

Allylic Resonance—When Is It Unimportant?

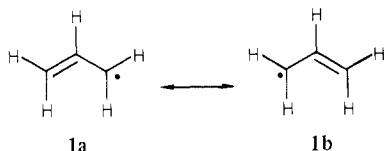
David Feller, Ernest R. Davidson, and Weston Thatcher Borden*

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195. Received September 12, 1983

Abstract: Second-order Jahn–Teller theory is used to show that electronegativity differences and cyclic conjugation can each minimize the importance of allylic resonance in radicals. However, it is also shown that electron repulsion causes resonance to be important in diradicals, even when they differ from radicals in which resonance is unimportant only by addition of an electron. Results of ab initio MCSCF and CI calculations on formyloxyl, $\text{O}(\text{CH}_2)_2^+$, and $\text{O}(\text{CH}_2)_2$ that support these predictions are reported. It is demonstrated how consideration of no-bond resonance structures can also be used to assess the importance of allylic resonance in heteroatom derivatives of allyl. The application of second-order Jahn–Teller theory and inspection of resonance structures to the prediction of the importance of resonance in nonallylic systems is also discussed briefly.

The theory of resonance in chemistry is an essentially qualitative theory, which, like the classical structure theory, depends for its successful application largely upon a chemical feeling that is developed through practice.¹

Experimentally, the allyl radical is found to have properties that are different from those expected for either of the two Kekulé structures (**1a** and **1b**) that can be drawn for it. In particular,



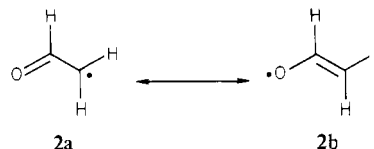
the EPR spectrum shows that the two ends of allyl are equivalent,² suggesting C_{2v} symmetry for the radical. EPR measurements have also found the barrier to rotation of one methylene group out of conjugation to be slightly in excess of 15 kcal/mol,³ rather than the extremely small value that would be predicted for rotation about the C–C single bond in either **1a** or **1b**. Additionally, formation of the allyl radical by C–H bond dissociation in propene has been determined to require 12 ± 2 kcal/mol less energy than formation of the 1-propyl radical from propane.⁴ Similar stabilization energies for allyl have been measured by kinetic studies of rotations about double bonds that result in the formation of allyl radicals.⁵

Resonance theory ascribes the structure and energetics of the allyl radical to the quantum mechanical result that at geometries with equal C–C bond lengths the wave functions for **1a** and **1b** contribute equally to the wave function for a species that is a hybrid of these two structures and whose energy is lower than that of either of them.⁶ Because a C_{2v} geometry would not be the equilibrium geometry for either **1a** or **1b**, the net “resonance energy” of allyl is the difference between the energy of the radical at its optimal C_{2v} geometry and the energy of one of the classical structures at its equilibrium (non- C_{2v}) geometry. Experimentally, the resonance energy may be measured as either the barrier to rotation of one methylene group in allyl out of conjugation, or as the difference between the primary C–H bond dissociation energies of propene and propane. The two definitions lead to

rather similar values for the resonance energy of allyl.

Radicals that are isoelectronic with allyl can be derived by replacing CH_2 and/or CH by isoelectronic atoms or groups of atoms (e.g., BH_2^- , NH , O , or F^+ for CH_2). If the replacement atoms have lone pairs of electrons, so that various states that differ in numbers of σ and π electrons are possible, only the lowest energy state among those in which three electrons occupy the π system is truly comparable with allyl. Because of their relationship to allyl, such radicals are often termed “allylic”.

Unsymmetrical allylic radicals, in which the two resonance structures corresponding to **1a** and **1b** are not identical, may, in general, be expected to have smaller resonance energies than allyl, since the two structures will not contribute equally to the resonance hybrid in such a radical. An example is the radical (**2**) derived from acetaldehyde by removal of a hydrogen from the methyl group. The two resonance structures are of unequal energy, with **2a** being preferred to **2b**, because of the greater strength of the



$\text{C}=\text{O}$ compared to the $\text{C}=\text{C}$ π bond. Consequently, **2a** contributes much more than **2b** to the actual resonance hybrid, a fact evidenced by both the computed⁷ and measured⁸ spin distribution in this type of radical.

Of course, for allylic radicals in which the two contributing structures are identical, symmetry demands that they contribute to the hybrid equally. Therefore, resonance might be expected to be of comparable importance to the structure and stabilization of such radicals as it is in allyl. Thus, we were surprised to discover in our calculations on the lowest π state of the formyloxyl radical (**3**) that there was little preference for a C_{2v} geometry, where resonance stabilization is maximized, over a geometry with unequal C–O bond lengths.⁹

In our preliminary communication on the general subject of allylic resonance,¹⁰ we used the theory of second-order Jahn–Teller effects¹¹ to explain the apparent lack of resonance stabilization of **3**. We also showed why one would similarly predict that substitution of O^+ for the central carbon in allyl should likewise confer upon **4** a very low resonance energy. Computational results

(1) Pauling, L. “Nature of the Chemical Bond”, 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 220.

(2) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(3) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.

(4) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223. DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *Ibid.* **1980**, *102*, 3334, and references cited therein.

(5) Doering, W. von E.; Beasley, G. H. *Tetrahedron* **1973**, *29*, 2231. Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48.

(6) This subject is discussed in most elementary organic chemistry textbooks. See, for example: Morrison, R. T.; Boyd, R. N. “Organic Chemistry”, 4th ed.; Allyn and Bacon: Boston, 1983; pp 402–407. For a more sophisticated treatment see: Wheland, G. W. “Resonance in Organic Chemistry”; Wiley: New York, 1955.

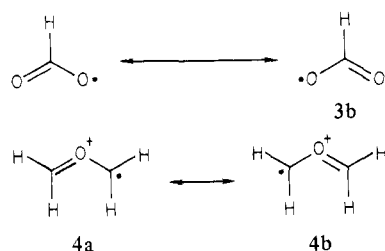
(7) Huyser, E. S.; Feller, D.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1982**, *104*, 2956.

(8) Camaioni, D. M.; Walter, H. F.; Jordan, J. E.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7978.

