Preferred Conformations of the Isobutyl, Cyclopropylcarbinyl, and Oxirylcarbinyl Cations, Radicals, and Anions as Determined by Semiempirical Intermediate Neglect of Differential Orbital Calculations[1]

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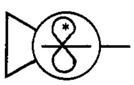
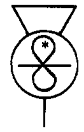
Abstract: Semiempirical INDO calculations have been performed on the isobutyl, cyclopropylcarbinyl, and oxirylcarbinyl cations, radicals, and anions, as well as several model compounds. Total energies, charge densities, and hyperfine coupling constants for the radical species are reported for various conformations of the molecules. It is found that the cyclopropylcarbinyl cation has a pronounced preference for the bisected conformation while the isobutyl cation shows a significantly diminished preference for this alignment. The oxiryl group is calculated to have a strong stabilizing influence on a cationic site from a slightly distorted bisected alignment (*cf.* **30**). An analysis of the calculated bond orders and atomic orbital electron densities is presented which reveals the nature of the stabilizing interactions. All three radicals are likewise calculated to have lower total energies in the bisected conformation than in the perpendicular, although the energy differences are greatly attenuated as compared to the cationic species. A partial energy minimization is performed on the cyclopropylcarbinyl radical and the mechanisms of spin distribution onto the β and γ hydrogens are discussed in some detail. For the anions, calculations are performed assuming both planar, sp^2, configurations and tetrahedral, sp^3, configurations about the carbon holding the "pair" of electrons. For the isobutyl and cyclopropylcarbinyl species there is a slight preference for the perpendicular conformations while the oxirylcarbinyl anion shows a definite favoring of the distorted bisected arrangement **35**. It is evident that such an alignment is most conducive to transferring electron density onto the electronegative oxygen atom. It is concluded that, in general, C–C hyperconjugation is more favorable than C–H hyperconjugation in cationic species while the reverse is true for carbanions.

It is well established that the cyclopropyl group is more effective at stabilizing an electron-deficient trigonal carbon from the bisected conformation **1** than from the perpendicular alignment **2**.[2-5] It is furthermore apparent that the degree of interaction of a cyclopropyl substituent is quite dependent upon the amount of cationic character on the attached carbon with the preference for **1** being rather powerfully attenuated by a decrease of positive charge.[6,7]



1, bisected

$* = +, \cdot,$ or $-$

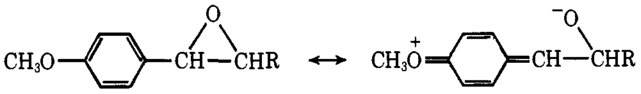


2, perpendicular

$* = +, \cdot,$ or $-$

Although there is considerably less data available for the analogous free-radical systems, the cyclopropylcarbinyl radical apparently exists largely in the bisected conformation **1** at least at −150°.[8] Bauld, *et al.*,[9,10] have investigated a variety of cyclopropyl-substituted radicals and have noted that the preference for conformation **1** is dampened considerably in going from radical cations to neutral radicals to radical anions. The possibility that anionic cyclopropyl conjugation may preferentially occur through the perpendicular conformation **2** was mentioned although there are little data to support such a conclusion.

In contrast to the rather large amount of data in the literature dealing with the cyclopropyl substituent, the electronic properties of the three-membered oxiryl ring have received considerably less attention.[11] Ultraviolet absorption studies appear to indicate that this group is electron withdrawing relative to the cyclopropyl substituent[12] and the conformational dependence of the ultraviolet absorption spectra of various stilbene oxides[13] indicates that resonance contributions of type **3b** are important at least for excited state species. However, our studies[11] of the radical anions of a number of *p*-nitrophenyl-substituted oxiranes



3a **3b**

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF No. 1123-Gl), for support of this work. Thanks are also due to Kansas State University for assistance in defraying the computing costs.

[2] For comprehensive literature bibliographies, see (a) Z. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971); (b) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (c) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).

[3] J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969).

[4] F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686 (1969).

[5] H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

[6] R. G. Pews, *ibid.*, **89**, 5605 (1967).

[7] W. H. Sachs and C. Rappe, *Tetrahedron Lett.*, 2317 (1968).

[8] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877 (1969).

[9] N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *ibid.*, **91**, 6666 (1969).

[10] N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967).

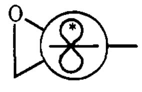
[11] W. C. Danen, C. T. West, T. T. Kensler, and T. J. Tipton, *ibid.*, **94**, 4830 (1972), and references cited therein.

[12] L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *ibid.*, **86**, 4628 (1964).

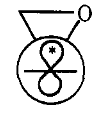
[13] L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966).

suggest that the electron-withdrawing characteristics of the oxiryl group lack a significant conformational dependence at least for the radical anion system. This conclusion is at least partially substantiated by the results of Pews[6] who concluded that resonance structures analogous to **3b** (methoxy group replaced by fluorine) are not important in describing the ground-state properties of the oxiryl substituent.

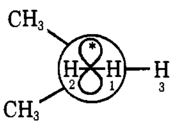
In the present work we have attempted to determine the relative ground-state energies of and charge delocalization in the bisected **1** and perpendicular **2** conformations of the cyclopropylcarbinyl cation, radical, and anion by INDO (intermediate neglect of differential overlap) calculations.[14] Similar calculations have been performed on the two conformations **4** and **5** of the oxirylcarbinyl cation, radical, and anion as well as the model noncyclic isobutyl species **6** and **7**.



4, bisected
* = +, ·, or −



5, perpendicular
* = +, ·, or −



6, bisected
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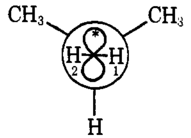

7, perpendicular
* = +, ·, or −

The cyclopropylcarbinyl cation has been subjected to calculations by a variety of semiempirical[15,16] and *ab initio* procedures[17] all of which lead, at least qualitatively, to the conclusion that the bisected conformation **1** is preferred, the stabilization being derived from overlap between the "empty" p orbital and the heavily p weighted C–C bond orbitals of the cyclopropane ring. However, no calculations have been reported on the corresponding cyclopropylcarbinyl radical or anion to allow a comparison of the three systems nor have any of the oxirylcarbinyl species been subjected to such calculations.

Although *ab initio* type calculations undoubtedly yield more accurate results on an absolute basis, the all-valence electron, semiempirical INDO procedure can be expected to give reasonable qualitative-semiquantitative estimates of the rotational barriers of interest here. The INDO method calculates a rotational barrier of 2.20–2.25 kcal/mol (depends on geometry) for ethane which compares well with the experimental value of 2.875 kcal/mol.[18] Moreover, as will be seen below, the INDO method generally is in at least fair agreement with more rigorous *ab initio* calculations where comparisons are possible. However, semiempirical methods can give quite misleading results on carbonium ions and even stable molecules when changes in connectivity are involved (cyclic *vs.* open structures).[19–21] The INDO and related semiempirical methods explicitly consider electron–electron and nuclear–nuclear repulsion interactions unlike the extended Hückel theory of Hoffman; the applicability of this latter method to charged species such as in the present study is questionable.[22] However, all semiempirical schemes, even the "best" available for carbonium ions at the semiempirical level,[23] neglect many two-electron integrals which are included in *ab initio* methods and, since these integrals represent electron repulsions and exchange interactions, their neglect gives too much weight to the forces remaining such as orbital overlap effects with the result that, in discriminating between two isomers, the structure displaying the greater number or bonds will oftentimes be incorrectly favored. Rotational barriers are expected to be much less subject to this kind of problem and the INDO method can probably be relied upon to give realistic trends in conformations of the species of interest in this work.

