[a]

occupation of 2π and state	molecule and ρ_b									
$2\pi^0$ ($^1\Sigma^+$)	CF⁺	2.249	NO⁺	4.137						
$2\pi^1$ ($^2\Pi$)	CF	1.973	NO	4.004	NF⁺	2.541				
$2\pi^2$ ($^3\Sigma^-$)			NO⁻	3.884	NF	2.308	OF⁺	2.625		
$2\pi^3$ ($^2\Pi$)					NF⁻	2.044	OF	2.491	F₂⁺	2.532
$2\pi^4$ ($^1\Sigma^+$)							OF⁻	2.276	F₂	2.494
R_e of neutral		1.271		1.151		1.317		1.321		1.336

[a] Calculated from wave functions with use of STO basis sets close to the Hartree-Fock limit: Cade, P. E.; Huo, W. M.; *At. Data Nucl. Data Tables* 1975, *15*, 1. Cade, P. E.; Wahl, A. C. *Ibid.* 1974, *13*, 339. O'Hare, P. A. G.; Wahl, A. C. *J. Chem. Phys.* 1970, *53*, 2469. R_e is in Å and ρ is in no. of e/Å³ ≡ Å⁻³.

essential to the orbital theory of electronic structure is the property of self-consistency—that each orbital be determined by its average repulsion and exchange interactions with the other orbitals in the system. Thus the density distributions derived from σ and π orbitals are not determined independently of one another. This coupling is very pronounced and is best illustrated by considering the change in ρ_b values for a given bond in vertical (no change in internuclear separation) ionization and electron attachment. Table II lists such values for a number of diatomic molecules whose ground electronic configuration involves occupation of the 2π *antibonding* orbital ($1\pi_g$ of homonuclear diatomics). It is a general observation that the vertical ionization of a π electron causes an increase in the σ-distribution along the internuclear axis while the addition of a π electron has the reverse effect.[16] As a result, the value of ρ_b *increases* with the removal of, and *decreases* with the addition of, a 2π electron. Thus unlike the increase in ρ_b and hence in n observed for the progressive filling of the *bonding* CC "π" orbital in hydrocarbons (Table III), the occupation of an *antibonding* π orbital leads to a decrease in ρ_b. These observations are in accord with the predictions of orbital theory regarding the opposing effects generated by the occupation of a bonding or an antibonding orbital. The effects of changing the 2π occupation are accentuated when the system relaxes to its new equilibrium geometry.[17]

Bond Ellipticity

As discussed above, a second important property of ρ at a bond critical point is the ratio λ_1/λ_2 of its negative curvatures along axes perpendicular to the bond path. The ellipticity $\epsilon = \lambda_1/\lambda_2 - 1$ provides not only an indication of the susceptibility of a CC ring bond to rupture but also a link with and a quantitative generalization of the concept of σ–π character of a bond. The axes associated with λ_1 and λ_2 are symmetrically equivalent for the CC bond in ethane, $\lambda_1/\lambda_2 = 1$ and $\epsilon = 0$, and a display of ρ in the plane perpendicular to the bond axis at its midpoint yields circular contours centered at r_c. As stressed some time ago by Coulson et al.,[18] the density of a π orbital is not spatially separate from that of the σ orbitals. Thus all bonds, including multiple bonds, are topologically equivalent and exhibit a single (3,–1) critical point with a maximum in ρ at r_c in the interatomic surface. However, the contours in a display of $\rho(r)$ in the CC interatomic surface for ethylene are elliptical in shape (Figure 3). Hence λ_1 and λ_2 are not degenerate in ethylene as they are in ethane and their associated eigenvectors define a unique pair of orthogonal axes, perpendicular to the bond path: the *minor axis* along which the magnitude of the negative curvature of ρ is a maximum (λ_1) and the *major axis* along which its magnitude is a minimum (λ_2). In ethylene the major axis is perpendicular to the plane of the nuclei and is coincident with the direction of the maximum in the π distribution of orbital theory.
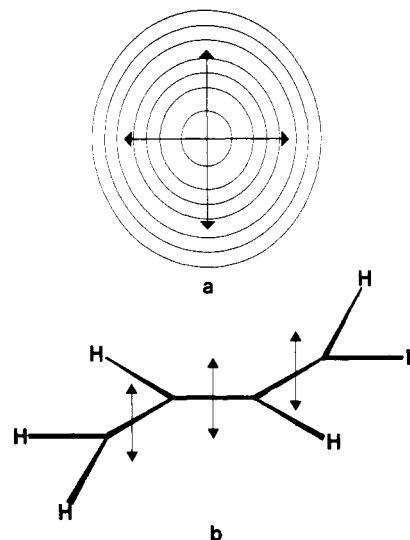

