

The Structure of Acetaldehyde Enolate Anion

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Non-empirical SCF-MO computations have been performed on $[\text{CH}_2\text{CHO}]^-$, the simplest enolate anion. Following a preliminary search of the conformational hypersurface using an STO-3G basis set to determine the C—C and C—O bond lengths as a function of rotation about the C—C bond, the rotation-inversion surface has been generated with an STO-4G basis set. The energy minimum of this surface is the all-planar anion whose C—C and C—O bond lengths are entirely compatible with the usual description $^-\text{CH}_2\text{CHO} \leftrightarrow \text{CH}_2=\text{CHO}^-$. The planar structure results from extensive conjugative stabilization amounting to over 30 kcal/mol (based on the C—C rotational barrier). When the CH_2 plane is perpendicular to the CHO plane, the conjugative interaction is symmetry forbidden and the electron-withdrawing inductive effect of the formyl substituent leads to a pyramidal carbanion. Experimental implications of these results are discussed.

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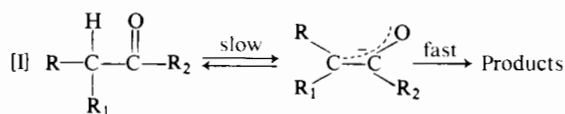
On a effectué des calculs SCF-MO non-empiriques sur $[\text{CH}_2\text{CHO}]^-$, l'anion énoate le plus simple. On a effectué une étude préliminaire de l'hypersurface conformationnelle utilisant une base STO-3G afin de déterminer les longueurs des liaisons C—C et C—O en fonction de la rotation du lien C—C; on a ensuite généré la surface de rotation-inversion utilisant une base STO-4G. Le minimum d'énergie de cette surface correspond à l'anion complètement plan pour lequel les longueurs des liaisons des liens C—C et C—O sont compatibles avec la description usuelle $^-\text{CH}_2\text{CHO} \leftrightarrow \text{CH}=\text{CHO}^-$. La structure planaire est le résultat d'une stabilisation importante provenant de la conjugaison et correspondant à plus de 30 kcal/mol (en se basant sur la barrière à la rotation C—C). Quand le plan du CH_2 est perpendiculaire au plan CHO, l'interaction de conjugaison n'est pas permise par la symétrie et l'effet inductif d'attraction des électrons par le groupe formyle conduit à un carbanion pyramidal. On discute des implications expérimentales de ces résultats.

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Introduction

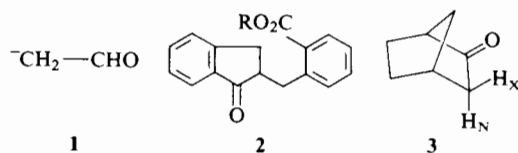
"The generally-accepted mechanism of racemization, hydrogen isotope exchange, and halogenation of carbonyl compounds is rate-determining enolization followed by fast reaction of the enol or enolate ion" (1) (Eq. 1). The classic experiments upon which this mechanism rests (2, 3) were designed to demonstrate that "if the carbon atom bearing mobile hydrogen is an asymmetric center of optical activity, and is the only one present in the molecule, then optical activity must be lost in the mesomeric anion" (4).

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The purpose of the present investigation is to examine theoretically the circumstances under which an enolate anion will have trigonal planar geometry at carbon and will, therefore, be achiral. The work was initiated because of the implications that may be drawn from three types of study: (i) the extensive literature on the symmetry properties of tricoordinated species (5) indicates that attachment of a carbonyl group to a carbanionic center will cause a lowering of the barrier to pyramidal inversion at

carbon if the conjugative effect of the carbonyl group dominates; however, the electron-withdrawing inductive effect of the carbonyl group operates in the opposite direction and will tend to increase the inversion barrier. Depending upon the balance between conjugative and inductive effects in this system, the barrier to pyramidal inversion at carbon in the anion of acetaldehyde (**1**) might be higher, lower, or equal to that in methylcarbanion. (ii) Although several claims that conjugated asymmetric carbanions had been generated (6) could not be confirmed (7), Marquet and co-workers (8) have succeeded in repeating and extending the observations of Leuchs (9). Thus the ketone **2** undergoes chlorination and bromination with retention of configuration at the asymmetric center, the degree of asymmetric induction depending upon the nature of the halogenating agent and the solvent. (iii) A number of examples now exist (10) of large differences in the rates of appearance of deuterium at the *exo* and *endo* methylene positions of certain bicyclic ketones (e.g. **3**), when these compounds are subjected to base catalyzed hydrogen-deuterium exchange.