There is some evidence to suggest that the INDO calculations of the present study might rather consistently overestimate the energy difference between conformations of various species.[24] Furthermore, except for the cyclopropylcarbinyl radical and the C_1–C_2 bonds in all the species, no geometry optimization has been attempted since such a procedure would be prohibitively expensive for the relatively large number of species under consideration in the present work although the importance of geometry optimization has been emphasized.[25] The C_1–C_2 bond was optimized to 0.01 Å for both the bisected and perpendicular conformations of all the species as it was felt that this parameter would exert a predominate influence on the relative energies of the two conformations. We had originally performed calculations assuming a C_1–C_2 distance of 1.51 Å for all the species; optimization of this bond did not invert any of the predictions on relative stabilities of conformations but only affected the magnitude of the energy difference. Although the optimum C_1–C_2 length usually varies slightly in going from the bisected to the perpendicular conformation for a given molecule, this variation has minimal effect on the relative energy of the two conformations.

Results

The calculations were performed on an IBM 360/50 computer utilizing the program of Pople, *et al.*,[14]

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[14] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967). A copy of this program was obtained from the Quantum Chemistry Program Exchange, Indiana University, No. 141.

[15] R. Hoffmann, *ibid.*, 40, 2480 (1964).

[16] K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

[17] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970), and references cited therein.

[18] W. England and M. S. Gordon, *ibid.*, **93**, 4649 (1971).

[19] E. I. Snyder, *ibid.*, **92**, 7529 (1970).

[20] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).

[21] H. Iwamura, K. Morio, M. Oki, and T. L. Kunii, *Tetrahedron Lett.*, 4575 (1970).

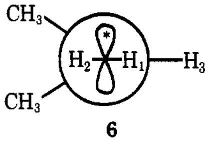
[22] T. Yonezawa, H. Nakatsuju, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

[23] (a) H. Fischer, H. Kollmar, H. O. Smith, and K. Millter, *Tetrahedron Lett.*, 5821 (1968); (b) H. Kollmar and H. O. Smith, *ibid.*, 1833 (1970); (c) H. Kollmar and H. O. Smith, *Angew. Chem., Int. Ed. Engl.*, **9**, 463 (1970).

[24] Wiberg[16] concludes that CNDO calculations probably overestimate the energy difference between cationic rotational isomers by a factor of *ca.* 3 while a factor of *ca.* 2–4 is likewise suggested by a comparison of several of the present INDO results with the more rigorous *ab initio* calculations. However, in some comparisons with *ab initio* results the INDO calculated differences are disturbingly large although the two methods appear to predict the same trends in all instances in the present work.

[25] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

Table I. INDO Calculated Energies, C_1–C_2 Bond Lengths, and Charge Densities for the Bisected and Perpendicular Conformations of the Isobutyl Cation, Radical, and Anion



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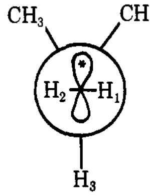
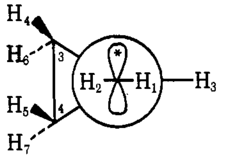


7

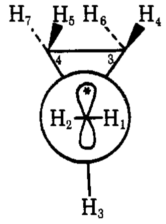
	Cation	Radical	Anion	Cation	Radical	Anion
Total energy, au[a]	−33.889491	−34.220264	−34.127298	−33.871454	−34.218518	−34.137475
Rel energy, kcal/mol[b]	0.0	0.0	0.0	+11.32	+1.10	−6.38
C_1–C_2, Å[c]	1.38	1.44	1.46	1.39	1.44	1.44
Charge density						
C_1	+0.3739	−0.0598	−0.5645	+0.3943	−0.0458	−0.5349
C_2	+0.0465	+0.0921	+0.1711	+0.0005	+0.0855	+0.1948
$C_3 = C_4$	+0.0972	+0.0623	+0.0385	+0.0632	+0.0592	+0.0588
H_1	+0.0780	−0.0002	−0.0844	+0.0721	−0.0039	−0.0868
H_2	+0.0770	+0.0029	−0.0789	+0.0721	−0.0039	−0.0868
H_3	+0.0404	−0.0323	−0.1025	+0.1761	−0.0202	−0.2067
H_{CH_3}	+0.0316[d]	−0.0212[d]	−0.0697[d]	+0.0264[d]	−0.0217[d]	−0.0662[d]

[a] In atomic units: 1 au = 627.502 kcal/mol. [b] Relative energy of **7** *vs.* **6** taken as 0.0 kcal/mol. [c] Energy-minimized C_1–C_2 bond length. [d] Average value.

Table II. INDO Calculated Energies, C_1–C_2 Bond Lengths, and Charge Densities for the Bisected and Perpendicular Conformations of the Cyclopropylcarbinyl Cation, Radical, and Anion



1



2

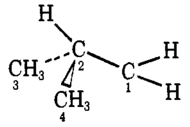
	Cation	Radical	Anion	Cation	Radical	Anion
Total energy, au	−32.360410	−32.660077	−32.566819	−32.294836	−32.648589	−32.569175
Rel energy, kcal/mol[a]	0.0	0.0	0.0	+41.15	+7.21	−1.48
C_1–C_2, Å	1.37	1.43	1.44	1.39	1.44	1.43
Charge density						
C_1	+0.2846	−0.0803	−0.5473	+0.4301	−0.0395	−0.5447
C_2	+0.0808	+0.0949	+0.1971	−0.0455	+0.0676	+0.1997
$C_3 = C_4$	+0.1062	+0.0320	−0.0471	+0.0836	+0.0318	−0.0080
H_1	+0.0796	−0.0001	−0.0840	+0.0694	−0.0047	−0.0855
H_2	+0.0716	+0.0036	−0.0704	+0.0694	−0.0047	−0.0855
H_3	+0.0520	−0.0272	−0.1075	+0.1701	−0.0154	−0.1986
$H_4 = H_5$	+0.0434	−0.0124	−0.0577	+0.0279	−0.0149	−0.0537
$H_6 = H_7$	+0.0661	−0.0150	−0.0892	+0.0417	−0.0186	−0.0810

[a] Relative energy of **2** *vs.* **1** taken as 0.0 kcal/mol.

The Cartesian coordinates for all the atoms in the molecule were calculated using the program described by Schwendeman.[26]

The following bond lengths in ångström units and bond angles were utilized.

(a) **Isobutyl:** C_2–C_3 = C_2–C_4 = 1.54, C_1–H = 1.08, C_2–H = C_3–H = C_4–H = 1.09 Å; HC_1H angle = 120°, all other angles = 109.471° (tetrahedral). Energy minimization of C_1–C_2 yields the values reported in Table I for the bisected and perpendicular conformations of the various species.



(b) **Cyclopropylcarbinyl:**[27] C_2–C_3 = C_2–C_4 = C_3–C_4 = 1.5096, C_1–H = 1.08, C_2–H = C_3–H = 1.0888 Å; HC_3H = HC_4H angle = C_1C_2H angle = 115.12°, HC_1H angle = 120.0°. Energy minimization of C_1–C_2 yields the values reported in Table II for the

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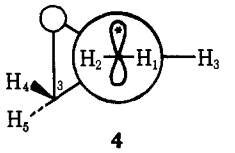
(26) R. H. Schwendeman, *J. Mol. Spectrosc.*, **6**, 301 (1961).