Figure 3. (a) A contour map of ρ for ethylene in a plane perpendicular to the plane of the nuclei and containing the carbon–carbon bond critical point. The value of ρ at the critical point is 2.2 Å⁻³ and the contours decrease from this maximum value outwards. The diagram illustrates the elliptical nature of the distribution of charge associated with the presence of a π bond. The magnitude of the curvature of ρ at the critical point is a minimum in the direction of the major axis, the axis perpendicular to the plane of the nuclei. (b) The major axes of the CC bonds in *trans*-butadiene are parallel to one another and perpendicular to the plane containing the nuclei. This observation is consistent with the orbital model of a delocalization of π density through conjugation.

One important quantity to be determined by estimating the amount of "π-character" in a bond is the extent to which the charge density is preferentially distributed in a particular plane containing the bond axis. The bond ellipticity provides a quantitative measure of just this effect. Furthermore, the directions of the axes defining the relevant planes are uniquely specified by the eigenvectors associated with the two negative curvatures of ρ at r_c.

In a covalent bond the charge density accumulated in the binding region is shared by both nuclei and hence λ_3, the positive curvature of ρ at the bond critical point along the bond path, is low in value. Equally characteristic of covalent binding is the radial contraction of the charge density toward the bond path, and the negative curvatures λ_1 and λ_2 are greater in absolute value than λ_3. Consequently, for a covalent bond the value of $\nabla^2\rho(r_c)$, which equals the sum of the three curvatures of ρ, is less than zero as its value is dominated by the negative curvatures λ_1 and λ_2. This result is to be contrasted with that for a bond at the ionic limit.[19] With the exception of the STO-3G basis set, the value

(16) Cade, P. E.; Bader, R. F. W.; Pelletier, J. *J. Chem. Phys.* **1971**, *54*, 3517–3533.

(17) For example, in CF⁺, ρ_b increases to 2.454 Å⁻³ at its R_e = 1.229 Å, and in NO⁺ ρ_b increases to 5.134 at its R_e = 1.062 Å. For $O_2(X^3\Sigma_g^-)$ ρ_b = 3.720 Å⁻³, R_e = 1.208 Å; for $O_2^+(X^2\Pi_g)$ ρ_b = 4.744 Å⁻³, R_e = 1.123 Å; for $O_2^-(X^2\Pi_g)$ ρ_b = 3.121 Å⁻³, R_e = 1.270 Å.

(18) Coulson, C. A.; March, N. H.; Altmann, S. *Proc. Natl. Acad. Sci. U.S.A.* **1952**, *38*, 372–378.

(19) For any bond resulting from the interaction of two closed-shell systems, ionic bonds, hydrogen bonds, and van der Waal's bonds, for example, the value of $\nabla^2\rho(r_c)$ is greater than zero. As a consequence of the Pauli exclusion principle, the charge density assumes low values in the interatomic surface in these cases and the positive curvature of ρ at the bond critical point along the bond axis is therefore large and dominant.

