

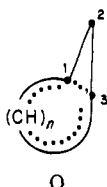
## Description of Homoaromaticity in Terms of Electron Distributions

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**Abstract:** This paper illustrates how the topological theory of molecular structure can be used to provide an answer as to whether or not homoaromatic conjugation is present in a given system. The study hinges upon the particular properties of a cyclopropyl ring. As a consequence of the proximity of the bond and ring critical points in this system, the ring possesses a surface of delocalized charge, thereby affording a number of possible modes of conjugative interaction with an unsaturated fragment. Depending upon the electronic requirements of the unsaturated system to which it is coupled, the charge distribution of the three-membered ring may be deformed so far as to cause its ring critical point to approach the critical point of one of the ring bonds thereby reducing its bond order and enhancing its ellipticity (i.e., its "π" character) or conversely cause the same critical point to migrate toward one of the ring nuclei thereby simultaneously imparting these same properties to two of the ring bonds. The former possibility occurs in the homotropylium cation ( $C_8H_9^+$ ) and this system is homoaromatic. The second possibility occurs in the cyclopropylcarbinyl cation ( $C_4H_7^+$ ) and to a lesser extent in the bicyclo[3.1.0]hexenyl cation ( $C_6H_7^+$ ). This bicyclic structure of  $C_6H_7^+$  corresponds to a conjugative coupling of a cyclopropyl ring to an unsaturated fragment involving the two external bonds of the three-membered ring. The properties of the charge distribution of the cyclobutenyl cation ( $C_4H_5^+$ ) calculated at both the STO-3G and 6-31G\* levels of approximation show that this system does not contain a three-membered ring. At these levels of approximation, this cation is not homoaromatic.

The concept of homoaromaticity was introduced into chemistry by Saul Winstein triggering numerous experimental investigations.<sup>1</sup> It has proven to be a useful tool for the rationalization of many chemical observations. Nevertheless, a theoretical formulation of homoaromaticity is still an unresolved problem. This has become obvious from attempts to elucidate the geometric and energetic requirements for the occurrence of homoaromatic interactions.<sup>2-4</sup> Various authors have pointed out that one essential feature of homoaromaticity is the union of a cyclopropane moiety with an unsaturated linear segment<sup>2-4</sup> as illustrated by O. It has



been found that the interactions of the Walsh orbitals of the three-membered ring with the frontier orbitals of the linear system play a key role in distinguishing between a homoaromatic, non-aromatic, or homoantiaromatic system. A similar analysis carried out for the union of a four-membered ring and a linear fragment gave no indication of homoaromaticity.<sup>3</sup>

The orbital interactions, which are governed by an appropriate alignment of π-type orbitals in positions 1 and 3, depend sensitively on the geometry of the fused ring system, and particularly on the 1,3 interatomic distance. So far, the geometry constraints for homoaromaticity have not been specified. From ab initio calculations it is only known that interactions occur for a "relatively closed" cyclopropane ring where no further specification of the allowable 1,3 bond length has been given.<sup>4</sup>

In this paper we shall illustrate how the topological theory of molecular structure may be used to obtain a definitive answer as to whether or not homoaromatic conjugation is present in a given system and if present obtain a quantitative description of the conjugation. Given a charge distribution for a system such as that illustrated by O, one may, by determining the position, number, and kind of its critical points assign a molecular structure. This

assignment of structure determines whether or not carbon nuclei 1 and 3 are linked by a bond path. If a C1-C3 bond is found to exist, its properties may be examined. In particular, as illustrated in the previous paper,<sup>5</sup> one may determine the extent to which it is conjugated with the rest of the system by determining the ellipticities of the bonds in the resulting unsaturated ring and the degree of alignment of their major axes.

A most important observation from the preceding paper<sup>5</sup> is that the CC bonds of cyclopropane possess significant ellipticities with their major axes coincident with the ring surface. This is a topological consequence of the proximity of the ring and bond critical points unique to a three-membered ring (3MR) structure. The delocalization of charge in an isolated cyclopropane molecule is, however, different in form and properties from that associated with a system of conjugated π bonds. In the latter case the delocalization, as determined by the ellipticities and the alignment of the major axes of the neighboring bonds, is a maximum in a ribbon-like surface that extends along the framework of conjugated CC bonds. The ribbon may be twisted (the major axes of neighboring bonds are not exactly parallel), but the twisting angle must be less than 90°. Such a π system, however, represents a one-dimensional coupling of bonds as the conjugation is determined by the degree of alignment of the major axis of one bond with that of its neighbor—a one-dimensional constraint. In cyclopropane the delocalization of charge, as determined by the ellipticities and major axes of the CC ring bonds, is necessarily two-dimensional, being a maximum in the *ring surface defined by the pair of eigenvectors* associated with the positive eigenvalues of the ring critical point. The result is a surface of delocalized charge containing the ring and CC bond critical points. In this case the extent of delocalization is not determined by the degree of alignment of major axes of the ring bonds (which by geometry

(1) For reviews, see: (a) Winstein, S. *Q. Rev., Chem. Soc.*, **1969**, *23*, 141-176. (b) Warner, P. M. In "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1976; Vol. 2. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106-117.

(2) Jorgensen, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 3082-3090; **1976**, *98*, 6784-6789.

(3) Haddon, R. C. *Tetrahedron Lett.* **1974**, 2797-2800; **1974**, 4303-4304; **1975**, 863-866; *J. Am. Chem. Soc.*, **1975**, *97*, 3608-3615.

(4) Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 5807-5809.

(5) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* previous paper in this issue.

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equals 0.5), for all three major axes lie in the ring surface and all three CC bonds contribute to the surface of delocalized charge. The possibilities of conjugative coupling are greater for such a two-dimensional system as the requirement for coupling is that the major axis of the bond to be coupled be parallel with the surface of delocalization rather than with a single major axis. The versatility of a 3MR in conjugating with an unsaturated fragment is illustrated in this paper.

The surface of delocalized charge is readily perturbed when the 3MR is linked to an unsaturated fragment because of the motility of the ring critical point. If, for example, a CC bond of cyclopropane is linked to an unsaturated fragment in the manner shown in O, the major axis of this bond will be approximately parallel to the axis of the unsaturated ring structure thus formed. This axis is in turn parallel to the major axes of the CC bonds of the unsaturated ring. A lengthening of the inserted CC bond of cyclopropane will cause the ring critical point to move closer to the CC bond critical point, thereby enhancing its ellipticity and reducing its bond order. A conceivable result of such an interaction is a ring of CC bonds, all with equal ellipticities and all with their major axes parallel to the ring axis—an aromatic system.<sup>5</sup> In this manner a bond of cyclopropane may enter into conjugation with an unsaturated system and one may thus predict the possibility of homoaromatic conjugation as originally envisaged by Winstein with use of only known properties of molecular charge distributions.