(27) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

Table III. INDO Calculated Energies, C_1–C_2 Bond Lengths, and Charge Densities for the Bisected and Perpendicular Conformations of the Oxirylcarbinyl Cation, Radical, and Anion



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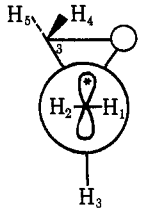

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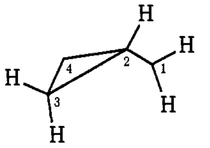
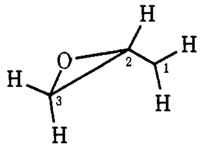
	Cation	Radical	Anion	Cation	Radical	Anion
Total energy, au	−41.469309	−41.814550	−41.755363	−41.419667	−41.802514	−41.741210
Rel energy, kcal/mol[a]	0.0	0.0	0.0	+31.15	+7.55	+8.88
C_1–C_2, Å	1.38	1.43	1.42	1.40	1.44	1.43
Charge density						
C_1	+0.2967	−0.0814	−0.5276	+0.4226	−0.0601	−0.5740
C_2	+0.1501	+0.2117	+0.3208	+0.0847	+0.1991	+0.3239
C_3	+0.2853	+0.1692	+0.0636	+0.2374	+0.1667	+0.1127
O	−0.0931	−0.2528	−0.4047	−0.1688	−0.2633	−0.3567
H_1	+0.0958	+0.0111	−0.0769	+0.1007	+0.0179	−0.0668
H_2	+0.0883	+0.0174	−0.0582	+0.0916	+0.0105	−0.0736
H_3	+0.0602	−0.0346	−0.1324	+0.1598	−0.0231	−0.2001
H_4	+0.0464	−0.0193	−0.0763	+0.0271	−0.0221	−0.0677
H_5	+0.0704	−0.0214	−0.1082	+0.0449	−0.0256	−0.0977

[a] Relative energy of **5** *vs.* **4** taken as 0.0 kcal/mol.

bisected and perpendicular conformations of the various species. No significance should be attached to the number of significant figures utilized for the C–C and C–H bond lengths. These values were simply used as reported for cyclopropane.[27]



(c) **Oxirylcarbinyl:**[28] C_2–C_3 = 1.471, C_2–O = C_3–O = 1.436, C_3–H = C_2–H = 1.082, C_1–H = 1.08 Å; HC_3H angle = C_1C_2H angle = 116.30°, HC_1H angle = 120.0°, angle between HC_3H plane and C_2–C_3 bond = 158.10°. Energy minimization of C_1–C_2 yields the values reported in Table III for the bisected and perpendicular conformations of the various species.



For the "sp³ hybridized" anions the geometry about C_1 was assumed tetrahedral with C_1–H = 1.09. No attempt was made to optimize these geometries with respect to an INDO energy minimization, except for C_1–C_2 and the cyclopropylcarbinyl radical (*vide infra*). Results of the calculations are presented in Tables I–IV.

The bond indices referred to in the text are calculated by summing the squares of density matrix elements between bonding atoms and are related to the bond character as discussed by Wiberg.[16] However, the bond index method fails to consider that some interactions may be bonding while others may be antibonding so that subtle errors may arise in this procedure and correlations between bond index and bond strength must be viewed with some caution.

Discussion

In this study we are primarily interested in determining the relative difference in energy between the bisected, **1** and **4**, and perpendicular, **2** and **5**, conformations of the cyclopropylcarbinyl and oxirylcarbinyl species as the electron density on the trigonal carbon is increased in going from the cation to the radical to the anion. As a model for the cyclopropylcarbinyl species, the analogous isobutyl has been chosen and we will discuss this compound first.

Isobutyl. (a) Cation. As can be seen from the data in Table I, the bisected conformation **6** of the isobutyl cation is more stable than the perpendicular arrangement **7** by 11.32 kcal/mol on the INDO scale. This result may be compared with the recent *ab initio* value of 2.68 kcal/mol determined by Pople, *et al.*[17] These authors have found that, in general, conformations of alkyl cations in which the "empty" p orbital is coplanar with a C–C bond are preferred over conformations allowing alignment with a C–H bond in contrast with the usual assumption that C–H hyperconjugation is more favorable than C–C hyperconjugation. The bisected conformation **6** of the isobutyl cation allows maximum C–C hyperconjugation. It is also apparent from the listed charge densities that C_1 of the isobutyl cation has calculated charge densities of only +0.3739 and +0.3943 for **6** and **7**, respectively, indicating appreciable delocalization of charge over the entire molecule in both conformations.

(b) Radical. In comparing the two extreme conformations of the isobutyl radical it is seen that the energy difference is substantially less than in the cation although the bisected form **6** is still preferred by 1.10

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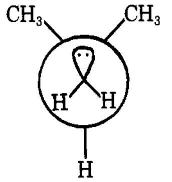
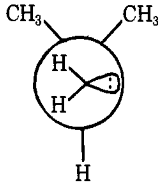
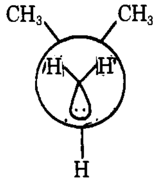
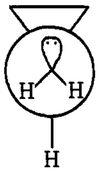
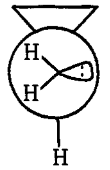
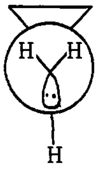
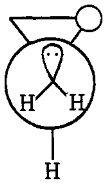
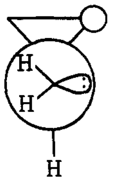
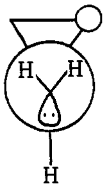
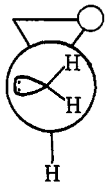
(28) J. D. Swalen and D. R. Herschbach, *J. Chem. Phys.*, **27**, 100 (1957).

Table IV. INDO Calculated Total and Relative Energies for Various Tetrahedral C_1 Conformations of the Isobutyl, Cyclopropylcarbinyl, and Oxirylcarbinyl Anions[a,b]

Isobutyl				
	8 (θ = 180°)	9 (θ = 90°)	10 (θ = 0°)	
Total energy[c]	−34.143122	−34.134721	−34.135634	
Relative energy[d]	0.0	+5.27	+4.70	
Cyclopropylcarbinyl				
	11 (θ = 180°)	12 (θ = 90°)	13 (θ = 0°)	
Total energy[c]	−32.573823	−32.568249	−32.565502	
Relative energy[d]	0.0	+3.50	+5.22	
Oxirylcarbinyl				
	14 (θ = 180°)	15 (θ = 90°, syn)	16 (θ = 0°)	17 (θ = 90°, anti)
Total energy[c]	−41.743953	−41.747861	−41.736513	−41.746366
Relative energy[d]	+2.45	0.0	+7.12	+0.94

[a] θ is the dihedral angle formed by the directed lone pair of electrons on C_1 and the C_2–H bond. [b] C_1–C_2 bond length = 1.51 Å for all compounds. [c] In atomic units: 1 au = 627. 502 kcal/mol. [d] In kcal/mol.

kcal/mol according to the calculations. This conclusion is at some variance with experiment, however. Both Fessenden[29] and Krusic and Kochi[30] have noted from esr studies that the isobutyl radical prefers the perpendicular alignment and exhibits a potential barrier to rotation of 0.295–0.300 kcal/mol. These latter workers have noted, however, that both quantum mechanical and classical treatments fail to accurately reproduce the experimentally observed slopes of the temperature dependences of β hydrogen esr hyperfine couplings in simple acyclic hydrocarbon radicals including the isobutyl radical. Although a detailed analysis was not attempted for the isobutyl radical, it was noted that a bent, distorted model, in which the axis of the $(CH_3)_2CH$– group is tilted so that the single β proton eclipses and is brought closer to the p orbital on C_1, gives a better fit to the experimental curves. Such a distortion might imply that C–H hyperconjugation is more effective than C–C hyperconjugation in alkyl radicals but it is also possible that the distortion could result from a decreased steric interaction between the two methyl groups and the α protons.