These latter observations have been interpreted in terms of a kinetic model which assumes a difference in the rates of protonation (deuteration) of an achiral intermediate (the enol or enolate anion) from *exo* and *endo* faces. However, there is an alternative interpretation of such observations if it is supposed that the asymmetry resides in the anionic intermediate itself, and not in the capture of this intermediate. In this event, the experimental observations would be consistent with either a greater rate of abstraction of the *exo* proton, or with exchange of the *exo* proton with retention of configuration and exchange of the *endo* proton with inversion of configuration (11). Analysis of experimental data in terms of such a mechanism would require a more complex kinetic model (12).

To assess the validity of these views, and the possible role of conformational effects in creating and maintaining asymmetry (i.e., non-planar geometry at carbon) in an enolate anion, we have

carried out a theoretical study of a portion of the conformational hypersurface of **1** corresponding to rotation about the carbon-carbon bond and pyramidal inversion at the carbanionic center. We were aware of the fact that formamide, H_2NCHO , which is isoelectronic with **1**, may have a non-planar configuration at nitrogen (13).

Method

The Hartree-Fock-Roothaan equations were solved using the Gaussian 70 program system (14). A preliminary search of the energy hypersurface was performed with an STO-3G basis set (15) and detailed investigation of the rotation-inversion surface was then carried out with the STO-4G basis set.² As a result of convergence problems, the computations could not be extended to the 4-31G level (16).

All computations were performed on a CDC 6600 computer at the University of Bologna.

Calculations

Because of the low (ca. 1 kcal/mol) inversion barrier in formamide (13), it was recognized that a crude optimization of the out-of-plane angle of **1** could well overlook a non-planar anion. In addition, the degree of non-planarity was expected to depend strongly upon both the C-C and C-O bond lengths. For example, shorter C-C and longer C-O bonds should enhance the conjugative effect and diminish any tendency towards a non-planar anion. The computations were, therefore, carried out in three stages.

In the first stage, the C-C and C-O bond lengths were varied with the carbanionic center non-planar ($\text{C-H} = 1.09 \text{ \AA}$; $\angle \text{CCO} = \angle \text{OCH} = 120^\circ$; $\angle \text{HCH} = \angle \text{HCC} = 115^\circ$; HCCO dihedral angle = 20° and both methylene hydrogens on the same side of the CCHO plane). These results are summarized in Table 1, together with a similar optimization with the carbanionic center planar. The second stage consisted of a complete optimization beginning with a slightly non-planar structure. Starting from $\angle \text{HCH} = \angle \text{HCC} = 119^\circ$, all bond lengths and angles were optimized, with the inversion coordinate varied last. This led to a fully planar structure for the energy minimum. In the third stage of the work, this optimized structure represented the starting point for the STO-4G calcu-

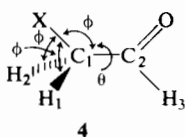
²Minimal basis sets tend to overestimate barriers to pyramidal inversion. Therefore, energy differences in this paper which deal with changes in the inversion coordinate should be regarded as upper limits of these values.

TABLE 1. Optimization of the C—C and C—O bond lengths of **1** with an STO-3G basis set

Bond length (Å)		Energy (hartree ^a)	
C—O	C—C	Non-planar ^b	Planar ^c
1.43	1.45	-150.102438	
1.35	1.50	-150.114595	
1.35	1.45	-150.121671	
1.35	1.40	-150.124948	-150.122763
1.25	1.50	-150.124957	
1.25	1.45	-150.130463	-150.129779
1.25	1.40	-150.132067	-150.133724
1.25	1.35	-150.128540	-150.132561
1.15	1.40	-150.106068	-150.106199

^a1 hartree = 627.71 kcal/mol.^bOptimum structure: C—O = 1.279 Å; C—C = 1.409 Å; E = -150.133502.^cOptimum structure: C—O = 1.272 Å; C—C = 1.386 Å; E = -150.134805.

lations of the rotation-inversion surface. The coordinates are defined as shown in **4**; in this structure, the point X is included to facilitate the definition of the inversion coordinate.