(9) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459.

(10) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347.

(11) For a lucid discussion and leading references see: Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947.



were reported in support of this prediction.

In this paper we amplify the previous arguments and demonstrate how they can be used to make some predictions about the importance of allylic resonance in a variety of radicals. We also discuss why allylic resonance is important in diradicals, even when they differ from radicals in which resonance stabilization is unimportant only by the addition of an electron. The results of computations that support these conclusions are presented in detail. Finally, we show how, in heteroatom derivatives of allyl, consideration of no-bond resonance structures can be used to predict the importance, or lack thereof, of allylic resonance.

Qualitative Theoretical Considerations

The effect of heteroatom substitution on the molecular orbital (MO) energies of the allylic π system is shown schematically in Figure 1 for replacement of the terminal CH_2 groups in allyl by the oxygen atoms of formylxyl. Since oxygen is more electronegative than carbon, all the MOs are stabilized by the substitution. Mixing between the two b_1 MOs increases the coefficients of $1b_1$ at the terminal atoms at the expense of those in $2b_1$. This is why $1b_1$ is stabilized more than $2b_1$ by the substitution of oxygen for CH_2 . However, the $1a_2$ MO is stabilized more than the two b_1 MOs, because $1a_2$ has all its density on the two terminal atoms.

Since $1a_2$ is stabilized more than $1b_1$, the energy gap between these two orbitals decreases, as shown schematically in the diagram. This effect is clearly seen in the orbital energies that emerge from calculations on allyl and formylxyl (*vide infra*). The energy difference between $1b_1$ and $1a_2$ of 3.4 eV in allyl is more than halved in formylxyl, where it is computed to be only 1.4 eV.

In the lowest energy configuration, 2A_2 , the $1a_2$ orbital is singly occupied. Excitation of an electron from the $1b_1$ MO, which is doubly occupied in 2A_2 , into $1a_2$ gives a 2B_1 configuration. These two configurations belong to different representations of the C_{2v} point groups, but they are mixed by a molecular distortion of b_2 symmetry, which shortens one of the two equivalent bonds to the central atom and lengthens the other.

According to the theory of the second-order Jahn-Teller effect,¹⁰ the mixing between these two configurations that occurs on a b_2 molecular distortion should reduce the force constant required for stretching one bond to the central atom and shortening the other. The magnitude of the reduction is predicted to depend inversely on the energy difference between 2A_2 and 2B_1 , so that the closer these two configurations are in energy, the easier this type of distortion from C_{2v} symmetry should be.

As noted above, the electronegativity difference between carbon and oxygen causes the energy difference between the $1b_1$ and $1a_2$ MOs to be much smaller in formylxyl than in allyl. This results in 2A_2 and 2B_1 being much closer energetically in formylxyl than in allyl, since these configurations differ only by the excitation of an electron from $1b_1$ to $1a_2$. The second-order Jahn-Teller effect thus predicts that distortion from C_{2v} symmetry to a geometry with unequal bond lengths between the heavy atoms should be much more facile in formylxyl than in allyl. The computational evidence that supports this prediction is discussed in the next section.

Because resonance between the two contributing structures for formylxyl (**3a** and **3b**) is maximized at C_{2v} geometries, the predicted ease of distortion of formylxyl from C_{2v} symmetry indicates that resonance is less important in this radical than in allyl. More generally, a small energy gap between the lowest 2A_2 and 2B_1 configurations in an allylic-type radical augers not only for a relatively low energetic cost in going to a bond-alternated

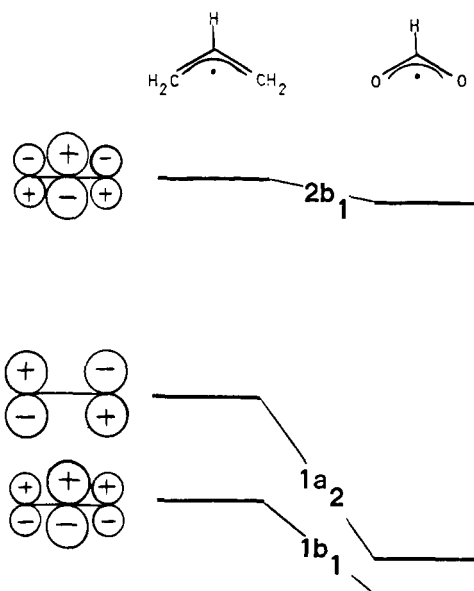


Figure 1. π MO energies in allyl and formylxyl.

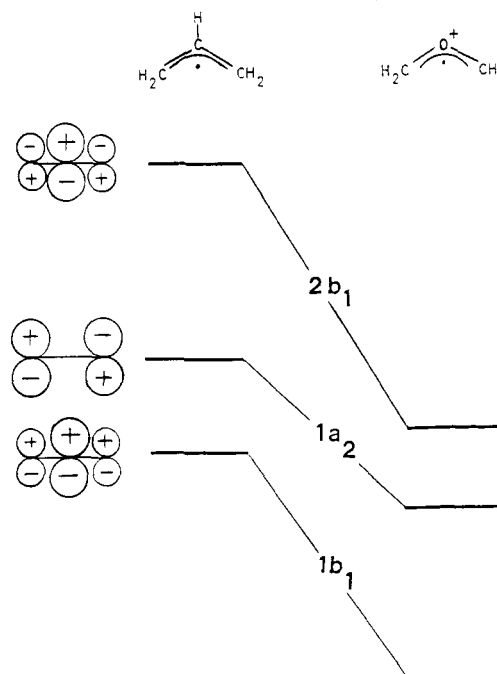


Figure 2. π MO energies in allyl and $\text{O}(\text{CH}_2)_2^+$.

geometry, but also for a low resonance energy. Thus, second-order Jahn-Teller considerations allow one to devise strategies for constructing allylic radicals with small resonance energies, by minimizing the energy difference between these two configurations.