A comparison of the C–H bond dissociation energies[31] for ethane and neopentane, 98.0 ± 1 and 99.3 ± 1 kcal/mol, respectively, reveals that $CH_3CH_2\cdot$ and $(CH_3)_3CCH_2\cdot$ must have about the same stabilization energies and that alkyl radicals are quite different than the corresponding carbonium ions which show a rather marked enhancement of stability due to β-methyl substitutions. Although the above two bond dissociation energies are the same within experimental error, if the value for ethane is indeed lower this would imply that C–H hyperconjugation might be slightly more effective than C–C hyperconjugation in hydrocarbon free radicals which is also the conclusion suggested by the esr results.[29,30] Although a completely energy-minimized geometry for the isobutyl radical might be a distorted structure as discussed above with an alignment more closely approximating the perpendicular conformation 7, both the present calculations and experimental evidence indicate that the barriers to rotation in alkyl radicals must be quite small.

(c) Anion. A changeover in preferred conformation occurs in the isobutyl anion as evidenced by the data in Tables I and IV. Now the prependicular form 7 is more stable than the bisected form 6 by 6.38 kcal/mol. Comparing the sp^3 hybridized C_1 species (Table IV)

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(29) R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964).

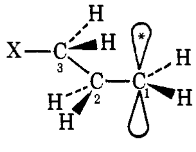
(30) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(31) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

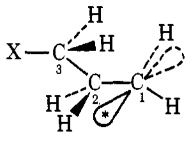
it is seen that the staggered conformation **8** with the lone pair anti with respect to the methine proton is more stable than **9** and **10** by 5.27 and 4.70 kcal/mol, respectively. These INDO calculated[24] differences in energy between the various conformations of the isobutyl anion are not insignificant and could conceivably be tested experimentally.

A comparison of the anions **7** and **8** (planar *vs.* pyramidal C_1 both with C_1–C_2 = 1.51 Å) reveals that the tetrahedral arrangement is more stable than the planar geometry by 8.0 kcal/mol, in agreement with the accepted view that carbanions are pyramidal, rapidly inverting ions.[32] This value may be considered a crude estimate[24] of the barrier to pyramidal inversion in this anion.

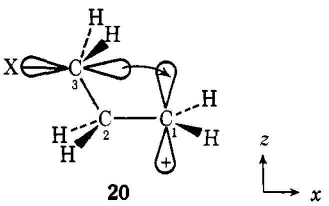
In order to gain an insight into the reasons for the changeover in conformational preference in going from the cation to the anion, we performed INDO calculations on the two conformations of "substituted" *n*-propyl species **18** and **19** in a manner analogous to that of Pople, *et al.*[33] For the cations, the conformations in which the "empty" p orbital on C_1 are aligned with the C_2–C_3 bond, *i.e.*, **18a** and **18b**, are predicted to be more stable than **19a** and **19b** by 14.02 and 12.35 kcal/mol, respectively. These differences are intuitively too large although the *decrease* in the potential barrier of 1.67 kcal/mol resulting from replacement of the $-CH_3$ group with $-C{\equiv}N$ compares quite favorably to a decrease of 2.86 kcal/mol (barriers of 3.73 and 0.87 kcal/mol for X = CH_3 and $-CN$, respectively) as determined by the *ab initio* LCAO-SCF calculations with the STO-3G basis set of Pople, *et al.*[33] By an analysis of overlap and atomic populations, these authors have concluded that the dominant effect producing the barrier is the preferential stabilization of conformation **18** through interaction of the "empty" 2p orbital on C_1 ($2p(C^+)$ orbital) with the CH_2X group. This interaction takes place by (a) overlap of the $2p(C^+)$ orbital of C_1 with the $2p_x$ orbital of C_3 (*cf.* **20**) and (b) increased overlap population (compared with the ethyl cation) of the $2p(C^+)$ with the $2p_z$ orbital of C_2 (*cf.* **21**).



18a, X = CH_3
b, X = CN
* = +, ·, or −



19a, X = CH_3
b, X = CN
* = +, ·, or −



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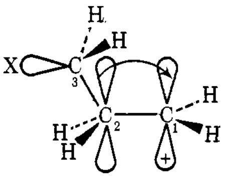
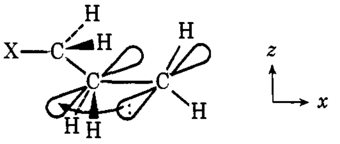


21

This latter observation indicates that C–C hyperconjugation is more favorable than C–H hyperconjugation. It is important to note that these modes of stabilization are more effective in conformation **18** and that both effects are enhanced when the substituent X is electron donating (X = CH_3) and diminished when X is electron withdrawing (X = CN).

Although it is not possible to obtain overlap populations and Mulliken gross populations directly from an INDO-type calculation, examination of the INDO calculated bond orders and atomic orbital electron densities, in general, supports the above conclusions derived from *ab initio* calculations although the differences are not pronounced. We have performed a similar analysis of the corresponding anions which reveals decidedly different results in that conformation **19** is now preferred over **18** for both X = CH_3 and CN. Assuming a trigonal "sp^2" hybridization about C_1 for the anions yields an INDO energy difference of 6.50 and 5.03 kcal/mol for the X = CH_3 and X = CN compounds, respectively. The calculated energy difference drops to 2.90 and 2.50 kcal/mol, respectively, for a tetrahedral, "sp^3" hybridization about C_1. From both calculations it is seen that the energy difference between conformations **18** and **19** is smaller for the X = CN compound. An analysis of the bond orders now reveals an almost negligible interaction involving overlap of the $2p(C^-)$ orbital on C_1 with the $2p_x$ orbital of C_3 (*i.e.*, similar to **20** except with donation of electron density from C_1 to C_3) even with X = CN. Likewise, there is a decrease (compared to both the cation and the ethyl anion) in bond order between the $2p(C^-)$ orbital with the $2p_z$ orbital on C_2. The predominant stabilizing influence for conformation **19** for these anions apparently arises from an interaction of the $2p_y$ orbital on C_1 with the $2p_y$ orbital on C_2 (*cf.* **22**). This indicates that anionic C–H hyperconjugation is somewhat more favorable than anionic C–C hyperconjugation. It should be noted, however, that the calculated potential barriers to rotation in these anions are considerably smaller than those calculated for the analogous cations.