**4**

Thus $\phi = 90$, $\theta = 0$ defines the all-planar conformation.

At each of three dihedral angles ($\theta = 0$, 45 , and 90°), the C—C and C—O bond lengths and the HC_1C_2 valence angles were reoptimized with ϕ maintained at 90° . Then the inversion cross-sections were scanned by permitting ϕ to vary. The relationship between the HC_1C_2 angles and

$$\begin{aligned}
 [3] \quad E = & C_0 + C_1(\phi - 90)^2 + C_2 \exp[-1.05(\phi - 90)^2] \\
 & + C_3 \sin \theta \cdot (\phi - 90) + C_4 \sin \theta \cdot (\phi - 90)^3 \\
 & + C_5 \sin^2 \theta + C_6 \sin^2 \theta \cdot (\phi - 90)^2 \\
 & + C_7 \sin \theta \cdot \exp[-1.05(\phi - 90)^2] + C_8 \sin^3 \theta \cdot (\phi - 90) \\
 & + C_9 \sin^3 \theta \cdot (\phi - 90)^3 + C_{10} \sin^4 \theta \\
 & + C_{11} \sin^4 \theta \cdot (\phi - 90)^2 + C_{12} \sin^4 \theta \cdot \exp[-1.05(\phi - 90)^2]
 \end{aligned}$$

Discussion

The all-planar structure is the minimum point on the rotation-inversion surface because of the overriding effect of the conjugative stabilization that is present in this conformation. The magnitude of this conjugative effect may be gauged

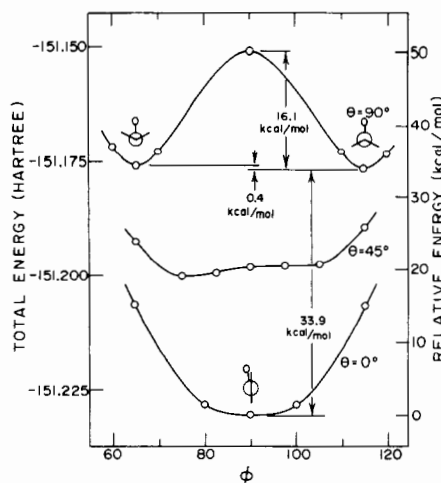


FIG. 1. Cross-sections of the rotation-inversion surface of **1** corresponding to $\theta = 0^\circ$ (the all-planar conformation), $\theta = 45^\circ$, and $\theta = 90^\circ$.

ϕ is given in Eq. 2, and corresponds to the assumption that the projected HC_1C_2 angle about the C_1X axis remains constant.

$$[2] \quad \cos(\angle \text{HC}_1\text{C}_2)_\phi = \cos^2 \phi + \cos(\angle \text{HC}_1\text{C}_2)_{90} \sin^2 \phi$$

These latter cross-sections are displayed in Fig. 1 and summarized in Table 2.

An analytical expression having the form shown in Eq. 3 was then fitted to the data of Table 2. The coefficients of Eq. 3 are given in Table 3. With the aid of this equation, a perspective view of the final rotation-inversion surface was generated, and is presented in Fig. 2.³

from the 33.9 kcal/mol barrier to rotation about the $\text{C}_1\text{—C}_2$ bond and the decrease in this bond length from 1.472 Å at $\theta = 90^\circ$ to 1.379 Å at

³This surface is generated by a series of computer programmes SURFPLOT, which may be obtained from the authors.