As discussed above, substitution of electronegative atoms at the termini of allyl reduces the $^2A_2 - ^2B_1$ energy difference in the resulting allylic π system by decreasing the energy difference between $1b_1$ and $1a_2$. Another method for creating a relatively low-lying 2B_1 configuration involves reducing the energy gap between $1a_2$ and $2b_1$, since excitation of the unpaired electron in 2A_2 from the former MO to the latter gives rise to a 2B_1 configuration. The energy difference between $1a_2$ and $2b_1$ can also be reduced from that in allyl by heteroatom substitution.

Shown schematically in Figure 2 is the effect on the allylic π MO energies of substituting for the central CH group in allyl the isoelectronic O^+ . Any realistic calculation would show that all the π MOs are stabilized by the presence of the additional proton in O^+ , but both the b_1 MOs are stabilized more than $1a_2$, since the latter MO has a node at the central atom. Indeed, in a Hückel-type calculation the a_2 MO would show no stabilization on central atom substitution.

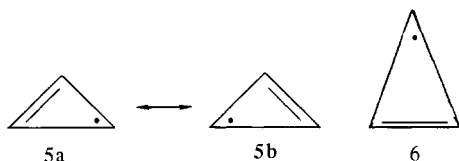
Since substitution of an electronegative atom, in this case O^+ , for the central CH group in allyl stabilizes $2b_1$ more than $1a_2$, the energy difference between these orbitals is reduced from that in allyl. This leads to the expectation that $O(CH_2)_2^+$ (**4**) should undergo a more facile distortion from C_{2v} symmetry and have a lower resonance energy than allyl.

Substitution of electropositive atoms for either the central or terminal carbons in allyl also produces low-lying 2B_1 configurations. However, the 2B_1 configuration that is stabilized, relative to 2A_2 , is the opposite of the one that is lowered by substitution of an electronegative atom for carbon at the same positions. For example, substitution of the terminal carbons by electropositive atoms raises the energy of $1a_2$ relative to that of the b_1 MOs. This decreases the energy gap between $1a_2$ and $2b_1$. In contrast, as shown in Figure 1, substitution of the terminal carbons by electronegative atoms decreases the gap between $1a_2$ and $1b_1$.

Because the substitution of electronegative atoms for the terminal CH_2 groups and an electropositive atom for the central carbon in allyl both serve to decrease the energy separation between the $1b_1$ and $1a_2$ MOs, a radical-like $FBHF^+$ would be expected to have a particularly low-lying $1b_1 1a_2^2$, 2B_1 configuration. Similarly, since the separation between $1a_2$ and $2b_1$ is decreased by substitution of an electronegative atom for the central CH and electropositive groups at the termini of allyl, H_2BFBH_2 would be anticipated to have a very low energy $1b_1 2b_1$, 2B_1 configuration. The lowest 2A_2 state of each radical would, as a consequence, be expected to distort easily to geometries with unequal F-B bond lengths, and the resonance energy of each should be small.

Heteroatom substitution provides one mode of creating a low-lying 2B_1 state in allylic radicals, but a small energy gap between $1a_2$ and $2b_1$ can also be produced by joining the terminal atoms of allyl by a bond to form the cyclopropenyl radical. The π interaction between the terminal atoms thus created destabilizes $1a_2$ while stabilizing both b_1 MOs. In fact, at a D_{3h} geometry $1a_2$ and $2b_1$ become degenerate by symmetry, and 2A_2 and 2B_1 become the two components of a degenerate $^2E'$ state.

Of course, the Jahn-Teller theorem¹² predicts that $^2E'$ will show first-order instability to a distortion of e' symmetry. Such a distortion can lead to two distinct C_{2v} geometries, the bonding in which can be depicted, respectively, as in **5** and **6**. The former



has a delocalized, allylic wave function, whereas in the latter the odd electron is largely localized at the unique carbon atom. Indeed, the other two possible choices for the unique carbon in **6** give the two resonance structures that contribute to **5**, each at the C_{2v} geometry appropriate to its localized bonding.

An important question concerns the relative energies of **5** and **6**. This question cannot be answered unequivocally using a qualitative theory like that of the second-order Jahn-Teller effect. However, one can predict that asymmetric C-C bond-length distortions in **5**, which lead to one of the two other localized structures that is equivalent to **6**, should be facile, if not actually favorable energetically. The prediction is based on the supposition that, even after distortion from a D_{3h} geometry to one of C_{2v} symmetry that is appropriate for **5**, 2B_1 must still be close in energy to the 2A_2 ground state. Consequently, the b_2 molecular distortion that takes **5** to the geometry appropriate for one of its two, localized, resonance contributors should be an easy one.¹³

Ab initio calculations on the cyclopropenyl radical find that the three equivalent structures that correspond to **6** are actually

Table I. MCSCF Vibrational Frequencies and CI Force Constants Calculated for Symmetric (a_1) and Asymmetric (b_2) Stretching of the Bonds between Heavy Atoms in Some Allylic Systems

molecule	$\nu(a_1)^a$	$\nu(b_2)^a$	$k(a_1)^b$	$k(b_2)^b$
allyl (1)	1093 ^c	1204 ^c	8.2	7.4
formyloxyl (3)	1328	586	10.1	5.4
$O(CH_2)_2^+$ (4)	1117	545i	7.3	-4.6
$O(CH_2)_2$ (7)	1068	1580	8.2	7.0

^a Frequency in cm^{-1} . ^b Force constant in $mdyn/\text{\AA}$. ^c Data from ref 16.

lower in energy than the three allylically delocalized structures that correspond to **5**.¹⁴ This is the case even without the pyramidalization at the unique carbon in **6** that further stabilizes it with respect to **5**. The ab initio results are in excellent agreement with the conclusions of Closs and co-workers from their experimental studies of the trimethylcyclopropenyl radical.¹⁵

Computational Results

In order to confirm the second-order Jahn-Teller effect predictions regarding the effect of electronegativity differences on allylic resonance energies, we carried out calculations on two oxygen substituted allylic systems, **3** and **4**. As noted in the introductory section, our calculations on the 2A_2 state of formyloxyl (**3**)⁹ were what first led us to consider the effect of electronegativity differences on allylic resonance. At all levels of theory a structure with one single and one double C-O bond length was computed to be nearly isoenergetic with the optimized structure with C_{2v} symmetry.