22

As discussed by Pople, *et al.*,[17] the preference for the β C–C bond of a cation to be coplanar with the "empty" p orbital also predicts the bisected conformation **6** of the isobutyl cation in which the two C–CH_3 bonds form dihedral angles of 30° with the "empty" p orbital to have a lower energy than the perpendicular arrangement **7**. A similar mode of reasoning explains the opposite preference for the anions. It should be mentioned that the *least* stable forms of the tetrahedral anions analogous to **18a** and **18b** have the lone pair of electrons anti to the β C–C bond in both instances. Such an alignment is less stable than the syn, even though eclipsing of the hydrogens on C_1 and C_2 is relieved. In this regard it may be noted from Table IV that **8** is appreciably more stable than **10**.

Cyclopropylcarbinyl. (a) Cation. The cyclopropylcarbinyl cation has been the subject of many experimental investigations as well as several molecular orbital calculations. The present results (Table II) indicate the bisected conformation **1** is more stable than the perpendicular arrangement **2** by 41.15 kcal/mol which

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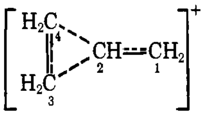
[32] J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

[33] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6987 (1970).

can be compared with the *ab initio* calculated value of 17.54 kcal/mol.[17] Although there has been no reported experimental determination of the rotational barrier in the cyclopropylcarbinyl cation itself, Kabakoff and Namanworth[34] have recently utilized a nuclear magnetic double resonance technique to determine a barrier of 13.7 ± 0.4 kcal/mol for the dimethylcyclopropylcarbinyl cation. It is reasonable to assume that the barrier to rotation of the primary cyclopropylcarbinyl cation will be somewhat greater than this value for the tertiary ion; the effect of the highly polar SO_2–SbF_5–HSO_3F solvent system on the experimentally determined value must also be considered when compared with the "gas-phase" calculations.

It is revealing to compare the bond indices for the bisected conformation **1** (C_1–C_2 = 1.5384, C_2–C_3 = C_2–C_4 = 0.7397, C_3–C_4 = 1.1169) with those for the perpendicular alignment **2** (C_1–C_2 = 1.2563, C_2–C_3 = C_2–C_4 = 0.9028, C_3–C_4 = 0.9841) and the isobutyl cation (bisected, **6**: C_1–C_2 = 1.3328, C_2–C_3 = C_2–C_4 = 0.8560; perpendicular, **7**: C_1–C_2 = 1.3031, C_2–C_3 = C_2–C_4 = 0.9437). It is seen that in the bisected alignment of the cyclopropylcarbinyl cation the value for the C_1–C_2 bond is greatly enhanced while that for the C_2–C_3 and C_2–C_4 bonds is quite diminished indicating rather extensive interaction of C_1 with the heavily p-weighted C–C bonds of the three-membered cyclopropane ring and lending credulence to the following description of the cyclopropylcarbinyl cation. An examination of atomic orbital electron densities and bond orders reveals that the electron density in the "empty" $2p_z$ orbital on C_1 almost doubles from 0.2979 to 0.5067 in going from the perpendicular conformation **2** to the bisected alignment **1**. The dramatic increase in stability and magnitude of the C_1–C_2 bond index for the bisected conformation appears to result primarily from an effective overlap of the $2p_z$ orbitals on C_1 and C_2 (*cf.* **24a**). The analogous interaction of the $2p_z$ orbitals in the perpendicular conformation (*cf.* **24b**) is much less significant. There is also a moderate interaction between the $2p_z$ orbital on C_1 in **24a** and the $2p_x$ (bond order of 0.2105) and $2p_y$ (bond order of 0.2433) orbitals on C_3 and C_4 which is analogous to **20** even though now the overlap is not as favorable. It is seen that the calculated C_1–C_2 and C_2–C_3 = C_2–C_4 bond indices in the isobutyl cation do differ greatly from one conformation to the other. However, the differences in charge distribution between the cyclopropylcarbinyl and isobutyl species are not as pronounced as might have been anticipated.



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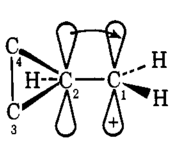
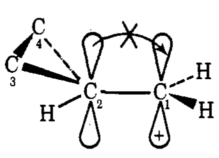


24a



24b

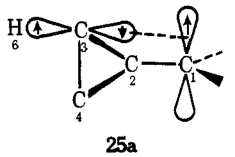
(b) Radical. The cyclopropylcarbinyl radical is predicted by the INDO calculations to prefer the bisected form **1** but by a significantly attenuated value of 7.21 kcal/mol. The experimental evidence agrees with the calculation in that an electron spin resonance investigation of this radical indeed shows it to exist as the bisected conformer at −150°;[8] no estimate of the rotational barrier in the cyclopropylcarbinyl radical could be obtained because of the occurrence of a rapid rearrangement to the allylcarbinyl radical at temperatures higher than −120°. A comparison of the observed and INDO calculated hyperfine coupling constants for the bisected and perpendicular conformations of the cyclopropylcarbinyl radical is given in Table V; it is apparent from the magnitude of the observed coupling of H_3 that the bisected conformer is indeed preferred.

Table V. INDO Calculated and Observed Hyperfine Coupling Constants for the Cyclopropylcarbinyl Radical

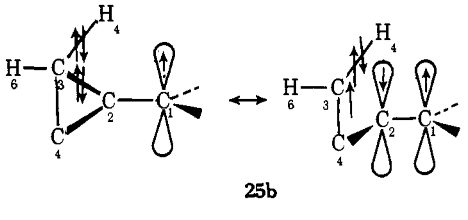
	Bisected conformation **1**		Perpendicular conformation **2**		
Atom	Assumed structure	Minimum energy structure[b]	Assumed structure	Minimum energy structure[c]	Obsd[a]
H_1	−19.31	−20.26	−20.69	−21.32	20.74
H_2	−19.45	−20.20	−20.69	−21.32	20.74
H_3	+1.70	+1.98	+60.58	+72.80	2.55
$H_4 = H_5$	−1.78	−1.57	−1.47	−1.92	2.01[d]
$H_6 = H_7$	+2.86	+3.16	−0.85	−1.50	2.98[d]
C_1	+36.17	+37.20	+38.85	+39.21	
C_2	−10.35	−10.39	−14.21	−15.43	
$C_3 = C_4$	+11.12	+10.79	+4.87	+4.85	

[a] Reference 8. [b] Structure **26**. [c] Same parameters as structure **26** except in perpendicular conformation. [d] Arbitrarily assigned.

It may be noted that the anti hydrogens H_6 and H_7 have a positive s-orbital spin density in the bisected conformation and a negative spin density in the perpendicular conformation; the syn hydrogens H_4 and H_5 have a negative value in both alignments. The unique behavior exhibited by the anti hydrogens in the bisected arrangement results from an interaction of the $2p_z$ orbital on C_1 with the $2p_x$ orbitals of C_3 and C_4 which causes an enhancement of α (↑) electron density on H_6 and H_7 (*cf.* **25a**). A similar interaction of these particular orbitals was noted above for the cyclopropylcarbinyl cation and is simply a three-center three-electron situation for the radical case. Such a mode of interaction is important for the anti hydrogens because of the large carbon $2p_x$ component in these C–H bonds. This interaction is much less significant for the syn



25a



25b

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(34) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970), and references cited therein.

hydrogens and the net negative electron density on H_4 and H_5 presumably results from spin polarization or a hyperconjugation–spin polarization mechanism as depicted in **25b**. Such a description also accounts for the enhanced α electron density on C_3 and C_4 in the bisected form which accumulates particularly in the $2p_y$ and 2s orbitals on these atoms. These conclusions are supported by similar calculations on the model *n*-propyl radical.