The resulting structure is predicted to be potentially unstable. A further increase in length of the CC bond of the cyclopropyl fragment will cause its bond critical point to coalesce with the 3MR critical point to produce a singularity in  $\rho$ .<sup>5</sup> As a consequence, the C1-C3 bond will vanish and the ring of conjugated major axes will be destroyed.




This analysis isolates important requirements for the formation of a homoaromatic system: (a) There has to be a C1-C3 bond path which closes a potentially aromatic ring of CC bonds. (b) The C1-C3 bond path must be longer than that in an isolated cyclopropane to give it substantial ellipticity and thereby enhance its conjugative interactions with the remainder of the system. This will lower the C1-C3 bond order to a value less than unity. (c) The angle between the plane of the 3MR and the unsaturated framework is clearly important if one is to obtain the proper alignment of major axes. This angle need not be 90°, however. The charge distribution can distort so that the ring critical point does not lie in the geometric surface of the 3MR and hence the major axis of the cyclopropane bond can be tilted out of this plane.

Thus if there is a C1-C3 bond present in a potentially aromatic system, with the appropriate  $n$  and  $\epsilon$  values we speak of it as a *homoaromatic bond*. If there is no such homoaromatic bond, there is no associated major axis and the distribution of charge is not of the form required for conjugation. As illustrated below, upon destruction of a homoaromatic bond, the conjugation in the remainder of the system reverts back to that of the corresponding isolated fragment.

We begin our investigation by first considering homoconjugation in an acyclic system, namely the homoallyl cation **1b**. This system is known to collapse without a barrier to the cyclopropyl carbanyl cation **1a** which is located at a local minimum of the potential energy surface of  $C_4H_7^+$ . A study of its electron distribution is also relevant in further illustrating the exceptional role of a three-membered ring as opposed to a four-membered ring.<sup>5</sup> Observations made for the  $C_4H_7^+$  system will be used to analyze the electron distribution of the homotropylium **2**, the cyclobutenyl **3**, and the bicyclo[3.1.0]hexenyl cations **4**, the first two of which have been discussed as being homoaromatic and the latter as homoantiaromatic.

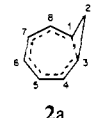
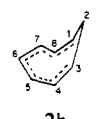
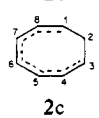
The charge distributions of these molecules are obtained from restricted Hartree-Fock calculations with use of the STO-3G, 4-31G, and 6-31G\* basis sets<sup>6</sup> and optimized geometries taken from the literature or obtained in this research. The structures **1a** through **4c** are drawn by using the standard symbols to denote bonds of order less than one (---), of one (—), and of two (==). They are meant to *partially* summarize, in terms of a familiar

Table I. Bond Properties for  $C_4H_7^+$  Structures: 6-31G\* Basis

structure	bond	$R,^a \text{ \AA}$	$\rho_b, \text{ \AA}^{-3}$	$n$	$\epsilon$	$\nabla^2\rho, \text{ \AA}^{-5}$
	C1-C4	1.347	2.378	1.91	0.28	-28.68
	C1-C2	1.664	1.161	0.60	6.74	-2.13
	C2-C3	1.412	2.067	1.42	0.18	-21.49
	C1-C4	1.357	2.340	1.85	0.25	-27.60
	C1-C2	1.522	1.603	0.91	0.32	-12.76
	C3-C2	1.456	1.893	1.20	0.19	-18.42
	C1-C2	1.435	1.984	1.31	0.16	-20.65
	C2-C3	1.650	1.271	0.66	0.36	-7.51



<sup>a</sup> Calculated at 4-31G geometries. Reference 7.

Table II. Bond Properties for  $C_8H_9^+$  Structures: STO-3G Basis

structure	bond	$R,^a \text{ \AA}$	$\rho_b, \text{ \AA}^{-3}$	$n$	$\epsilon$	$\nabla^2\rho, \text{ \AA}^{-5}$
	C1-C3	1.576	1.347	0.71	0.34	-8.88
	C1-C2	1.506	1.588	0.95	0.09	-13.70
	C3-C4	1.468	1.765	1.18	0.13	-16.90
	C4-C5	1.366	2.022	1.62	0.53	-17.05
	C5-C6	1.414	1.882	1.36	0.31	-16.89
	C1-C2	1.515	1.645	1.02	0.00	-15.38
	C3-C4	1.348	2.085	1.75	0.55	-19.28
	C4-C5	1.435	1.834	1.29	0.22	-16.90
	C5-C6	1.395	1.935	1.46	0.37	-17.60
	C1-C2	1.524	1.622	0.99	0.03	-15.11
	C3-C4	1.337	2.081	1.74	0.83	-15.57
	C4-C5	1.447	1.776	1.20	0.25	-15.15
	C5-C6	1.386	1.941	1.47	0.54	-14.89

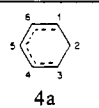
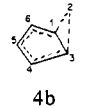
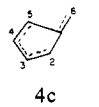
<sup>a</sup> Reference 13.

Table III. Bond Properties for  $C_4H_5^+$  Structures: 6-31G\* Basis

structure	bond	$R,^a \text{ \AA}$	$\rho_b, \text{ \AA}^{-3}$	$n$	$\epsilon$	$\nabla^2\rho, \text{ \AA}^{-5}$
	C1-C4	1.373	2.244	1.68	0.24	-24.20
	C1-C2	1.507	1.743	1.04	0.14	-16.05
	C1-C4	1.380	2.271	1.73	0.23	-26.23
	C1-C2	1.524	1.753	1.05	0.00	-17.16

<sup>a</sup> Reference 13.