As discussed above, the second-order Jahn-Teller effect really predicts only that formyloxyl should undergo a relatively easy distortion to a bond-alternated geometry. The inference that the resonance energy of formyloxyl is small is drawn from this fact. We therefore set out to obtain some quantitative computational data on how easy it is to distort the C-O bond lengths in formyloxyl from C_{2v} symmetry.

One indication of the ease of such a distortion is the frequency of the asymmetric (b_2) C-O stretching motion, compared with that for symmetric (a_1) C-O stretch. The lower the relative frequency for asymmetric stretch, the easier is a distortion to a bond-alternated geometry where resonance is relatively unimportant. Since Takada and Dupuis have computed vibrational frequencies for the allyl radical,¹⁶ we carried out similar calculations for formyloxyl.

Unless correlation is provided between the unpaired electron in allylic systems and the pair in the lowest π MO, spuriously localized wave functions are obtained, even for allyl. This is known as the "doublet instability problem", and it has been discussed frequently in the literature by us^{7,9,17} and by others.¹⁸ In order to make our calculations on formyloxyl comparable with those of Takada and Dupuis on allyl, we correlated the π electrons with the same type of multiconfiguration (MC) SCF wave function, involving all possible assignments of the π electrons to the lowest three π orbitals.

To further make our calculations comparable to theirs, we employed the same 3-21G basis set¹⁹ and calculated the force constants by taking finite differences between analytically evaluated first derivatives. Also like Takada and Dupuis, we carried out these calculations, using GAMESS.²⁰ The vibrational fre-

(14) Davidson, E. R.; Borden, W. T. *J. Chem. Phys.* **1977**, *67*, 2191. Poppinger, D.; Radom, L.; Vincent, M. A. *Chem. Phys.* **1977**, *23*, 437. Baird, N. C. *J. Org. Chem.* **1975**, *40*, 624.

(15) Closs, G. L.; Evanochko, W. T.; Norris, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 350.

(16) Takada, T.; Dupuis, M. *J. Am. Chem. Soc.* **1983**, *105*, 1713.

(17) Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

(18) Paldus, J.; Veillard, A. *Mol. Phys.* **1978**, *35*, 445, and references therein.

(19) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(20) Dupuis, M.; Spangler, D.; Wendolowski, J. J. *NRCC Software Catalog*, Vol. 1, 1980, Program GG01.

(12) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220.

(13) The first-order Jahn-Teller effect predicts equal energy lowering on going from a D_{3h} geometry to that of either **5** or **6**, but higher order effects can favor one C_{2v} structure over the other. For a discussion see: Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

quencies obtained are shown in Table I, along with the comparable frequencies for allyl.

Because C–O π bonds are both stronger and stiffer than C–C, the symmetrical stretching frequency that is computed for formyloxyl is higher than the calculated for allyl. However, whereas the asymmetric stretch in allyl is of even higher frequency than the symmetric stretch, the asymmetric C–O stretching frequency in formyloxyl is less than half of that computed for symmetric stretch.

Stretching frequencies can be somewhat misleading, because they include a number of different effects. For example, in allyl and in most AB_2 molecules, the asymmetric stretching frequency is higher than that for symmetric stretch, despite the fact that the force constant for asymmetric stretch is lower. The higher frequency for asymmetric stretch is a result of the fact that the central atom moves less in this mode, which makes the reduced mass for this mode smaller. In order to more directly compare the ease of distorting both radicals from C_{2v} symmetry, we also computed the force constants for symmetric and asymmetric bond stretching in each.

In examining symmetry breaking molecular distortions, it is essential to carry out calculations at a level of theory that produces the same energy at the point of highest symmetry, whether or not symmetry is imposed on the MOs. If the energy depends on whether or not symmetry is imposed on the MOs, the energy will exhibit a discontinuous change on a symmetry-lowering molecular distortion. Previous work in these laboratories has demonstrated that in charged π systems charge polarization of the σ core by the π electrons can lead to such discontinuity, unless σ – π correlation is included.^{17,21}

Since some charge separation is present in formyloxyl, calculations that correlate only the π electrons might be expected to show a discontinuous change in the energy on reduction of the symmetry from C_{2v} . Therefore we anticipated that it might be necessary to include σ – π as well as π – π correlation. Because of the large number of configurations necessary to provide even a modicum of σ – π correlation, it proved expedient to carry out such calculations using configuration interaction (CI) rather than MCSCF methodology.

In order to test whether the inclusion of σ – π CI is, in fact, important in formyloxyl, CI calculations were performed at the MCSCF optimized C_{2v} geometry. The calculations were carried out using two different sets of restricted Hartree–Fock (RHF) orbitals. One set was obtained by imposing C_{2v} symmetry on the orbitals. The other was obtained with the plane of the molecule as the only symmetry element imposed. Because of the doublet instability problem, the orbitals in the latter wave function did not emerge with C_{2v} symmetry.

In a nonpolar molecule, in which the σ core should be the same for both sets of π MOs, complete π CI with either set of MOs should give the same wave function and, hence, the same energy. For instance, we found for allyl that both the C_{2v} and C_s constrained sets of MOs did, in fact, give the same π CI energy of –115.8431 hartrees. However, for formyloxyl the π CI energy of –187.1084 hartrees with C_{2v} constrained MOs was 0.0009 hartree (0.6 kcal/mol) lower than that with the C_s constrained MOs. Consequently, π CI calculations on formyloxyl would, indeed, exhibit a discontinuous change in the energy on moving away from C_{2v} symmetry.

CI calculations that included all single σ excitations for all possible π configurations were also carried out for formyloxyl. These larger CIs yielded as energy of –187.2128 hartrees, starting from either the C_{2v} or C_s constrained molecular orbitals. Consequently, calculations at this level of theory do not exhibit discontinuities on symmetry breaking and so should be capable of yielding meaningful force constants.