TABLE 2. Rotation-inversion surface of **1** with an STO-4G basis set

Geometry ^a						
θ (deg.)	ϕ (deg.)	r_{CO} (Å)	r_{CC} (Å)	$\angle H_1C_1C_2$ (deg.)	$\angle H_2C_1C_2$ (deg.)	Energy ^b
0	90 ^c	1.270	1.379	122.4	121.7	-151.230542
0	100	1.270	1.379	119.3	118.7	-151.228334
0	115	1.270	1.379	105.2	104.7	-151.206895
45	90	1.261	1.404	122.5	121.2	-151.198504
45	65	1.261	1.404	105.2	104.3	-151.192742
45	75	1.261	1.404	115.7	114.6	-151.200313
45	82.5	1.261	1.404	120.7	119.5	-151.199681
45	97.5	1.261	1.404	120.7	119.5	-151.198338
45	105	1.261	1.404	115.7	114.6	-151.197877
45	115	1.261	1.404	105.2	104.3	-151.189213
90	90	1.233	1.472	119.8	119.8	-151.150814
90	60	1.233	1.472	97.0	97.0	-151.171749
90	65	1.233	1.472	103.2	103.2	-151.175878
90	70	1.233	1.472	108.8	108.8	-151.172916
90	110	1.233	1.472	108.8	108.8	-151.172703
90	115	1.233	1.472	103.2	103.2	-151.176521
90	120	1.233	1.472	97.0	97.0	-151.173670

^aAdditional parameters: $r_{C_2H_3} = 1.12$ Å; $r_{C_1H} = 1.075$ Å; $\angle C_1C_2O = 126.8^\circ$; $\angle H_3CO = 118.0^\circ$.

^bIn hartree units.

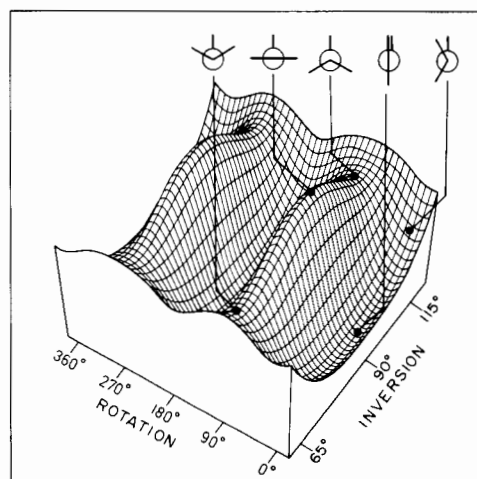
^cPlanar structure.

TABLE 3. The parameters of Eq. 3, employed in the generation of the rotation-inversion surface^{a,b}

Parameter	Value
C_0	-151.863773
C_1	0.726856
C_2	0.633231
C_3	0.012411
C_4	-0.001579
C_5	0.177172
C_6	-0.203588
C_7	-0.128697
C_8	-0.010458
C_9	-0.012292
C_{10}	-0.833062
C_{11}	0.645908
C_{12}	0.864296

^a θ, ϕ in radians; E in hartree units.

^bMaximum deviation 0.000081. Root mean square deviation 0.000031.

FIG. 2. The rotation-inversion surface of **1**.

$\theta = 0^\circ$, accompanied by a lengthening of the C_2-O bond from 1.233 to 1.270 Å. Inspection of the π -type molecular orbitals (Fig. 3) reveals that conjugation is achieved by a four-electron three-orbital interaction between the carbon lone pair and the π and π^* C_2-O orbitals. Even when the methylene group is rotated 45° out of the plane of the formyl group, substantial conjugation remains, as indicated by the short C_1-C_2 bond (1.404 Å). However, at $\theta = 90^\circ$, this conjugative interaction is now symmetry

forbidden and the methylene group behaves normally, *i.e.*, it is pyramidal. The inversion barrier is 16.1 kcal/mol, which may be compared to the 21.7 kcal/mol barrier computed for CH_3^- with the same basis set.