Table IV. Bond Properties for  $C_6H_7^+$  Structures: STO-3G Basis

structure	bond	$R,^a \text{ \AA}$	$\rho_b, \text{ \AA}^{-3}$	$n$	$\epsilon$	$\nabla^2\rho, \text{ \AA}^{-5}$
	C1-C2	1.502	1.700	1.09	0.04	-16.36
	C1-C6	1.358	2.062	1.70	0.56	-17.30
	C4-C5	1.421	1.872	1.35	0.29	-16.18
	C1-C3	1.501	1.646	1.02	0.12	-14.95
	C1-C2	1.535	1.497	0.85	0.16	-11.80
	C3-C4	1.492	1.713	1.10	0.11	-15.41
	C4-C5	1.392	1.956	1.50	0.47	-15.59
	C1-C6	1.471	1.696	1.09	0.01	-12.90
	C1-C2	1.523	1.599	0.96	0.02	-14.31
	C2-C3	1.348	2.120	1.83	0.46	-21.05
	C3-C4	1.459	1.811	1.25	0.13	-17.81

<sup>a</sup> Reference 17.

representation, the structural properties of these systems as determined by their charge distributions. Each of these structures is a representation of the system's molecular graph. The properties of each CC bond are summarized in the corresponding Tables

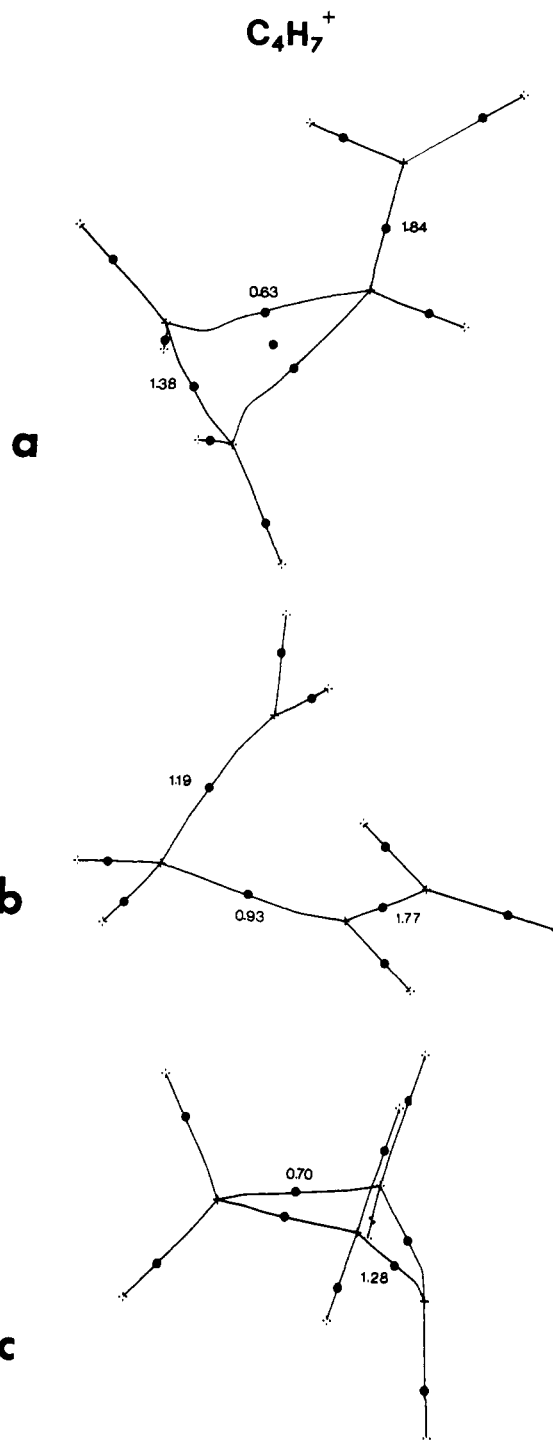
I–IV in terms of the properties of  $\rho$  at the bond critical point.<sup>5</sup> In those cases where the bond paths exhibit exceptional properties, the molecular graph itself is shown in a separate figure.

### Structures of $C_4H_7^+$

Both the STO-3G<sup>7a,b</sup> and 4-31G<sup>7c</sup> levels of approximation predict the bisected cyclopropylcarbanyl cation **1a** to be a minimum energy geometry on the  $C_4H_7^+$  potential energy surface. Levi et al.<sup>7</sup> have investigated this surface at the 4-31G level and have given energies at the 6-31G\* level for 4-31G optimized geometries. The structures for this system are shown in Figure 1 in terms of their defining molecular graphs and their bond properties are listed in Table I.

The most notable property of the  $C_4H_7^+$  system is its facile interconversion among a number of different structures. Thus Levi et al.<sup>7</sup> find a second minimum energy geometry **1b** whose energy is 0.5 kcal/mol (at 6-31G\*) above that of **1a**. In terms of the properties of its charge distribution,  $C_4H_7^+$  is found to have the most labile bonds of the equilibrium structures so far investigated. The two long bonds C1–C2 and C1–C3 in structure **1a** are of order 0.6 and exhibit extreme ellipticities, equal to 6.7. Their corresponding bond paths displayed in the molecular graph, Figure 1a, are very curved and their bond path lengths  $R_b$  exceed the internuclear separations by 0.20 Å. The structure verges on instability through the annihilation of either of the bond critical points associated with the long bonds. The curvature of  $\rho$  at the ring critical point, which, as indicated in Figure 1a, lies almost on a line joining these two bond critical points, is close to zero ( $0.48 \text{ \AA}^{-5}$ ) and, correspondingly, the associated negative curvature of each of the two bond critical points is equally small in magnitude. The values of  $\rho$  at the bond and ring critical points differ by only  $0.007 \text{ \AA}^{-3}$ . As anticipated for long bonds, the positive curvature of  $\rho$  at the bond critical points is relatively large ( $6.26 \text{ \AA}^{-5}$ ) and equal to the other positive curvature of  $\rho$  in the ring surface at the ring critical point. Thus there is a trough in the distribution of charge in the plane of the ring linking these three critical points and little energy is required to change its form to yield the open structure shown in **1b**. While the order of the remaining labile bond is increased to 0.9 in **1b**, Figure 1b, it still possesses a substantial ellipticity and its major axis is directed toward the region between C3 and C1. Hence  $\rho$  is still relatively flat along this line and close to forming a singularity and a weak unstable link between C1 and C3. The resulting structure would coincide with Winstein's<sup>9</sup> suggestion that  $C_4H_7^+$  could exhibit homoconjugation and exist as the "homoallyl" cation.