The force constants for both allyl and formyloxyl radicals were computed from the σ – π CI energies by quadratic fitting. The results are shown in Table I. The force constants provide the same

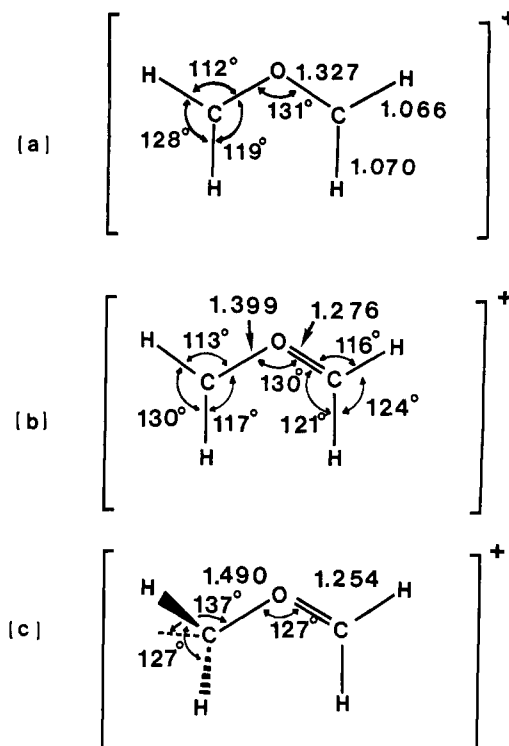


Figure 3. MCSCF optimized geometries for $O(CH_2)_2^+$ with (a) C_{2v} symmetry imposed, (b) C_s symmetry imposed, and (c) C_s symmetry imposed and one CH_2 group twisted out of conjugation.

qualitative picture as the frequencies. As expected, the force constant for symmetric (a_1) stretch in formyloxyl is larger than that in allyl. In allyl the force constant for asymmetric (b_2) stretch is only 10% lower than that for symmetric stretch, but in formyloxyl the former is barely half of the latter. Even comparing just the force constants for asymmetric stretch, it is considerably easier to distort formyloxyl than allyl to a geometry with unequal bond lengths between the heavy atoms.

Also shown in Table I are the π MCSCF vibrational frequencies and the σ – π CI force constants computed for $O(CH_2)_2^+$ (**4**). The optimal C_{2v} geometry for this radical, shown in Figure 3a, was obtained by the same type of π MCSCF calculation used for allyl and formyloxyl. The calculated energy was –151.7364 hartrees.

The imaginary frequency, computed at the π MCSCF level, for asymmetric stretching in **4** is consistent with the negative force constant obtained by σ – π CI calculations. At both levels of theory resonance is predicted to play such a small role in stabilizing **4** that a geometry with unequal C–O bond lengths is preferred.

The optimal geometry with unequal C–O bond lengths was also obtained by three-electron, three-orbital MCSCF calculations and is shown in Figure 3b. The surface for asymmetric C–O stretching is apparently rather flat, since, despite the substantial change in C–O bond lengths between the geometries in Figures 3a and 3b, the latter is lower in energy than that former by only 0.0006 hartree (0.4 kcal/mol). Because the computed surface is flat, more sophisticated calculations (e.g., ones that included polarization functions in the basis set) could conceivably change the role of the C_{2v} structure from that of being a transition state which connects two, mirror image, C_s minima to being the only minimum on the potential surface.²²

The ease of asymmetrically distorting the C–O bond lengths away from C_{2v} symmetry in **4** suggests that the resonance energy of this radical is quite small, compared with that of allyl. We

(21) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *103*, 5302; **1981**, *103*, 5725.

(22) CI calculations, carried out with polarization functions included in the basis set, did, in fact, find the C_{2v} geometry shown in Figure 3a to be slightly lower in energy than the C_s geometry shown in Figure 3b. However, since the geometries were not reoptimized with the larger basis set, we hesitate to regard these results as definitive, especially in view of the flatness of the computed surface for C–O bond-length distortions from C_{2v} symmetry.

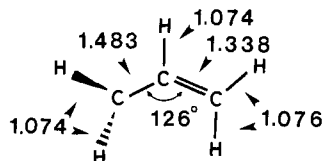


Figure 4. MCSCF optimized geometry of the allyl radical with one CH_2 group twisted out of conjugation.

decided to investigate the magnitude of the resonance energy in planar **4** by calculating the energy change on twisting one CH_2 group out of conjugation. Further motivation for carrying out these calculations was provided by the finding of Radom and co-workers that, at the RHF and UHF levels of theory, a geometry with one CH_2 group twisted out of conjugation is preferred for **4**.²³

A C_s geometry with one methylene group twisted out of conjugation was optimized with an MCSCF wave function that correlated two of the four electrons in π orbitals (double bond plus out-of-phase combination of C-H bonding orbitals on the twisted CH_2 group). The resulting geometry is shown in Figure 3c. The MCSCF energy was 0.0030 hartree (1.9 kcal/mol) higher than that at the planar C_s geometry with unequal C-O bond lengths. Thus, our calculations, in contrast to those reported by Radom et al.,²³ suggest that **4** does prefer a planar geometry. Nevertheless, the resonance energy of about 2 kcal/mol that we compute for **4** is only a very small fraction of the approximately 15 kcal/mol that EPR studies have found to be necessary to twist one methylene group out of conjugation in allyl.³

In order to verify the accuracy of our method for computing the energy required to twist one methylene group out of conjugation in **4**, we carried out a geometry optimization on allyl with one methylene group also twisted out of conjugation. The same type of MCSCF wave function that correlated one π pair of electrons was again employed. The optimal geometry, shown in Figure 4, was 0.0225 hartree (14.1 kcal/mol) higher than the three-electron, three-orbital, MCSCF energy of -115.8402 hartrees for the planar radical. The excellent agreement between this type of calculation²⁴ and experiment³ for allyl suggests that the computational prediction of a very small barrier to methylene group rotation in **4** is correct.

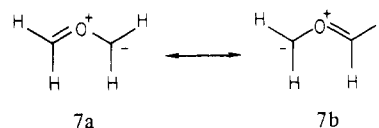
This prediction can, in principle, be tested experimentally, for the radical cation of ethylene oxide apparently undergoes ring opening to **4**, both in the gas phase²⁵ and in solid freon solutions.²⁶ The EPR spectrum in solid solutions indicates that the radical has C_{2v} symmetry on the EPR time scale at 77 K. This finding is consistent with the planar structure and very flat potential surface for asymmetric C-O bond-length distortions found by our calculations.