Since the spin density at the anti 6 and 7 hydrogens undergoes a changeover in sign from a positive value in the bisected conformation to a negative value in the perpendicular alignment, it would be expected that the esr hyperfine coupling to these hydrogens would become vanishingly small at some intermediate conformation.

The presently calculated barrier to rotation in the cyclopropylcarbinyl radical invites comparison with the values derived by Bauld, *et al.*,[9] for a variety of cyclopropyl-substituted aromatic radicals. Calculated potential barriers ranged from +2.22 kcal/mol for cyclopropyl phenyl ketyl to −1.25 kcal/mol (perpendicular conformer preferred) for the 9-cyclopropylanthracene radical anion. However, these barriers are influenced by both the unpaired electron density and the charge density on the attached trigonal carbon as well as steric effects in some cases and it is difficult to compare these results with the calculated results for the simple cyclopropylcarbinyl radical. These authors concluded that the cyclopropyl group preferentially adopts a bisected conformation except in sterically crowded environments but that this preference is rather powerfully attenuated by negative and accentuated by positive charge on the attached trigonal carbon in agreement with the present calculations.

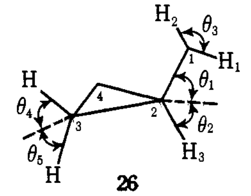
The present INDO calculations also shed light on another aspect of the work of Bauld, *et al.*[9,35] In

$$\alpha_\beta{}^{H} = (B_0 + B_2 \cos^2 \theta)\rho$$

applying the Heller–McConnell relationship, which relates the beta hydrogen coupling constant $a_\beta{}^{H}$ to the spin density ρ on the α carbon, to the cyclopropyl methine hydrogens in *p,p′,p′′*-tricyclopropyltrityl radical, these authors found it necessary to invoke a negative value for B_0 to achieve correspondence between the calculated and experimental potential barriers. A factor of $B_0/B_2 = -0.043$ was found to give good agreement between calculation and experiment. However, instead of simple B_0, these workers preferred to use a term $B_0\ \langle\sin^2\theta\rangle_{av}$ to account for the presence of a presumed orientation-dependent positive spin density at the tertiary cyclopropyl carbon which was attributed to contributions of cyclobutyl radical canonical forms to the resonance hybrid.

These conclusions are not substantiated by the present INDO calculations which indicate a positive s-orbital spin density at the β hydrogen of the cyclopropylcarbinyl radical even when it lies orthogonal to the axis to the p orbital holding the unpaired electron. From the calculated β-hydrogen s-orbital spin densities of +0.0032 and +0.1122 in the bisected **1** and perpendicular **2** conformations, respectively, of the cyclopropylcarbinyl radical it is found that $B_0/B_2 = +0.0294$. This value is identical in sign and similar in magnitude to that calculated in an analogous manner for the ethyl radical, +0.0367.[36] This latter value agrees at least in sign with that determined experimentally for the methyl group, +0.074[37] and +0.113,[38] and by the method of Bauld, *et al.*, for the isopropyl group, +0.119.[9,35]

In order to determine if the geometry assumed for the cyclopropylcarbinyl radical was drastically affecting the results, we performed a partial INDO energy minimization study on this species. The following structure was obtained by starting with the geometry given above and systematically varying the ring C–C distances, C_1–C_2, the cyclopropyl C–H lengths, the C_1–H distances, θ_1, θ_2, and θ_3 in that order. The optimum values for these parameters are 1.49, 1.43, 1.12, 1.11 Å, 54.7, 59.2, and 114.0°, respectively. No attempt was made to optimize θ_4 and θ_5. The calculated hydrogen hyperfine interactions for the partially energy minimized structure are given in Table V. It may be noted that the bisected conformation is predicted to be more stable than the perpendicular conformation by 6.05 kcal/mol which is very similar to the energy difference calculated above utilizing the standard geometry; B_0/B_2 is virtually unchanged at +0.0282. A similar analysis for the INDO energy-minimized structure for the ethyl radical[39] yields a B_0/B_2 value of +0.0408.[40] Thus, the B_0/B_2 values do not appear to be particularly sensitive to the chosen geometry and it must be concluded that the calculations do not suggest any unique behavior on the part of the β hydrogen in the cyclopropylcarbinyl radical. As in the ethyl radical and presumably alkyl radicals in general, both hyperconjugation and spin polarization place positive spin density at the β hydrogen according to the INDO calculations. Furthermore, it appears that the mechanism of hyperfine coupling to the β hydrogen in the cyclopropylcarbinyl radical is roughly 94% hyperconjugation and 6% spin polarization which is virtually identical with the calculated partitioning in the ethyl radical.[36]



26

Although the INDO calculations predict both the methyl[41] and ethyl radicals to be slightly nonplanar about the α carbon, the present study indicates that C_1 in the partially energy minimized structure **26** is indeed planar. It might be noted that an *ab initio* calculation utilizing an extended basis set[42] gives the planar form of

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[35] N. L. Bauld, C. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, **54**, 1834 (1971).

[36] J. A. Pople, D. L. Beveridge, and P. A. Dobash, *ibid.*, 47, 2026 (1967).

[37] A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **5**, 115 (1962).

[38] J. R. Morton, *J. Chem. Phys.*, 41, 2956 (1964).

[39] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 108.

[40] The INDO minimum energy structure for the ethyl radical does not have the α carbon exactly planar but with an angle ϕ of 4.3° in which (180 − ϕ) is the angle between the C–C bond and the bisector of the $HC_\alpha H$ angle. For an angle $\phi = -4.3°$, B_0/B_2 is calculated to be +0.0396.

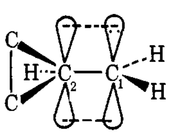
[41] Reference 39, p 100.

[42] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

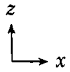
the methyl radical as most stable, although an appreciably nonplanar geometry is predicted for the ethyl radical.

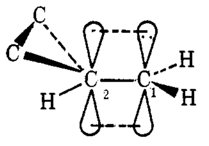
(c) Anion. The cyclopropylcarbinyl anion is calculated to have a slight preference for the perpendicular conformation **2** probably as anticipated from the results for the substituted *n*-propyl anions **18** and **19** discussed above. For planar sp^2 hybridization about C_1, the calculated energy difference is only 1.48 kcal/mol (Table II) while for the tetrahedral sp^3 arrangement the energy difference amounts to 3.50 kcal/mol (Table IV). It may be noted that the tetrahedral structure **13** (Table IV) with the pair of electrons anti to the cyclopropyl ring is highest in energy.

The energy difference between the two conformations of the planar cyclopropylcarbinyl anion is actually less than that calculated for the *n*-propyl anions **18** and **19** and the isobutyl anion. Both the total charge on C_1 and the electron density in the 2p orbital holding the "pair" of electrons in the anion is virtually unchanged in going from one conformation to the other and analysis of the C_1–C_2 bond indices and bond orders reveals but small differences between the two. Inspection of the bond order between the $2p_z$ orbitals on C_1 and C_2 shows a value of 0.3887 for the bisected conformation (*cf.* **27**a) which is essentially identical with that between the $2p_z$ orbitals 0.3935 for the perpendicular alignment **27b**.