As noted in the previous paper,<sup>5</sup>  $\nabla^2\rho(r_c)$  at a bond critical point becomes less negative as the bond order decreases from 3 to 1. The labile bonds of order 0.6 in structure **1a** provide the first evidence that this trend continues for values of  $n$  less than 1. The magnitude of  $\nabla^2\rho$  for these bonds,  $2.1 \text{ \AA}^{-5}$ , is considerably less than the corresponding value of  $15.9 \text{ \AA}^{-5}$  recorded in Table III of the previous paper<sup>5</sup> for the CC bond in ethane. (Note as well that the values of  $\nabla^2\rho$  for the other bonds in **1a**, those of order 1.9 and 1.4, are as anticipated by the values listed in Table III<sup>5</sup>.) Unlike the bond ellipticity which may exceed zero for  $n >$  and  $<$  1, the value of  $\nabla^2\rho$  is directly linked to  $n$  for reasons easily understood. As two nuclei separate and  $\rho_b$  decreases in value, the positive curvature of  $\rho$  at  $r_c$ , the curvature along the bond axis, increases in value relative to the magnitudes of the two negative curvatures of  $\rho$  perpendicular to the bond axis, and  $\nabla^2\rho$  increases in value. Extending and weakening a CC bond will cause its  $\nabla^2\rho$  value to increase regardless of the value of  $\epsilon$ . If the ellipticity of



**Figure 1.** Planar projections of the molecular graphs defining structures **1a**, **1b**, and **1c** of  $C_4H_7^+$  obtained from 4-31G calculations. The bond orders given in the diagram should be compared with those calculated by using the 6-31G\* basis given in Table I. The bond critical points are denoted by solid circles in this and succeeding figures. The position of the ring critical point is also shown in part a.

the bond increases simultaneously with the lengthening as a consequence of the approach of a ring critical point, thereby causing the magnitude of one of the negative curvatures to rapidly decrease, then the rate of increase in  $\nabla^2\rho$  is enhanced. Such a bond is not only weak but also labile as the formation of a singularity in  $\rho$  and a change in structure are then imminent.

Besides reforming **1a** by linking C3 and C1, structure **1b** can also form the puckered cyclobutyl cation **1c** by linking C3 to C4. The geometry of **1c** is energetically unstable. Its energy is  $10.9^{\text{7c}}$  kcal/mol above that of **1a** at 4-31G and 3.7 kcal/mol at 6-31G\*. The ring critical point, which is situated on the C3 side of the

(6) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1969**, *54*, 724–728. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(7) (a) Hehre, W. J.; Hibierty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 302–304. (b) *Ibid.* **1972**, *94*, 5917–5918. (c) Levi, D. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537–5539.

(8) There are no significant changes in the bond orders when different basis sets are used. Compare, for example, the values listed in Table I with those shown in Figure 1 which are calculated with use of the 4-31G basis set.

(9) Winstein, S. *Spec. Publ. Chem. Soc.* **1967**, *21*, 5–45.

C2–C4 axis, has a  $\rho$  value only  $0.40 \text{ \AA}^{-3}$  less than that of the labile bonds and a very soft curvature of  $\rho$  in the ring surface. Hence these bonds are of low order and possess substantial ellipticities and this structure is also close to an instability. An opening of either of the long ( $R_b = 1.65 \text{ \AA}$ ) labile bonds in this structure will result in a scrambling of the methylene groups.<sup>10</sup> Note that the lability of the C2–C3 bonds is also reflected in their low  $|\nabla^2\rho|$  values, a consequence of the large positive curvature of  $\rho$  along the bond path axis.

The degree of co-linearity of the major axes of neighboring CC bonds (the charge density analogue of the extent of “ $\pi$  overlap”) is easily determined by taking the scalar product of the unit vectors which define the major axes (in each case, the eigenvector of the Hessian of  $\rho$  at a bond critical point associated with  $\lambda_2$ , the negative curvature of smallest magnitude).

In structure **1a** the major axis of the C1–C4 bond has an overlap of 0.97 with the corresponding axes of the two long bonds which lie in the surface of the ring. The major axis of the C2–C3 bond is also directed toward the ring critical point. Thus this structure contains a delocalized distribution of charge in the plane of the ring, contiguous with the  $\pi$  distribution along the C1–C4 bond axis. The charge delocalization extends over the entire carbon framework. The overlap between C1–C4 and C1–C2 is maintained in the open structure and is increased to 0.99. The major axes of the bonds C1–C2 and C1–C4 ( $n = 1.3$ ) in structure **1c** are directed almost perpendicularly to the plane of the C1, C2, and C4 nuclei. Hence these bonds exhibit partial “ $\pi$ ” character in the usual sense and they have an overlap of 0.97. The ellipticities of the two labile bonds C2–C3 and C3–C4 ( $n = 0.7$ ), however, result from their interaction with the ring critical point. Hence their major axes lie in the ring surface. The overlap between the major axes of the two sets of bonds is close to zero.

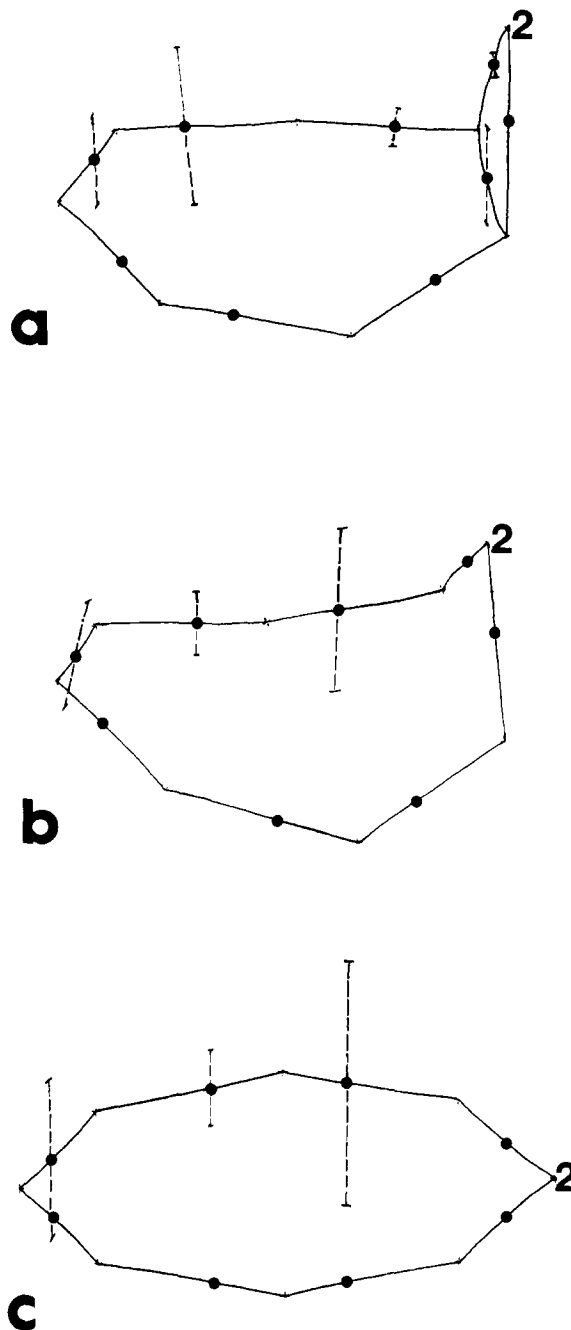
In summary, the extent of delocalization as determined by the degree of overlap of the major axes of the CC bonds is greatest for the structure of lowest energy, **1a**. Because of the low energy barriers separating structures **1a**, **1b**, and **1c** and the corresponding ease with which the molecular structure changes from a 3MR to an open system or to a 4MR, experimental observations made on this system would reflect some average of these possible structures.<sup>10</sup>