Table III. Bond Critical Point Data for CC Bonds

molecule	R_e(calcd), Å	ρ_b, Å^{-3}	$\nabla^2\rho(r_c)$, Å^{-5}	λ_1, Å^{-5}	λ_2, Å^{-5}	λ_3, Å^{-5}	n	ϵ
			STO-3G Basis					
ethane	1.538	1.628	−15.72	−9.75	−9.75	3.78	1.00	0.00
benzene	1.387	2.002	−19.96	−12.36	−9.19	1.58	1.58	0.34
ethylene	1.306	2.217	−21.69	−13.85	−7.95	0.10	2.08	0.74
acetylene	1.168	2.484	−17.05	−6.82	−6.82	−3.42	2.88	0.00[b]
			4-31G Basis					
ethane	1.529	1.518	−10.27	−9.14	−9.14	8.01	1.00	0.00
benzene	1.384	2.029	−17.60	−14.17	−12.47	9.04	1.59	0.14
ethylene	1.316	2.286	−22.42	−16.68	−13.63	7.89	2.00	0.22
acetylene	1.190	2.737	−31.25	−16.21	−16.21	1.17	3.01	0.00
			6-31G Basis					
ethane	1.530	1.520	−9.94	−9.11	−9.11	8.28	1.00	0.00
benzene	1.388	2.012	−17.55	−13.90	−12.29	8.64	1.59	0.13
ethylene	1.322	2.252	−22.30	−16.12	−13.23	7.04	1.99	0.22
acetylene	1.194	2.691	−30.46	−15.46	−15.46	0.46	3.01	0.00
			6-31G*					
ethane	1.527	1.702	−15.94	−11.50	−11.50	7.06	1.00	0.00
benzene	1.386	2.205	−24.42	−17.04	−13.85	6.46	1.62	0.23
ethylene	1.317	2.451	−28.73	−19.66	−13.60	4.54	2.05	0.45
acetylene	1.185	2.820	−30.88	−14.16	−14.16	−2.56	2.92	0.00
			BA+P STO[a]					
HCCH	1.207	2.803	−29.66	−15.55	−15.55	1.45		0.00
LiCCH	1.201	2.982	−39.99	−21.81	−21.81	3.63		0.00
FCCH	1.198	2.668	−17.37	−12.80	−12.80	8.23		0.00

[a] Calculated from STO wave functions by: McLean, A. D.; Yoshimine, Y. *IBM J. Res. Dev.* 1967, Nov. They are the "best atom" sets plus d and f polarizing functions. [b] See ref 11.

of $\nabla^2\rho(r_c)$ becomes increasingly more negative as n increases from 1 to 3 for the basis sets listed in Table III. This decrease in $\nabla^2\rho(r_c)$ results from an enhancement of the general behavior noted above for covalent bonds: as an increasing amount of charge is accumulated in the binding region corresponding to an increase in n, the absolute values of λ_1 and λ_2 become increasingly greater than λ_3. In addition, as n increases from 1 to 2, the difference between $|\lambda_1|$ and $|\lambda_2|$ increases and the ellipticity ϵ attains a maximum value at $n = 2$. The ellipticity should undergo a continuous decrease from its value at $n = 2$ to zero at $n = 3$, corresponding to the progressive filling of the second "π" orbital and the eventual attainment of axial symmetry in acetylene.[20]

The use of ϵ as a measure of the π character of a bond necessarily fails for acetylene if this molecule is viewed as possessing two π orbitals. Conjugative and hyperconjugative interactions which remove the axial symmetry in acetylene, however, again result in the formation of a plane in which charge is preferentially concentrated. This plane and the extent of concentration are faithfully reflected in the direction of the major axis and the ϵ value of the CC bond.

In general the trends in the behavior of ρ_b, $\nabla^2\rho(r_c)$, and ϵ are preserved between basis sets. The bond orders in Table III are calculated from the ρ_b values with use of the parameters given in Table I. All four basis sets reproduce the n values 1.0, 1.6, 2.0, and 3.0 to within ±0.1. Thus by changing from the ρ_b values, which are basis set dependent, to n one may compare bond orders obtained from different basis sets with an uncertainty of ±0.1. The ellipticities must be compared to the standard values for an aromatic and a double bond within a given basis set. With the exception of triple bonds,[12] the STO-3G set yields the same trends in ρ_b, n, ϵ, and $\nabla^2\rho(r_c)$ as the more flexible basis sets. The study of conjugation presented in the next section is primarily concerned

with bonds of order 1 to 2, and for these the STO-3G basis set is of sufficient quality to reveal the correct trends in the bond parameters, n, ϵ, and $\nabla^2\rho(r_c)$.