Investigations of the geometry of and force constants in this radical by other spectroscopic techniques are desirable. Most importantly, however, from EPR studies on **4**, analogous to those carried out for allyl, it should be possible to confirm our prediction that the barrier to methylene group rotation in **4** is but a small fraction of that in allyl. An experimental determination of this

barrier would provide a critical test of our qualitative predictions and quantitative calculations.

Diradicals

Since both second-order Jahn-Teller considerations and the results of MCSCF and CI calculations indicate that the resonance stabilization of the $\text{O}(\text{CH}_2)_2^+$ radical (**4**) is quite small, it is natural to assume that resonance would also play a minor role in the neutral species (**7**), where one electron is added to the nonbonding ($1a_2$) MO.



In second-order Jahn-Teller terms, the mixing between the $1a_2$ MO in 2A_2 and the $2b_1$ MO in 2B_1 is what provides electronic relaxation on b_2 molecular distortion from C_{2v} to C_s symmetry. The mixing stabilizes the $1a_2$ MO. If a second electron occupies the $1a_2$ MO, the total stabilization energy should be twice as large.

Equation 1 gives the expression for the stabilizing effect of mixing the 1A_1 ground state of a four-electron π system like that in **7** with the 1B_2 excited state that arises from exciting an electron from $1a_2$ to $2b_1$.

$$\Delta E = \left[\int \Psi(^1A_1) H \Psi(^1B_2) \right]^2 / [E(^1A_1) - E(^1B_2)] \quad (1)$$

With

$$\Psi(^1A_1) = |1b_1^2 1a_2^2\rangle \quad (2)$$

and

$$\Psi(^1B_2) = |1b_1^2 1a_2 2b_1(\alpha\beta - \beta\alpha)/2^{1/2}\rangle \quad (3)$$

the numerator of eq 1 is, in fact, twice as large as the numerator in the corresponding expression for the energy lowering on mixing 2A_2 with 2B_1 in a radical like **4**.

It is essential to note, however, that the denominator of eq 1 also changes in going from a radical to a molecule containing an additional electron in the nonbonding MO. For an open-shell singlet wave function, like that for 1B_2 , the energy expression contains the exchange integral between the two, singly occupied MOs. This term occurs with a positive sign, because the electrons in the two, singly occupied MOs are anticorrelated. If the two orbitals span the same region of space, as they generally will in an allylic system when the two MOs are similar in energy, the exchange integral is large. The high energy calculated for 1B_2 under these circumstances corresponds physically to the fact that the wave function for the electrons in the singly occupied MOs is highly ionic, with a large probability for both electrons simultaneously occupying the same atomic orbital.²⁷

Although coulombic repulsion between the electrons in the singly occupied MOs in 1B_2 tends to raise its energy, 1A_1 is not similarly destabilized. In fact, the closer in energy that the $2b_1$ MO is to $1a_2$, the smaller is the coulombic repulsion energy between the nonbonding electrons in 1A_1 .

This is a consequence of the fact that, in addition to the configuration in eq 2, there is another 1A_1 configuration in which both the electrons in $1a_2$ are excited into $2b_1$. The mixing between the two configurations correlates these two electrons in the lowest 1A_1 state, thus reducing their coulombic repulsion energy. Indeed, if $1a_2$ and $2b_1$ were both confined entirely to the terminal atoms, as would be the case with an infinitely electronegative central atom, the probability of finding the two nonbonding electrons in the same atomic orbital would be essentially zero.²⁷

Because 1A_1 is expected to have a much lower coulombic energy than the highly ionic 1B_2 , the denominator of eq 1 can be anticipated to be much larger when there are two nonbonding electrons

(23) Bouma, W. J.; Macleod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540. **Added in Proof:** Radom's more recent calculations find, in agreement with our results, that a planar geometry is preferred and that the potential surface for distortion from C_{2v} symmetry is very flat. Bouma, W. J.; Poppinger, D.; Saebo, S.; Macleod, J. K.; Radom, L. *Chem. Phys. Lett.* **1984**, *104*, 198.

(24) A similar type of calculation, using a minimal basis set of STO-3G orbitals and CI to provide correlation, affords a comparable value for the barrier to rotation in the allyl radical: Baird, N. D.; Gupta, R. R.; Taylor, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 4531.

(25) Corderman, R. R.; LeBreton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929. Bouma, W. J.; Macleod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724.

(26) Snow, L. D.; Wang, J. T.; Williams, F. *Chem. Phys. Lett.* **1983**, *100*, 193. The same EPR spectrum has been reported (Symons, M. C. R.; Wren, B. W. *Tetrahedron Lett.* **1983**, *24*, 2315), but it has been interpreted in terms of a closed structure for the radical cation. These latter authors apparently failed to consider the possibility of ring opening to **4**, which readily rationalizes the observed magnitude of the hyperfine coupling constants.

(27) For a discussion of the wave functions for diradicals see: Borden, W. T. In "Diradicals"; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1-72. Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

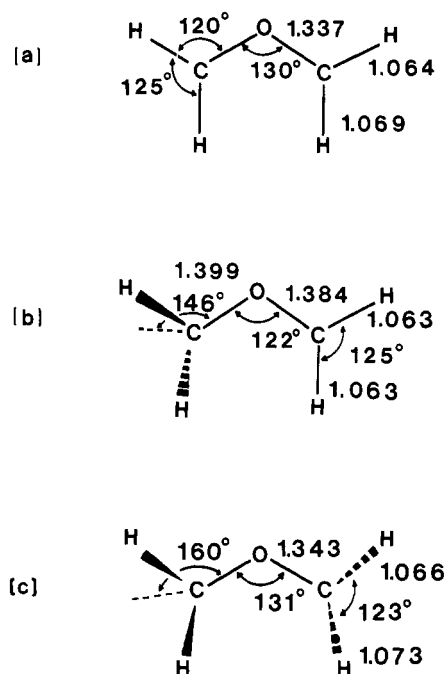


Figure 5. MCSCF optimized geometry for $\text{O}(\text{CH}_2)_2$ with (a) C_{2v} symmetry imposed (b) one CH_2 group twisted out of conjugation, and (c) anti pyramidalized CH_2 groups.

than when there is one. Consequently, in the diradical case, electron repulsion effects, manifested in the increase in the size of the denominator, can, in principle, overwhelm the doubling of the one-electron stabilization energy in the numerator. Since the difference in the coulombic repulsion energies between 1A_1 and 1B_2 can easily be in excess of 5 eV in diradicals where $1a_2$ and $2b_1$ are effectively degenerate, molecular distortion from C_{2v} symmetry can be much less favorable in a diradical than in the corresponding radical species. Thus, when cognizance is taken of electron repulsion, second-order Jahn–Teller considerations lead to the expectation that addition of an electron to an allylic radical might enhance the importance of resonance in the resulting diradical.