### Structures of $C_8H_9^+$

In 1967 Winstein<sup>9</sup> concluded that then available data were compelling in favor of a nonclassical homotropylium structure for the  $C_8H_9^+$  ion. Childs et al. reach the same conclusion on the basis of a recent X-ray diffraction study of 2-hydroxyhomotropylium hexachloroantimonate.<sup>11</sup> Haddon<sup>12</sup> on the basis of a theoretical study concluded that  $C_8H_9^+$  was best represented by a structure intermediate between one in which the C1–C3 bond of the cyclopropane ring was a single bond and another in which it was represented by a dashed homoaromatic bond.

Haddon<sup>13</sup> has recently obtained carefully optimized geometries for  $C_8H_9^+$  at the STO-3G level of approximation: for the equilibrium situation, for the planar transition state of the ring flip, and for the geometry of an intermediate on this reaction path. Haddon's calculated equilibrium geometry is in good general agreement with that determined by Childs et al. in their X-ray diffraction study.<sup>11</sup> In particular the C1–C3 separation is calculated to be  $1.58 \text{ \AA}$  compared to the experimental value of  $1.62 \text{ \AA}$ . The molecular graphs for this system are shown in Figure 2.

A homoaromatic bond does exist between C1 and C3 in the lowest energy structure **2a**. It possesses an order less than 1, a substantial ellipticity, a  $\nabla^2\rho$  value whose magnitude is approximately half of that of a normal CC single bond, and a bond path



**Figure 2.** Planar projections of the molecular graphs defining structures **2a**, **2b**, and **2c** of  $C_8H_9^+$ . The bond paths linking the protons are not shown. The methylenic carbon is labeled 2 as in Table II. The dashed lines through bond critical points denote the directions of the corresponding major axes. The length of each dashed line is proportional to the magnitude of the bond ellipticity. The angle between the plane of the 3MR and the plane containing nuclei C1, C3, C4, and C8 in part a is  $112.5^\circ$ .

which is noticeably curved (see Figure 2a), being bent below the plane of the 7MR. This latter characteristic is anticipated on the basis of the orbital descriptions of a homoaromatic bond as resulting from an overlap of orbitals on two centers which is intermediate between the overlap of a pair of  $\sigma$  and a pair of  $\pi$  orbitals.<sup>9</sup> Each of the CC bonds of the 7MR ring possess an ellipticity and their major axes are all approximately parallel to one another. For full realization of an aromatic system all seven bond orders and ellipticities should be equal and all major axes should be parallel to the 7MR axis (see, for example, the properties of  $C_7H_7^+$  in the previous paper<sup>5</sup> for which  $n = 1.5$  and  $\epsilon = 0.21$  for all CC bonds). In **2a** the relative alignment of the major axes around the 7MR is rather good (see Figure 2a). The dot products

(10) Staral, J. A.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016–8018 and references therein.

(11) Childs, R. F.; Varadarajan, A.; Lock, C. J. L.; Faggiani, R.; Fyfe, C. A.; Wasylshen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 2452–2456.

(12) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608–3616.

(13) Haddon, R. C., personal communication; now published: Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1983**, *105*, 118–120.

of the unit vectors defining neighboring major axes, beginning with the pair C1–C3 and C3–C4, are 0.89, 0.98, 0.99, and 0.97. The delocalization, however, is less than complete. The bonds C3–C4 and C1–C8 which link the homoaromatic bond to the pentadienyl fragment have relatively low bond orders and ellipticities. The bond orders of the 7MR sum to 9.0, a value equivalent to six single bonds and a six-electron  $\pi$  system.

In summary,  $C_8H_9^+$  is a homoaromatic system. The C1–C3 bond of cyclopropane is present in the equilibrium structure and it possesses the characteristics of a homoaromatic bond as originally put forth by Winstein:<sup>9</sup> a bond closing a potentially aromatic system with order less than 1 and an "orbital overlap intermediate between  $\sigma$  and  $\pi$ " as indicated here by  $n < 1$  and  $\epsilon > 0$ . Although the homoaromatic bond is conjugated with the unsaturated system in the 7MR, the delocalization of charge around the ring is less than complete.

The present theory predicts the homoaromatic bond to be labile. Its low bond order and its substantial ellipticity are both consequences of the proximity of a ring critical point and hence it is potentially unstable. In the equilibrium structure of  $C_8H_9^+$  the distance between the critical points of the C1–C3 bond and the 3MR is 0.44 Å and their values of  $\rho(r_c)$  differ by only 0.015 Å<sup>-3</sup>.<sup>14</sup>

Because of the migration of the ring critical point toward C1–C3, the ellipticities of the other two bonds of the 3MR are greatly reduced. Their properties are close to those of a normal CC bond of order 1. Thus the migration of the ring critical point from the ring center toward the bridging bond greatly reduces the extent of the delocalization of charge in the surface of the 3MR and only the bridging bond of the 3MR participates significantly in the conjugation of the 7MR.

The extension of the C1–C3 internuclear separation from its value of 1.576 Å in the equilibrium geometry to 2.324 Å to form the intermediate (Figure 2b) found by Haddon<sup>12</sup> to lie on the minimum energy path to the planar transition state (Figure 2c) leads to the coalescence of these two critical points, to the breaking of the C1–C3 bond, and to the destruction of the 3MR. The rupturing of the C1–C3 bond leads to a gross reorganization of the charge density in the remaining bonds that formed the 7MR. Thus the bond is not broken in isolation. Because of the concomitant charge reorganization which accompanies the breaking of the ring of conjugated bonds, only 6.4 kcal/mol separate the two structures. This energy may be taken as a measure of the homoaromatic stabilization.<sup>12</sup>

Another 19.0 kcal/mol is required to attain the planar transition-state geometry, Figure 2c. Its bond orders and the extent to which the charge is delocalized differ little from that for the intermediate **2b** and the energy difference between them is primarily caused by the bending motion. The bond orders (excluding the two single bonds) sum to 9.0 for the intermediate and 8.8 for the planar geometry indicating that the charge density of the ruptured C1–C3 bond has been transferred into the remaining delocalized system. It is interesting to note that the bond orders, ellipticities, and relative positioning of the bond critical points of the C5–C6–C7 fragment in structures **2b** and **2c** are almost identical with those found in the allyl cation,  $C_3H_5^+$ . At STO-3G the CC bonds in this cation have  $n = 1.48$  and  $\epsilon = 0.48$ .