27a



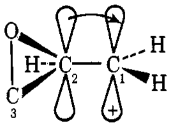


27b

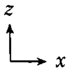
Although the present calculations predict but a rather feeble preference for the perpendicular conformation of the cyclopropylcarbinyl anion, this conclusion is in accord with the recent report of Bauld, *et al.*,[10] who noted such a preference in cyclopropyl-substituted radical anions. However, these workers concluded from a study of various cyclopropyl- and isopropyl-substituted hydrocarbon radical anions that these two substituents behaved differently with the former preferentially adopting the perpendicular alignment. Our calculations indicate that the cyclopropyl and isopropyl substituents interact with an anionic center in a similar manner with no apparent unique mode of interaction such as through the internal Walsh cyclopropane orbitals as suggested by Bauld, *et al.*[9,10] In fact, the present calculations suggest a less pronounced preference for the perpendicular alignment in the cyclopropylcarbinyl anion as compared to the isobutyl for an assumed trigonal configuration at C_1 (Tables I and II) although the two species are more similar for tetrahedral C_1 conformations (Table IV).

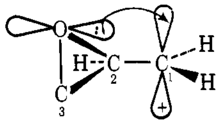
There is some kinetic evidence that the cyclopropyl group can stabilize a carbanion[43] but the most recent data[44] indicate that the stabilizing effect is weak and apparently not very conformationally dependent. These results would appear to be in agreement with the present calculations.

Oxirylcarbinyl. (a) Cation. The oxirylcarbinyl cation exhibits a rather pronounced preference for the bisected conformation just as does the cyclopropylcarbinyl species. The INDO calculated difference in energy between the bisected **4** and symmetrical **5** conformations amounts to 31.15 kcal/mol for the oxirylcarbinyl cation. These alignments do not, however, correspond to the calculated highest and lowest energy conformations of the oxirylcarbinyl cation (*vide infra*). An examination of the bond indices (bisected, **4**: C_1–C_2 = 1.4645, C_2–C_3 = 0.8031, C_2–O = 0.7272, C_3–O = 1.0232; perpendicular, **5**: C_1–C_2 = 1.2433, C_2–C_3 = 0.9430, C_2–O = 0.9079, C_3–O = 0.9224) reveals an enhanced value for the C_1–C_2 bond and diminished values for the C_2–C_3 and C_2–O bonds for the bisected conformation as compared to the perpendicular alignment. As in the cyclopropylcarbinyl case the enhanced stability and increased C_1–C_2 bond index in the bisected conformation arise primarily from effective overlap of the $2p_z$ orbitals on C_1 and C_2 (*cf.* **28**a). It should be noted that depictions such as **24**a and **28**a do not imply transfer of electron density only from the orbital indicated but rather from the C_2–C_3 and C_2–C_4 (or C_2–O) "bent" bonds of which the p orbital depicted is an integral part. Indeed, the electron density of the $2p_z$ orbital on C_2 is actually greater than unity, 1.0706 and 1.0314 for **24**a and **28**a, respectively. Most of the electron density is actually removed from appropriate orbitals on C_3 and C_4 (or O). There is also evidence from the calculations for partial electron donation of the lone pair electrons in the $2p_x$ orbital on oxygen into the $2p_z$ orbital of C_1 which is particularly favored from the bisected conformation (*cf.* **28b**).



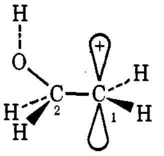
28a



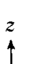


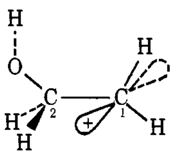
28b

It is interesting to note that INDO calculations on the 2-hydroxyethyl cation predict that the conformation with the p orbital on C_1 aligned with the C–O bond, **29**a, to be less stable than the orthogonal alignment, **29b**, by 12.42 kcal/mol. Analysis reveals that although there is a slightly diminished electron density in the oxygen $2p_x$ orbital in **29**a as compared to **29b** presumably as a result of electron donation into the "empty" 2p orbital on C_1 (*cf.* **28b**), this effect is not sufficient to counteract the decrease in the bond order between the $2p_z$ orbitals on C_1 and C_2 due to the intrinsic electronegativity of the oxygen atom. These results indicate that hyperconjugation involving C–O is less effective than that involving C–H. However, it must be noted that no attempt was made to optimize the geometry in the present case and **29b** may not even approximate a true energy minimum.[25] Radom and Pople have carried out *ab initio* calculations on structures similar to **29**a and **29b**



29a





29b

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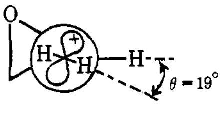
(43) M. Charton in "The Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 511.

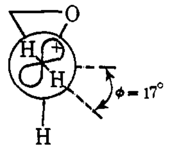
(44) M. J. Perkins and P. Ward, *Chem. Commun.*, 1134 (1971).

except that the hydroxyl hydrogen is oriented anti to the C_1–C_2 bond. Using assumed geometries, the barrier to rotation is calculated to be 7.67 kcal/mol with the conformation corresponding to **29b** being the more stable in agreement with the INDO results.[45]

The lower degree of symmetry inherent in the oxirylcarbinyl species as compared to the cyclopropylcarbinyl prompted us to determine whether the bisected conformation is truly the lowest in energy. Rotation about C_1–C_2 reveals an energy minimum when the $H_1C_1H_2$ plane makes an angle of 19° with the C_2–H_3 bond (*cf.* **30**). This conformation is calculated to be more stable than the true bisect alignment (**30**, $\theta = 0°$) by 3.26 kcal/mol. It is evident that the p orbital on C_1 prefers to align itself with the C_2–C_3 bond rather than the C_2–O bond in accord with the discussions above indicating the importance of cationic C–C hyperconjugation as compared to cationic C–O hyperconjugation or interaction with the lone pair on the oxygen atom. Likewise, the highest energy conformation is not the perpendicular form (**31**, $\phi = 0°$) but rather a slightly different alignment in which $\phi = 17°$. The difference in energy between the highest and lowest energy forms is calculated to be 39.07 kcal/mol which is similar to that calculated for the bisected and perpendicular conformations of the cyclopropylcarbinyl cation. It is to be emphasized, however, that these results are not derived from a complete energy minimization.[25]

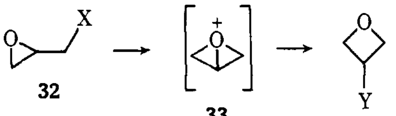


30, low energy



31, high energy

In summary, it appears that the epoxide substituent should be almost as effective as the cyclopropyl in stabilizing a cationic center with a more or less bisected conformation being preferred. The only experimental data relating to this conclusion is a report by Richey and Kinsman who investigated the solvolysis reactions of esters of several 2,3-epoxy-1-propanols **32**.[46] Esters of 3-oxetanols, **34**, were observed as products and 1-oxabicyclobutonium cations, **33**, were postulated as intermediates in the rearrangements. Quite rapid first-order rate constants were observed but it was not possible to ascertain whether the acceleration was due to a direct participation by the oxygen lone pairs in the rate-determining step or by an acceleration of ionization due to the conjugative effect of the oxirane ring similar in nature to that exhibited by the cyclopropyl ring, or by a combination of these factors. The present calculations indicate that both these factors are probably operative but that the conjugative effect of the three-membered oxirane ring is dominant.