In order to test this qualitative prediction, we carried out calculations on the parent carbonyl ylide (7). The computational methodology was the same as that used for the radical cation (4). The optimized planar geometry is shown in Figure 5a. The MCSCF vibrational frequencies and $\sigma-\pi$ CI force constants in Table I reveal that there is a strong preference for equal C–O bond lengths in 7, unlike the case in the radical cation (4), where a bond-alternated geometry is lower in energy. The force constants found for 7 are quite comparable to those computed for the allyl radical.

Although the force constant for b_2 distortion of the C–O bond lengths in 7 proved to be large and positive, negative force constants were found for a_2 and b_1 modes of pyramidalizing the two methylene groups. We optimized the geometry for the anti (a_2) mode of pyramidalization. The structure is shown in Figure 5c. Its energy of -151.9737 hartrees is only 0.0008 hartree (0.5 kcal/mol) below that of the planar diradical. Presumably, the pyramidalization of the methylene groups results from the fact that they have some carbanionic character. A Mulliken population analysis finds each methylene to have 1.2 π electrons in the optimal planar geometry.

Because the force constant for asymmetric distortion of the bond lengths between the heavy atoms in 7 is similar to that in the allyl radical, one might expect the resonance energy of 7 to be comparable to that in allyl. The resonance energy was obtained by calculating the energy necessary to twist one methylene group out of conjugation. The MCSCF optimized C_s structure, containing one unpaired σ and one unpaired π electron, is shown in Figure 5b.²⁸ The two-configuration π MCSCF energy was 0.0265

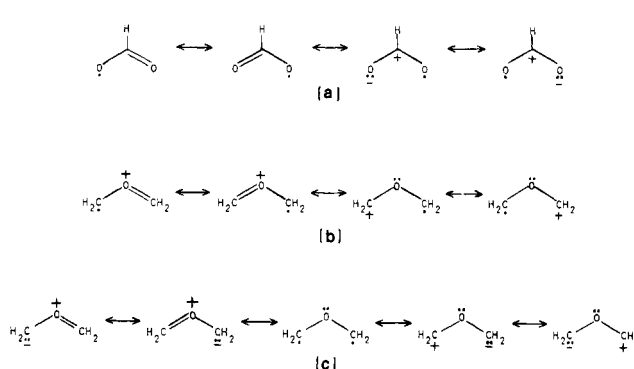


Figure 6. Principal contributing resonance structures for (a) formyloxyl, (b) $\text{O}(\text{CH}_2)_2^+$, and (c) $\text{O}(\text{CH}_2)_2$.

hartree (16.6 kcal/mol) higher than that of the structure shown in Figure 5c. The MCSCF optimized structures in Figures 5a and 5b and the energy difference between them are comparable to those found by the CI calculations of Jean and co-workers.²⁹

Discussion

In the foregoing paragraphs it has been shown how, from the perspective of the second-order Jahn–Teller effect, it can be predicted that: (1) allylic resonance in radicals will decrease in importance with increasing differences between the electronegativities of the central and terminal heavy atoms and (2) electron repulsion effects will cause allylic resonance to be more important in diradicals than in the corresponding radical species containing one less π electron. It seems that it should be possible to reach the same conclusions within the context of resonance theory. Indeed, this is the case, provided that no-bond resonance structures, which localize electron pairs on the most electronegative atoms, are considered.³⁰

In Figure 6a are shown four resonance structures for the lowest π state of the formyloxyl radical. The first two are perfectly analogous to those for the allyl radical. However, the second pair of structures, each of which localizes the electron pair in the carbonyl π bond on an oxygen atom, have no low-energy equivalent in allyl. Nevertheless, because oxygen is considerably more electronegative than carbon, these structures do contribute substantially in formyloxyl. Indeed, in resonance theory, the chemical and physical differences between C–C and C–O double bonds are attributed to the contribution of such polar resonance structures to the carbonyl group.

To the extent that the latter two structures in Figure 6a do contribute to the resonance hybrid for formyloxyl, it can be predicted that formyloxyl will have a low allylic resonance energy. The latter two structures differ by the exchange of a π electron between nonbonded oxygen atoms. Because of the large distance and, hence, small overlap between the $p\pi$ orbitals on the terminal oxygen atoms, "through-space" electron delocalization between them has but a small stabilizing effect. Moreover, since the central atom is not involved in this type of resonance, it is not really allylic resonance. Thus, were it not for the contribution of the first two structures, the allylic resonance stabilization would be so small that a structure with unequal C–O bond lengths might well be preferred to one with C_{2v} symmetry.

(28) It is interesting to note that both C–O bonds lengthen on twisting one CH_2 group out of conjugation. A Mulliken population analysis at the twisted geometry finds less π donation from oxygen to the CH_2 group that remains conjugated, consistent with the lengthening of the bond to this group. The synergistic effect of CH_2 group conjugation on enhancing π C–O bond strength can be demonstrated even at the level of simple Hückel theory. This rather surprising result is due to the fact that, on twisting one methylene group out of conjugation, a nonbonding electron is placed in a π MO that is antibonding between oxygen and the remaining planar CH_2 group.

(29) Volatron, F.; Anh, N. T.; Jean, Y. *J. Am. Chem. Soc.* **1983**, *105*, 2359.

(30) The effect of electronegativity on electronic structure has previously been considered for diradicals like 7, where the no-bond resonance structure does not separate charge: Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504. Hayes, E. F.; Siu, A. K. Q. *Ibid.* **1971**, *93*, 2090.