### Structure of $C_4H_5^+$

Winstein first discussed the possibility of observing homoaromaticity in an interrupted cyclopropenyl cation. The simplest such system is the cyclobutenyl cation  $C_4H_5^+$ , structure **3a**. The bond properties for this molecule for an optimized equilibrium geometry obtained by Haddon,<sup>13</sup> using the 6-31G\* basis set, are given in Table III. The C1–C3 distance of 1.787 Å is in fair agreement with an experimental value of 1.775 Å obtained from X-ray studies of an aluminum chloride salt of the tetramethyl-substituted derivative of  $C_4H_5^+$ .<sup>15</sup> This distance of 1.78 Å is significantly larger, by 0.20 Å, than the corresponding distance

in  $C_8H_9^+$ . The angle made by the two faces at the C1–C3 axis is 148.1°. Structure **3b** is for the optimized planar geometry, the transition state to ring flipping, again obtained by Haddon.<sup>13</sup> This geometry is 4.4 kcal/mol higher in energy than the equilibrium geometry.

There is no C1–C3 bond critical point and hence no C1–C3 bond in the equilibrium geometry. Thus  $C_4H_5^+$  is predicted not to be homoaromatic at the 6-31G\* level of approximation. The same molecular graph and hence the same structure is obtained at the STO-3G level of approximation. Decreasing the C1–C3 distance to 1.59 Å does not yield a change in structure when the 6-31G\* basis is used, nor does a change occur when this decrease is accompanied by an increase in the puckering of the ring and a relaxation of the CC internuclear separations. The charge density in the region between C1 and C3 is not on the verge of forming a singularity in  $\rho$  which would then bifurcate into a bond critical point and a second ring critical point. Instead the existing ring critical point lies only 0.11 Å away from the midpoint of the C1–C3 axis and its  $\rho$  value of 0.893 Å<sup>-3</sup> and curvatures are typical of a four-membered ring system.

The C1–C4 and C1–C3 bonds have bond orders,  $\epsilon$ , and  $\nabla^2\rho$  values similar to those for a CC bond in the allyl cation at the 6-31G\* level. The remaining two bonds, those linked to the saturated carbon, are normal single bonds in terms of their  $n$  and  $\nabla^2\rho$  values<sup>5</sup> but have significant ellipticities, far in excess of the value anticipated because of the presence of a ring critical point in a 4MR system. The major axes of the single bond ellipticities are therefore not found to lie in the ring surface defined by the C1C2C3 nuclei, but instead are tilted up from this surface and have an overlap of 0.74 with the major axes of the two allyl bonds. These latter axes, in turn, are not perpendicular to the C1C3C4 surface as might be anticipated for normal unsaturated bonds, but instead are tilted away from the perpendicular direction in such a way as to increase their alignment with the major axes of the single bonds. Thus the ellipticities of the single bonds are induced by the presence of the neighboring unsaturated bonds. This is typical of a hyperconjugative interaction between a  $CH_2$  group and a  $\pi$  system.<sup>5</sup>

Aside from the small increases in the bond lengths, the only significant changes incurred by the system in attaining the planar geometry of the transition state are the vanishing of the induced ellipticities of the single bonds and the tilting of the major axes of the unsaturated bonds perpendicular to the plane of the nuclei. While orbital models offer no explanation as to why the induced ellipticities vanish in the planar geometry, the result remains that only in the puckered equilibrium geometry is there an interaction between the unsaturated and single bonds.

It is possible that by including electron correlation one might obtain a structure for **3** with a C1–C3 bond path. For example, second-order Møller–Plesset perturbation calculations lead to a decrease of the distance C1–C3 and an increase of the puckering of **3a** accompanied by an increase of the barrier to inversion.<sup>13,16</sup> Nevertheless, the C1–C3 distance of **3a** is still considerably larger (by  $\sim 0.2$  Å) than that of **2a** and the calculated charge distributions give no indication of the incipient formation of a C1–C3 bond path. Such a bond path, of course, could be generated by decreasing the C1–C3 separation to values less than 1.5 Å yielding a cyclopropane rather than a homoaromatic bond, a localization of positive charge at C2, and a considerable increase in energy. Thus, we conclude that the cyclobutenyl cation **3a** is not homoaromatic in the sense defined above. This statement does not exclude the existence of weak interactions in **3a**, which may lead to a change in certain molecular properties (e.g., the <sup>13</sup>C chemical shifts).

### Structure of $C_6H_7^+$

A number of different isomers of  $C_6H_7^+$  have been prepared as stable species. The two lowest energy isomers are the benzenium ion **4a** and the bicyclo[3.1.0]hexenyl cation **4b**. The conversion of structure **4b** to the more stable **4a** is a ground-

(14) The value of  $\rho$  at the 7MR critical point is 0.371 Å<sup>-3</sup>.

(15) Kruger, C.; Roberts, P. J.; Tsay, Y.-H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69–74.

(16) Cremer, D., to be published.

state-forbidden process according to the rules of orbital symmetry. The structures for this system were derived from charge densities obtained by optimizing the carbon framework in each structure, starting from the partially optimized STO-3G results given by Hehre.<sup>17</sup> This level of approximation places the geometry of **4b** 21 kcal/mol above that of **4a**, which may be compared with a recent experimental value, obtained from a thermochemical study of the hexamethyl-substituted derivatives, of 8.9 kcal/mol.<sup>18</sup>

The benzenium ion is anticipated<sup>9</sup> and found to be a classical carbenium ion. The bonds linking the saturated carbon are close to order 1 and their ellipticities are relatively small, typical of values induced by hyperconjugation.<sup>5</sup> The remaining carbon bonds are strongly conjugated, and all major axes are parallel to the ring axis. The bond orders for the unsaturated fragment are precisely those obtained by averaging over the three valence bond structures of the pentadienyl cation.

The interesting property of the methyl-substituted derivatives of **4b** is the ease of migration of a cyclopropane ring around the cyclopentenyl ring. Childs and Winstein<sup>19</sup> have concluded that the chemistry of such ions demands that the charge delocalization involve the two external cyclopropane bonds, rather than the internal C1–C3 bond. Indeed, as noted by these authors, if there was a homoconjugative C1–C3 bond as in  $C_8H_9^+$  the resulting system would be homoantiaromatic. This does not occur. The properties of the C1–C3 bond in **4b**, including its length, are those of a CC bond in an isolated cyclopropane (see Table IV of ref 5). One finds instead the two external bonds, C1–C2 and C3–C2, to be extended and to be the most labile bonds in this molecule: they are of order less than 1, they possess relatively low  $|\nabla^2\rho|$  values, and they exhibit ellipticities whose major axes have substantial overlaps with the corresponding axes of the neighboring bonds of the 5MR. Their properties are similar to, but less extreme than, those of the C1–C3 homoaromatic bond in  $C_8H_9^+$ , structure **2a**. Thus the ring of the six outer CC bonds forms a conjugated system. Their bond orders sum to 6.9, equivalent to four single bonds and a  $\pi$  system of approximately six electrons.