The final entries in Table III are for the CC triple bonds in a number of acetylenic molecules obtained from wave functions constructed from large STO basis sets including d and f polarizing functions. For these functions, close to the Hartree–Fock limit, the CC triple bond critical point is always found to be a (3,−1) critical point.

The Interaction between CC Bonds in Terms of ρ

Table IV summarizes the properties of CC bonds at the STO-3G level of approximation[21] for a variety of systems in terms of n, ϵ, and $\nabla^2\rho(r_c)$. The values of ϵ for propane and isobutane are less than 0.010, results that remain true for the 6-31G** basis as well.[22] The reduction in symmetry obtained when a hydrogen is replaced by a methyl group in ethane does not induce a significant ellipticity into the CC bond. With the exception of systems containing three-membered rings, carbon–carbon bonds in saturated hydrocarbons exhibit nearly autonomous behavior; they are of order 1, with zero ellipticity and essentially constant values for $\nabla^2\rho$. This is no longer true for a CC bond adjacent to an unsaturated system where a nonzero ellipticity in one bond can be transmitted to a neighboring bond. An example of this effect is found in *trans*-1,3-butadiene. The central bond in this molecule exhibits partial double bond character as evidenced by $n > 1$ and $\epsilon > 0$ and an increase in $|\nabla^2\rho|$. Correspondingly, the n, ϵ, and $|\nabla^2\rho|$ values of the two terminal bonds are decreased from the values found in ethylene. Of equal importance is the observation, as illustrated in Figure 3b, that the major axis of the ellipticity induced in the central bond is parallel to the major axes of each of the terminal bonds. These observations are consistent with the orbital model of conjugation—a delocalization of π electrons from the double bonds to the single bond.

In orbital theories, aromaticity in benzene is viewed as complete delocalization of the π electrons through conjugation. In terms

(20) Plots of ρ_b vs. internuclear separation, R, about the appropriate R_e value for a CC bond of given order also yield curves with negative slopes. These slopes are in general greater than those obtained in plots of ρ_b vs. R_b for bonds of different order. The near linear relationship between ρ_b and R_b is not a simple consequence of an increase in ρ_b as R is decreased. Bonds of different order differ not only in their ρ_b values but also in the manner in which the charge density is distributed in the binding region as reflected in the behavior of ϵ and $\nabla^2\rho(r_c)$. Thus the CC bond in ethane may be compressed to yield a ρ_b value equal to that for ethylene (at a smaller R than R_e of ethylene) but ϵ remains equal to zero and the value of $\nabla^2\rho(r_c)$ is greater than that for ethylene.

(21) Pople, J. A. In "Applications of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, Chapter I. Hehre, W. J. *Ibid.*, Chapter VII.

(22) The values of ρ_b in Å^{-3} and ϵ for the CC bonds in C_2H_6, C_3H_8, and i-C_4H_{10} at the 6-31G* level are respectively $\rho_b = 1.707$, $\epsilon = 0.000$; $\rho_b = 1.714$, $\epsilon = 0.007$; $\rho_b = 1.656$, $\epsilon = 0.008$.

Conjugation and Hyperconjugation

J. Am. Chem. Soc., Vol. 105, No. 15, 1983 5067

Table IV. CC Bond Properties in Hydrocarbons[a]