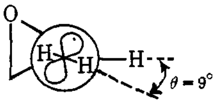
32 **33** **34**

(b) Radical. The calculations indicate that the bisected conformation of the oxirylcarbinyl radical is more stable than the perpendicular form by 7.55 kcal/mol which can be compared with a difference of 7.21 kcal/mol for the corresponding cyclopropylcarbinyl radical. The calculated hyperfine coupling constants for the two conformations of the oxirylcarbinyl radical are given in Table VI. A comparison of the data in Tables II, III, V, and VI reveals that there is a great deal of similarity between the cyclopropylcarbinyl and oxirylcarbinyl radicals. The anti H_5 in the oxirylcarbinyl radical is seen to have a positive coupling constant in the bisected conformation which becomes very small in the perpendicular alignment although it does not actually become negative as in the cyclopropylcarbinyl radical. The slight negative spin density on the oxygen atom in the bisected conformation is unexpected; by analogy with C_3 in this radical and C_3 and C_4 in the cyclopropylcarbinyl radical one would have predicted somewhat of an increase in spin density in changing from the perpendicular to the bisected forms (*vide supra*). An investigation of the two conformations of the 2-hydroxyethyl radical analogous to **29a** and **29b** reveals that the radical with the C–O bond aligned with the p orbital on C_1 holding the unpaired electron has a significantly higher ^{17}O hyperfine interaction than the conformation in which the bond and the orbital are perpendicular to each other (hyperfine splitting constants of +6.15 and −0.25, respectively).

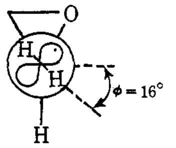
Table VI. INDO Calculated Hyperfine Coupling Constants for the Oxirylcarbinyl Radical

Atom	Bisected conformer **4**	Perpendicular conformer **5**
H_1	−19.40	−20.51
H_2	−19.04	−21.27
H_3	+3.11	+52.42
H_4	−2.28	−1.41
H_5	+2.10	+0.18
C_1	+35.84	+38.71
C_2	−13.81	−14.26
C_3	+12.15	+6.40
O	−2.62	+0.82

Calculations involving rotation about the C_1–C_2 bond in the oxirylcarbinyl radical reveal that the perfectly bisected **4** and perpendicular **5** conformations do not represent the lowest and highest energy alignments. Instead, an energy minimum is realized when the $H_1C_1H_2$ plane makes an angle of 9° with the C_2–H_3 bond (*cf.* **35**) while the highest calculated energy for this rotation occurs when the p orbital on C_1 is rotated 16° toward the C_2–O bond from the perpendicular alignment (*cf.* **36**). Conformation **35** is observed to be 0.21 kcal/mol more stable than the true bisected alignment (**35**, $\theta = 0°$) and the difference in energy between **35** and **36** is



35, low energy



36, high energy

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(45) Private communication from Professor P. v. R. Schleyer.

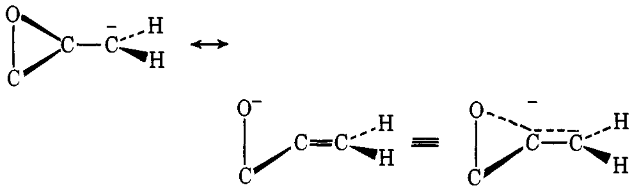
(46) H. G. Richey, Jr., and D. V. Kinsman, *Tetrahedron Lett.*, 2505 (1969).

calculated to be 8.51 kcal/mol which is similar to that calculated for the true bisected and perpendicular conformations; it is obvious that **35** and **36** represent very shallow minimum and maximum on the rotational potential surface.

An esr study of the oxirylcarbinyl radical has not, to our knowledge, been reported to allow a comparison with the present calculations. The accompanying paper[11] describes an investigation of a series of substituted *p*-nitrophenyloxirane radical anions; these are discussed briefly in the following section.

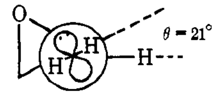
(c) Anion. The oxirylcarbinyl anion appears to prefer the bisected conformation in contrast to the analogous isobutyl and cyclopropylcarbinyl anions. From Table III which a trigonal configuration about C_1 is assumed it can be seen that the INDO method predicts a preference for the bisected alignment amounting to 8.88 kcal/mol. Likewise, in Table IV it is seen that both "bisected" forms **15** and **17** of an assumed tetrahedral C_1 are calculated to be more stable than either "perpendicular" conformation **14** or **16**.

The changeover to a preference for the bisected conformation in the oxirylcarbinyl anion as compared to the lower energy perpendicular alignment in the cyclopropylcarbinyl anion must obviously be due to the presence of the oxygen in the three-membered ring. A survey of the data in Table III indicates a lowered electron density on C_1 and an increased electron density on the oxygen atom while the bond indices (bisected, **4**: C_1–C_2 = 1.2557, C_2–O = 0.7490, C_2–C_3 = 0.9639, C_3–O = 0.9133; perpendicular, **5**: C_1–C_2 = 1.1851, C_2–O = 0.8291, C_2–C_3 = 1.0031, C_3–O = 0.9352) indicate an enhanced C_1–C_2 value and a decreased C_2–O value for the bisected conformation relative to the perpendicular alignment. Although these differences are not nearly so pronounced as for the corresponding cations, they do support a description of the oxirylcarbinyl anion in which a portion of the negative charge is transferred to the oxygen atom as depicted in the following.

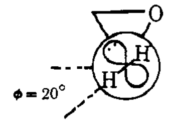


37

Calculations on the 2-hydroxyethyl anion (*cf.* **29a** and **29b** except anion) reveal the conformer with the p orbital on C_1 aligned with the C_2–O bond to be preferred over the orthogonal arrangement by 2.60 kcal/mol indicating that the C–O hyperconjugation is more effective than C–H interaction. Moreover, the true bisected (**38**, θ = 0°) and true symmetrical (**39**, ϕ = 0°) conformations of the oxirylcarbinyl anion are not the respective lowest and highest energy C_1–C_2 rotomers. Instead, the lowest energy conformation for trigonal C_1 is calculated to have the p orbital rotated 21° toward the oxygen atom (*cf.* **38**, θ = 21°) while the highest energy alignment is predicted to have this orbital rotated 20° toward C_3 (*cf.* **39**, ϕ = 20°). The energy difference between these two conformations amounts to 11.78 kcal/mol which is somewhat greater than that calculated assuming truly bisected and perpendicular alignment. Of course, the calculated energies for the various alignments of the tetrahedral C_1 anions reported in Table IV are probably more realistic than assuming a trigonal configuration about C_1.



38, low energy



39, high energy

Although the oxirylcarbinyl anion is calculated to prefer a more or less bisected conformation, it is apparent that this preference is not nearly as great as that exhibited between the two conformations of the oxirylcarbinyl cation. There are some experimental data which appear to support the present calculations. Strait, *et al.*,[12] have examined the ultraviolet spectra of a series of para-substituted styrene oxides and related compounds and have invoked resonance structures analogous to **37** to describe the excited state species. In our accompanying paper[11] we have investigated a number of substituted *p*-nitrophenyloxirane radical anions by electron spin resonance spectroscopy. Although such species are both radical and anion in nature, a measure of the magnitude of the hyperfine coupling constant of the nitrogen atom of the nitro group is expected to reflect the electron-donating or -withdrawing properties of the oxiryl substituent. It was concluded that the oxiryl and substituted oxiryl groups are moderately effective electron-withdrawing groups but that there is only a small conformational dependency for the effect. This conclusion would appear to be in general accord with the present calculations.

Acknowledgments. The author would like to express his appreciation to J. A. Pople and K. F. Purcell for helpful discussions.