The ellipticity of the labile bonds in **4b** is of course primarily the result of the proximity of the ring critical point which is 0.50 Å from their bond critical points. Their major axes have an overlap of 0.78 with the major axes of the two neighboring bonds C1–C6 and C3–C4, which are tilted off the perpendicular axis of the 5MR. The major axes of the remaining two bonds in the conjugated system, those of C4–C5 and C5–C6, are parallel to the axis of the 5MR and have an overlap of 1.0 with each other and of 0.93 with the neighboring bonds. Clearly the major axes of C3–C4 and C1–C6 are rotated to maximize the conjugative coupling of the two labile bonds with the bonds which terminate at C5. The allyl fragment, whose existence was noted in structures **2b** and **2c** of  $C_8H_9^+$ , is again evident in structure **4b**.

The value of  $\rho$  at the ring critical point of the 3MR differs by  $0.31 \text{ \AA}^{-3}$  from the  $\rho_b$  values of the two long bonds. While not as labile as the C1–C3 bond in homotropylium (**2a**), they are predicted to be the least stable bonds in **4b**. The rupture of either of these external bonds yields the structure **4c**, the transition state for the migration of a cyclopropyl ring. The extent of charge delocalization is radically reduced in attaining the transition state. The three bonds which terminate at C1 are essentially single bonds and are no longer involved in the conjugation which is now restricted to the remaining four carbon atoms with a butadiene-like pattern of delocalization.<sup>5</sup>

Thus in the bicyclo[3.1.0]hexenyl cation there is a conjugative coupling of a cyclopropane ring with an unsaturated fragment

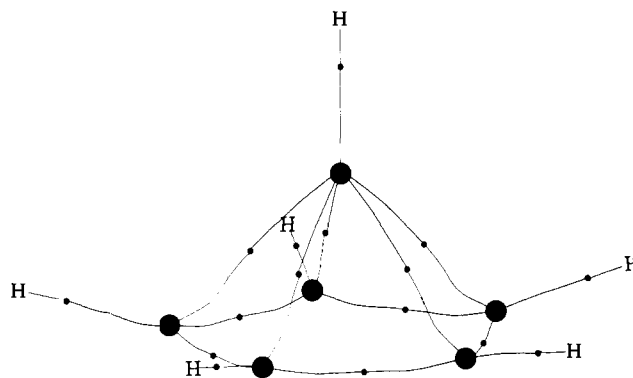


Figure 3. A planar projection of the molecular graph of  $C_6H_6^{2+}$ . The positions of the carbon nuclei are denoted by large solid circles.

to yield a cyclic system of delocalized charge. This situation is obtained not through the participation of the 1–3 bond of cyclopropane as in  $C_8H_9^+$  which would yield in this case a four-electron antiaromatic system, but rather primarily through a delocalization of the charge of the external bonds of the cyclopropane ring to yield a system of six electrons. In identifying these external bonds in **4b** as being labile, the present analysis thereby accounts as well for the perambulatory properties of the cyclopropane ring in this system. The relative motion of the ring critical point is not as great in  $C_6H_7^+$  as in  $C_8H_9^+$  and consequently all three bonds of the 3MR in **4b** exhibit substantial ellipticities. Unlike the case of  $C_8H_9^+$  where the external bonds of the 3MR are effectively removed from the conjugated system, the delocalization of charge over the entire surface of the 3MR persists in **4b** and this surface is conjugated with the remaining  $\pi$  distribution of the 7MR.<sup>20</sup> An eigenvector of the ring critical point contained in the ring surface has an overlap of 0.93 with the major axes of the C3–C4 and C1–C6 bonds.

## Discussion

Cyclopropane is unique among carbon ring systems in possessing a surface in which the charge is delocalized to a significant extent. The changes in the distribution of charge resulting from the conjugation of the 3MR to an unsaturated system give rise to a number of possible patterns of delocalization as determined by the effect these changes in  $\rho$  have on the position of the ring critical point. When linked by a single bond to an unsaturated system, such as the  $CH_2=CH-$  group,<sup>5</sup> the perturbation of the ring charge density is relatively slight, the position of the ring critical point is essentially unchanged, and the surface of delocalization in the 3MR is preserved. In this case the  $\pi$  density of the vinyl group forms a continuous delocalized system with the surface of the 3MR. When bonded to a cationic center such as in structure **1a**, the ring critical point migrates away from the C2–C3 critical point as a consequence of the transfer of charge to the  $CH_2^+$  group. The ellipticities of the two associated ring bonds are greatly increased and these bonds are labile. The surface of delocalized charge is, however, maintained and the  $\pi$  density of the external bond and the ring surface again form a continuous delocalized system. The same relative motion of the ring critical point occurs with the same consequences in structure **4b** of  $C_6H_7^+$ , but to a lesser extent. In the homotropylium cation, **2a**, the ring critical point migrates toward just one bond critical point, that of the bridging bond. This enhances the ellipticity of this bond at the expense of that of the remaining two ring bonds. The surface of delocalization is in this case essentially destroyed and replaced by a single  $\pi$ -like distribution as defined by the ellipticity and single major axis of the bridging bond. The resulting "homoaromatic coupling" of a cyclopropane ring so obtained is thus but one of a number of possible ways in which a 3MR can be conjugatively

(17) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 8908–8910. The STO-3G energies obtained here for structures **4a**, **4b**, and **4c** are respectively  $-228.26152$ ,  $-228.22793$ , and  $-228.15960$  au. Hehre assumed planar rings. We find C5 and C2 to be tilted out of the plane in the same direction by  $0.17^\circ$  and  $0.04^\circ$ , respectively, in **4a**. In **4b**, C5 is tilted up by  $1.2^\circ$  and C2 by  $74.8^\circ$ . In **4c**, the angle between the plane 1,2,5 and C1–C6 is  $109.45^\circ$  and the angle between this plane and the plane of 2,3,4,5 is  $179.16^\circ$ .

(18) Childs, R. F.; Mulholland, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 96–99.