molecule	bond	R	ρ_b	n	ϵ	$\nabla^2\rho$
propane	$CH_3-CH_2CH_3$	1.541	1.626	1.00	0.00	−15.6
isobutane	$CH_3-CH(CH_3)_2$	1.540	1.633	1.01	0.00	−15.7
trans-1,3-butadiene	$CH_2CH-CHCH_2$	1.488	1.721	1.11	0.10	−16.8
	$CH_2=CHCHCH_2$	1.313	2.200	2.00	0.72	−21.4
benzene	C_6H_6	1.400*	1.957	1.52	0.34	−19.3
tropylium cation	$C_7H_7^+$	1.398	1.958	1.50	0.21	−19.8
cyclopentadienyl anion	$C_5H_5^-$	1.395	1.973	1.53	0.55	−18.6
1,3-cyclobutadiene ($^1A_{1g}$)	CHCH−CHCH	1.569	1.512	0.98	0.04	−13.2
	CHCH=CHCH	1.313	2.227	2.10	0.82	−21.8
propene	CH_3-CHCH_2	1.520	1.653	1.03	0.03	−16.0
	$CH_3CH=CH_2$	1.308	2.213	2.06	0.84	−20.2
toluene	$C_6H_5-CH_3$	1.52*	1.656	1.03	0.04	−16.0
ethyl cation	$CH_3-CH_2^+$	1.484	1.606	0.98	0.03	−7.5
2-propyl cation	$CH_3-CHCH_3^+$	1.500	1.601	0.97	0.03	−10.1
methylacetylene	CH_3-CCH	1.484	1.676	1.06	0.00	−15.5
	$CH_3C≡CH$	1.170	2.456	2.78	0.00	−4.0
but-1-yn-3-ene	$CH_2=CHCCH$	1.320	2.166	1.95	0.72	−20.4
	$CH_2CH--CCH$	1.459	1.720	1.12	0.10	−15.6
	$CH_2CHC≡CH$	1.171	2.472	2.81	0.05	
cyclopropane	C_3H_6	1.502	1.626	1.01	0.11	−14.8
cyclobutane	C_4H_8	1.554	1.613	0.98	0.02	−15.3
cyclobutene	CHCH−CH_2CH_2	1.526	1.655	1.03	0.06	−15.7
	CHCH_2−CH_2CH	1.565	1.574	0.94	0.02	−14.6
	CH_2CH=CHCH_2	1.314	2.234	2.11	0.74	−22.1
cyclopropene	CH_2−CHCH	1.493	2.261	0.97	0.13	−12.9
	CH_2CH=CH	1.277	1.599	2.19	0.65	−21.4
methylcyclopropane	$C_3H_5-CH_3$	1.52*	1.670	1.05	0.04	−16.2
cyclopropylcarbinyl cation (bisected)	$C_3H_5-CH_2^+$	1.384	1.946	1.48	0.56	−12.5
cyclopropenylium cation	$C_3H_3^+$	1.377	1.954	1.50	0.04	−18.5
vinylcyclopropane	$C_3H_5-CHCH_2$	1.52	1.645	1.02	0.09	−15.5
	$C_3H_5CH=CH_2$	1.34	2.122	1.83	0.74	−20.1

[a] R in Å, ρ_b in Å^{-3}, and $\nabla^2\rho$ in Å^{-5}. STO-3G geometries are used. Starred values correspond to standard geometries.

of the properties of ρ, the limiting case of complete delocalization of the π electrons in a cyclic carbon system corresponds to each bond having the same values for n, $\nabla^2\rho$, and ϵ, all with their major axes parallel to the axis of the ring critical point, i.e., perpendicular to the plane of the ring. Benzene fits this description, as do $C_7H_7^+$ and $C_5H_5^-$. The cyclopropenium ion, another Hückel $4n + 2$ system, does as well, but the detailed discussion of this ion is presented in the section dealing with the particular properties exhibited by three-membered rings.

If one wishes to associate empirically the extra thermodynamic stability of an aromatic system with this particular set of bond critical point properties, they should be compared with and found different from those for a system that Hückel theory predicts to be antiaromatic. An example is cyclobutadiene in its singlet ground-state geometry.[21] One anticipates that if this molecule is antiaromatic, the extent of its conjugation as measured by n and ϵ should be suppressed relative to that found in the related conjugated system, butadiene. The data in Table IV show this to be the case. With reference to the usual canonical structures for these molecules, the single bonds in the cyclic molecule possess only a small induced ellipticity and an order less than 1, as opposed to $n > 1$ and $\epsilon \gg 0$ for the single bond in butadiene. The double bonds of the cyclic molecule have n and ϵ values greater than those for ethylene, while conjugation decreases the values of these same parameters for the double bonds in butadiene.[23]