Similarly, resonance between the last two structures for $\text{O}(\text{CH}_2)_2^+$ in Figure 6b affords negligible stabilization and makes no contribution to the allylic resonance energy of the radical. Unlike the analogous two structures in Figure 6a, in which the C–O π bond is broken and the electron pair localized on the more electronegative oxygen atom, these two structures in Figure 6b do not separate charge. Therefore, they should contribute more to the hybrid representing $\text{O}(\text{CH}_2)_2^+$ than the analogous two structures in Figure 6a are expected to contribute to the hybrid representing formyloxyl. Consequently, it is possible to predict that $\text{O}(\text{CH}_2)_2^+$ will be less stabilized by allylic resonance than the isoelectronic formyloxyl radical and that the former is thus more likely to have a non- C_{2v} equilibrium geometry than the latter. This prediction of resonance theory is, of course, confirmed by our computational results.

The resonance structures in Figure 6c for the neutral carbonyl ylide can be derived from those in Figure 6b by addition of one more electron. Electron repulsion effects are expected to disfavor the last two, no-bond, resonance structures, relative to the third structure in Figure 6c. In fact, analysis of the CI wave function for this diradical shows that the third structure constitutes more than half of the wave function, whereas the fourth and fifth each comprise only about 1%.²⁹

Because electron repulsion effects keep the last two structures in Figure 6c from contributing significantly to the wave function, the fact that there is no significant stabilization arising from resonance between them is of little consequence. There are, however, strong stabilizing interactions between the central oxygen and terminal carbons in the first three structures. As a result, it can be predicted that resonance in the neutral carbonyl ylide should be important, despite the lack of allylic resonance stabilization of the same molecule lacking one nonbonding electron. Once again, the computational results described above support this conclusion.

Predictions regarding the effect of electronegativity differences on allylic resonance can be made by judicious application of either the second-order Jahn–Teller effect or resonance theory, but the latter perspective does not allow the immediate prediction that the allylic wave function for the cyclopropenyl radical (**5**) will easily localize to one of the two structures that is equivalent to **6**. This prediction can, however, be made from the fact that, to first order, distortion from D_{3h} symmetry stabilizes **5** and **6** equally.¹³ If **5** and **6** have the same energy, the stabilization provided by resonance between the two structures in **5** is zero.

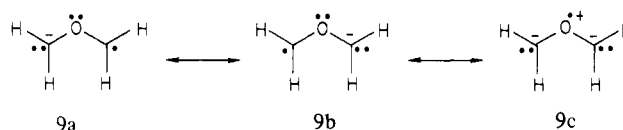
Although in this paper we have focused on allylic resonance, the perspectives that we have applied to predict the relative importance of resonance in such systems can be applied to other radicals and diradicals. For example, the theoretically computed³¹ and experimentally measured³² ease of pseudorotation in cyclopentadienyl radical, from geometries with delocalized 2A_2 wave functions (**8**) to geometries that are optimal for the more localized



2B_1 contributing structures (**8a** and **b**), is expected from second-order Jahn–Teller considerations that are completely analogous to those discussed above for cyclopropenyl radical.

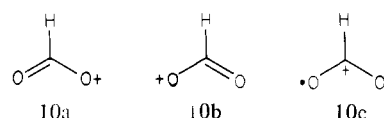
Electronegativity effects can also be anticipated to reduce the importance of resonance in radicals containing more than three

electrons, whenever such effects result in a small energy gap between the singly occupied MO and either filled or unfilled MOs. For instance, the small energy difference between the singly occupied $1a_2$ MO and the empty $2b_1$ MO causes $\text{O}(\text{CH}_2)_2^+$ to distort readily from C_{2v} symmetry. The same small energy gap should have a similar effect in the radical anion (**9**), wherein $1a_2$ is doubly occupied and $2b_1$ contains the unpaired electron.



The identical prediction of a small resonance energy can be made for this radical, containing five π electrons, from resonance theory. To the extent that the **9a** and **9b** predominate over the **9c**, the resonance stabilization is expected to be small. Thus, like the carbonyl ylide radical cation (**4**), the radical anion (**9**) is anticipated to have a small force constant for b_1 distortion of the C–O bond lengths, and little energy should be required to rotate one methylene group out of conjugation.

Predictions regarding diradicals with π electron counts other than four can also be easily made. For instance, on removing a π electron from formyloxyl, the cation **10**, with two π electrons, is formed. Because of the small $1b_1$ – $1a_2$ energy gap, from the MO point of view it seems appropriate to call this species a diradical. However, despite the smallness of the energy separation between these two MOs, electron repulsion effects, of the same type discussed above for the four-electron π system in **7**, should tend to confer on **10** a substantially larger force constant for



asymmetric stretch than that in the neutral formyloxyl radical (**3**).

The same prediction of a strong preference for a C_{2v} geometry for **10** can be made on the basis of resonance structures. The principal resonance structure (**10c**) has C_{2v} symmetry and strong resonant interactions with the two that resemble those of a typical allylic cation. Not shown are the two structures which simultaneously place the pair of π electrons on the same oxygen. These structures have little resonance interaction, and they provide no allylic resonance stabilization. However, they do not contribute substantially to the structure of **10**, because of their high coulombic repulsion energy.

The examples discussed above illustrate how the importance of resonance can be assessed in radicals and in diradicals, either by using second-order Jahn–Teller considerations or by drawing resonance structures. These techniques allow qualitative predictions to be made rapidly about many more molecules than can be discussed here. It is hoped that such predictions will lead to computational tests, such as those reported here for **4**, and will serve to stimulate experimental determinations of the importance of resonance in heterosubstituted radicals and diradicals.

Acknowledgment. We thank the National Science Foundation for support of this research, part of which was carried out while W.T.B. was a Fellow of the John Simon Guggenheim Memorial Foundation.

Registry No. **3**, 16499-21-1; **4**, 74427-28-4; **7**, 61518-27-2.

(31) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1979**, *101*, 3771.

(32) Liebling, G. R.; McConnell, H. M. *J. Chem. Phys.* **1965**, *45*, 3931.