(19) Childs, R. F.; Sakai, M.; Parrington, B. D.; Winstein, S. *J. Am. Chem. Soc.* **1974**, *96*, 6403–6409. Childs, R. F.; Winstein, S. *Ibid.* **1974**, *96*, 6409–6417. Childs, R. F.; Zeya, M. *Ibid.* **1974**, *96*, 6418–6424.

(20) Structure **4b** has been called homoantiaromatic.<sup>4,19</sup> Within the present approach such a description appears to be unnecessary.

linked to an unsaturated system.

A wide range of structures can now be viewed as possessing a surface of delocalized charge density. Consider, for example, the molecular graph shown in Figure 3 for the  $C_6H_6^{2+}$  cation, whose hexamethyl derivative was first synthesized by Hogeveen and Kwant.<sup>21</sup> The molecular graph is determined by a charge density obtained from an STO-3G wave function for an optimized geometry constrained to  $C_{5v}$  symmetry. The energy and geometrical parameters so obtained agree with those previously reported by Jemmis and Schleyer.<sup>22</sup>

This structure of  $C_6H_6^{2+}$  consists of five fused three-membered rings.<sup>23</sup> Each CC bond in the plane of the five carbons has  $n = 1.19$  and  $\epsilon = 0.05$ . Each of the long ( $R_e = 1.711 \text{ \AA}$ ), curved bonds terminating at the apical carbon has a low bond order of 0.44, a large ellipticity equal to 1.84, and a low value of  $|\nabla^2\rho| = 0.10 \text{ \AA}^{-5}$ . These bonds are labile. The values of  $\rho$  at the critical points of the three-membered rings are only  $0.004 \text{ \AA}^{-3}$  less than the values of  $\rho_b$  for the long CC bonds. There is therefore a ring of charge density of low and almost constant value,  $\sim 0.07 \text{ \AA}^{-3}$ , linking the bond and ring critical points in the atomic surface of the apical carbon atom. Associated with each 3MR is a surface

(21) Hogeveen, H.; Kwant, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 2208-2214.

(22) Jemmis, E. D.; Schleyer, P. V. R. *Ibid.* **1982**, *104*, 4781-4788. These authors have recently reviewed and extended the use of the  $4n + 2$  rule of aromaticity to account for the stabilities of capped structures.

(23) The surface of the apical carbon atom extends through the plane of the five carbon nuclei and there is no associated ring critical point. Hence the structure is not closed and does not form a cage.

of delocalized charge density and each such surface is coupled with its neighboring surface by the major axes of the common ring bonds. Thus the apical carbon is bonded to the remaining five carbon atoms by one continuous surface or cap of delocalized charge. A summation of the CC bond orders shows that approximately six electrons contribute to this delocalized system. The topological theory of molecular structure enables one to identify the existence of three-membered rings and their associated surfaces of delocalized charge in such capped structures. The relationship between the energy of a system and the one- and two-dimensional mechanisms of charge delocalization is currently under investigation using expressions which relate the quantity  $\nabla^2\rho(r)$  to the quantum mechanical stress tensor and kinetic energy density.<sup>24</sup>

**Acknowledgment.** We wish to thank Dr. R. F. Childs for many useful discussions and Dr. R. C. Haddon for kindly providing us with the optimized geometrical parameters for structures of  $C_8H_9^+$  and  $C_4H_5^+$  prior to publication. One of us (D.C.) wishes to acknowledge a research grant from the Deutsche Forschungsgemeinschaft and support provided by the Fonds der Chemischen Industrie and the "Rechenzentrum der Universität Köln".

**Registry No.** **1a**, 14973-56-9; **1b**, 25268-58-0; **1c**, 19067-43-7; **2a**, 39419-88-0; **2b**, 32731-02-5; **3b**, 12316-90-4; **4a**, 26812-57-7; **4b**, 32730-99-7; **4c**, 86013-58-3.

(24) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871-2883. Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.*, **1981**, *14*, 63-124.

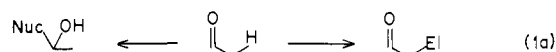
## Enol Thioethers as Enol Substitutes. An Alkylation Sequence

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**Abstract:** Ionic bromination of enol phenyl thioethers forms predominantly to exclusively 2-(phenylthio)-3-bromo-1-alkenes, an enolonium equivalent. The allylic bromide participates in displacements with stabilized and nonstabilized nucleophiles. The ability to hydrolyze the enol thioethers to their corresponding ketones equates this sequence to an equivalence of an enolonium ion. The versatility of the sulfur in selective introduction of allylic hydroxyl and amino groups as well as the ability to directly replace the sulfur substituent by hydrogen or alkyl imparts special significance to this approach. The sequence is highly regio- and chemoselective. Applications include the synthesis of lanceol and bisabolene and the introduction of steroid side chains.

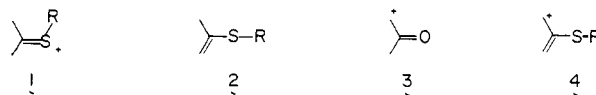
The carbonyl group represents one of the most important functional groups in organic chemistry because of the ability to achieve selective nucleophilic additions to the carbonyl carbon atom and electrophilic substitution at the  $\alpha$ -carbon atom (eq 1a).



Limitations posed by these direct processes have initiated searches for substitutes. For example, the catalytic effect of secondary amines in nucleophilic additions to carbonyl groups underpins the classical Doebner modification of the Perkin condensation in which the higher susceptibility of iminium ions to nucleophilic addition enhances the rate of addition of the weakly nucleophilic malonate anion.<sup>1</sup> The use of enamines or metalloenamines to mediate  $\alpha$ -substitution mainly derives from a concern for selectivity—chemoselectivity and diastereoselectivity.<sup>2</sup> From the above ex-

amples, nitrogen-based substitutes clearly have become imbedded into synthetic methodology.

The versatility offered by sulfur chemistry suggests that related sulfur systems may also have special roles to play. For carbonyl additions, the sulfur equivalent becomes a thionium ion **1**; for



$\alpha$ -substitutions, the critical intermediate becomes a vinyl sulfide, **2**. Further, the direct methods of synthesis of **1** and **2** without necessarily proceeding through carbonyl compounds provide even more incentive to explore this chemistry. For example, thioketals,

(2) Cook, "Enamines": Synthesis, Structure, Reactions"; Marcel Dekker: New York, 1969. Dyke, S. F. "The Chemistry of Enamines"; Cambridge University Press: London, 1973. Kuehne, M. E. *Synthesis* **1970**, 510. Wittig, G.; Reiff, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 7.

(1) Johnson, J. R. *Org. Reactions* **1942**, *1*, 210.