Orbital models predict the possibility of another mechanism for inducing partial double bond character into what is formally

a single bond. This is the so-called hyperconjugative mechanism of electron release from a methyl group that is linked to an unsaturated system or to a carbon with a single orbital vacancy. This mechanism has been invoked to explain the small observed decrease in the length of a CC bond adjacent to a double bond, as in propene for example[24] (see Table IV). The n, ϵ, and $\nabla^2\rho$ values indicate that the C−CH_3 bond exhibits partial double bond character, and its major axis is parallel to the corresponding axis of the double bond. Unlike the cases of direct conjugation discussed above, the ellipticity of the double bond in propene is increased to a value greater than that found for ethylene, while its bond order remains essentially unchanged. This increase in ϵ results from a further lessening in the curvature λ_2 along the major axis with no change in the value of λ_1. These obserations are consistent with the orbital model of an electron release from the methyl group into the π system which is delocalized over all three carbon atoms. Also consistent is the finding that the electron populations of the hydrogen atoms of the methyl group are lower in propene than in propane or other saturated hydrocarbons.[9] A corresponding effect of similar magnitude is observed in toluene for the C−CH_3 bond.

An ellipticity, again of similar magnitude to that found in propene, is found for the CC bond linking a methyl group to the carbon bearing the formal charge in carbocations. The examples in Table IV are the ethyl and 2-propyl cations. The methyl hydrogens in these cations bear net positive charges.[9] Finally, a similar delocalization is observed in methylacetylene. Because of the axial symmetry present in this system, ϵ is necessarily zero, but both λ_1 and λ_2 for the C−CH_3 bond are decreased from their values in ethane, yielding an effective ellipticity (λ_2(ethane)/

(23) It might be argued that the decrease of ϵ for the CC single bonds in 1,3-cyclobutadiene is a result of the long R_e values (1.569 Å vs. 1.488 Å in *trans*-butadiene) imposed by the STO-3G basis. Calculations on model geometries show that for a continuous approach to a square-planar geometry (R_e = 1.40 Å) the ϵ values of the CC single bonds do not change. Inclusion of CI, however, may influence ρ and its properties.

(24) See, for example: Wilson, E. G. *Tetrahedron* **1962**, *17*, 191–198. Mulliken, R. S. *Tetrahedron* **1959**, *5*, 253–274.

λ_1(methyl acetylene) − 1) of 0.04. Thus each π bond of acetylene is conjugated to approximately the same extent as it is in propene and the resultant increase in bond order for the C–CH$_3$ bond is twice that found in propene.

There is evidence of delocalization by conjugation in but-1-yn-3-ene, where formally a CC single bond links a double to a triple bond. As in butadiene, the orders of the unsaturated bonds are reduced from their corresponding values in ethylene and acetylene, while n for the central bond is increased substantially. The major axis of the ellipticity induced in the central bond is parallel to that of the double bond. This conjugation destroys the radial symmetry of the triple bond and the major axis exhibited by this bond is perpendicular to those of the other two CC bonds.

Ellipticities of CC Bonds in Three-Membered Rings

Most important for the understanding of the chemistry particular to three-membered rings is the observation that their CC bonds exhibit substantial ellipticities. As previously discussed, the close proximity of a bond and ring critical point reduces the magnitude of the negative curvature of the bond critical point which lies in the ring surface. Thus the CC bonds of cyclopropane, whose bond paths are noticeably curved outside of the geometrical perimeter of the ring, also as a consequence of the proximity of the ring critical point, exhibit substantial ellipticities (Table IV) with their major axes coincident with the ring surface.

In four-membered and larger rings, the ring critical point is sufficiently distant from the critical points of the perimeter bonds that there is only a small or insignificant interaction between them. In cyclobutane the value of $\rho(\mathbf{r})$ at the ring critical point is only 0.53 Å^{-3}, considerably less than the values of ρ_b of the CC bonds that are of order 1 and for which $\epsilon = 0.02$ (Table IV). In cyclobutene the major axes of the bond ellipticities are parallel with that of the double bond rather than directed at the ring critical point, and the conjugative interaction (as found in propene) overrides the interaction with the ring critical point. In cyclopropene on the other hand, while the magnitude of λ_1 (the curvature perpendicular to the ring surface) of the bonds of order 0.97 is decreased because of the conjugation of these bonds with the double bond, the interaction of λ_2 with the ring critical point is dominant—the major axes of these bonds are perpendicular to that of the double bond and lie in the ring surface. The ellipticity of the double bond is also considerably reduced in this case because of the proximity of the ring critical point. Thus the observation of substantial in-plane ellipticities in equilibrium geometries is a property unique to three-membered rings and their chemistry should in turn be unique among ring systems in exhibiting behavior consistent with a "π-like" charge distribution in the plane of the ring.

Ascribing the properties of an unsaturated system to cyclopropane as determined by its in-plane ellipticities leads to immediate predictions: ellipticities with major axes parallel to the ring surface should be induced in CC bonds linking a methyl group or a CH$_2^+$ cationic group to the ring system. These predictions are borne out (Table IV). In terms of the induced ϵ value in methylcyclopropene, the cyclopropyl group is equal to a double bond (compare with propene) in its ability to interact with a neighboring methyl group.[25] The interaction of the cyclopropyl group with the (formally) vacant 2p orbital in –CH$_2^+$ is very large as seen by the data for the bisected geometry of the cyclopropylcarbinyl cation. We emphasize that the major axis of the ellipticity of the C–CH$_2^+$ bond has an overlap of 0.97 with the corresponding axes of the neighboring CC bonds of the cyclopropyl group. (The overlap is determined by taking the scalar product

of the eigenvectors defining the major axes of the two bond critical points.) This molecule is discussed in detail in the following paper.[5] The relatively small ellipticities found for the CC bonds in the cyclopropenylium cation are the result of two competing effects—a charge buildup perpendicular to the plane of the ring (the bonds are of order 1.5) and the interaction of the curvatures in the ring surface with the ring critical point. The former effect is dominant and the major axes are aligned with the ring axis. The results for vinylcyclopropane indicate that a cyclopropyl group can take the place of a double bond to realize a delocalization of charge through conjugation.

Electron delocalization involving a cyclopropane ring is accounted for within molecular orbital theory through the choice of a particular orbital representation, the so-called Walsh orbitals.[4] In this way, the many similarities between a cyclopropane ring and a double bond, as documented for example by their comparable roles as effective neighboring groups in enhancing the rates of solvolysis reactions, are rationalized.[26] An important result of this study of the charge density is that the "π nature" of the cyclopropane bonds can be directly related to a property of ρ at the bond critical point. In addition, the study provides a physical basis for the origin of the π functionality of the cyclopropane ring in terms of the proximity of a bond and a ring critical point.

Conclusions

This paper demonstrates that chemical properties of a bond can be characterized in terms of the properties of ρ at a bond critical point and of the bond path which it defines. The values of ρ_b, ϵ, and $\nabla^2\rho(\mathbf{r_c})$ enable one *to translate the predicted electronic effects of orbital theories into observable consequences in the charge distribution*. The present study has concerned itself with static effects—the characterization of bonds in equilibrium structures. In the following paper[5] it is shown that the proximity of a bond and a ring critical point in three-membered ring systems not only accounts for their conjugative interaction with an unsaturated system but also enables one to predict the interesting structural consequences obtained when this interaction involves the participation of a CC bond of the cyclopropyl fragment to yield a homoconjugated or homoaromatic system.[27] It is clear from the introductory discussion that a slight lengthening of a cyclopropyl CC bond participating in such a system will result in a further decrease in the distance separating the bond and the ring critical points. The consequences are a reduction in the order of the bond to a value less than 1 and an increase in the ellipticity of its charge distribution which enhances its conjugative ability. In such a situation the bond and ring critical points are poised for mutual annihilation. Because of the near vanishing of the curvatures in ρ along their path of approach, little energy is required to achieve their coalescence, to break the bond and change the structure.

(25) The substantial ellipticities and their particular alignments in methylcyclopropane should be contrasted with the essential absence of any CC bond ellipticities in isobutane, which differs from it by the presence of a CC bond forming the three-membered ring.

(26) Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976.
(27) Winstein, S. *Spec. Publ. Chem. Soc.* **1967**, *21*, 5–45.