Our expectation that the electron-withdrawing formyl substituent might bring about some stabilization of the pyramidal configuration at the methylene group is thus not confirmed, either at $\theta = 0^\circ$ (the all-planar structure) or at $\theta = 90^\circ$. The reason for this can be seen upon considera-

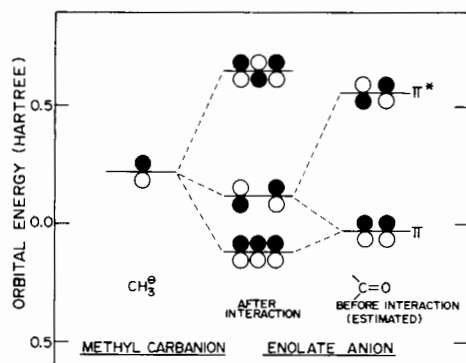


FIG. 3. Interaction of the π -type molecular orbitals in the energy minimum of **1**.

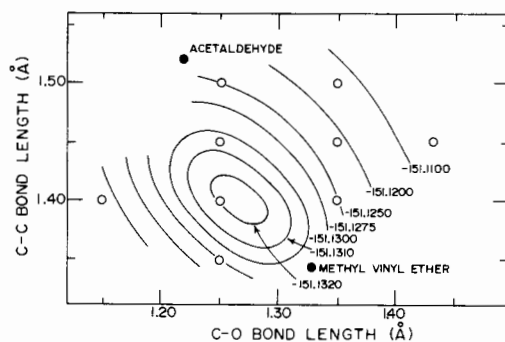
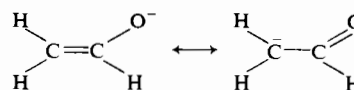


FIG. 4. The relationship between the computed (STO-3G) C—C and C—O bond lengths of **1**. Experimental data for methyl vinyl ether and acetaldehyde are indicated by ●.

tion of the nature of the charge transfer between the methylene and formyl groups. Within the framework of the Mulliken population analysis, there is, in the all-planar structure, a π charge transfer of 0.47 electron from CH_2^- to CHO, and a σ charge transfer of only 0.04, illustrative of the dominating influence of the conjugative interaction. In the $\theta = 90^\circ$ conformation, the σ charge transfer is 0.27 electron from CH_2^- to CHO, but some π charge transfer, amounting to 0.05 electron in the same direction, or 18% of the σ charge transfer, remains. This is caused by a hyperconjugative interaction between the methylene group and the formyl group. This hyperconjugative interaction works against the inductive (*i.e.* σ) effect of the formyl group, and it leads to a net destabilization of the pyramidal configuration, as compared to CH_3^- .

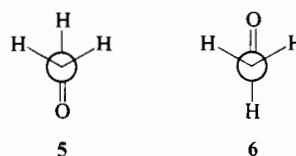
The C—C and C—O bond lengths are strongly coupled to each other (*cf.* Table 1). The contour plot of Fig. 4 shows this coupling for the STO-3G

calculations. For comparison, the experimental bond lengths of acetaldehyde (C—C and C=O) and methyl vinyl ether (C=C and C—O) are included in this figure. It is clear that the structure of acetaldehyde enolate anion is very well represented by the usual resonance description



The C—C and C—O bond lengths are also coupled to the out-of-plane bending of the methylene group. In the 0° rotational structure, for instance, the out-of-plane bending allows the orbitals of H_1 and H_2 to mix with the π orbitals and withdraw charge from them. In doing so, the π conjugation is reduced and the net effect is to lengthen both the C—C bond and the C—O bond as the geometry at C_1 is made non-planar. However, the stabilization gained by this out-of-plane bending is unable to overcome the concomitant destabilization of the π system.

The rotation-inversion surface shows in some detail the dependence of the energy on the rotation and inversion coordinates. It is noteworthy that the more stable of the two pyramidal structures has the Y conformation **5**. Such behavior has been found previously in $^-\text{CH}_2\text{OH}$ (**17**), whose C—O bond length is similar to the C_1 — C_2 bond length of the enolate anion. The Y conformation is favored when the structure is dominated by the nuclear component of the total energy. However, in the $\theta = 45^\circ$ cross-section, the structure is dominated by the electronic component of the total energy (*i.e.*, the conjugative effect), and the more crowded W conformation (**6**) is favored.

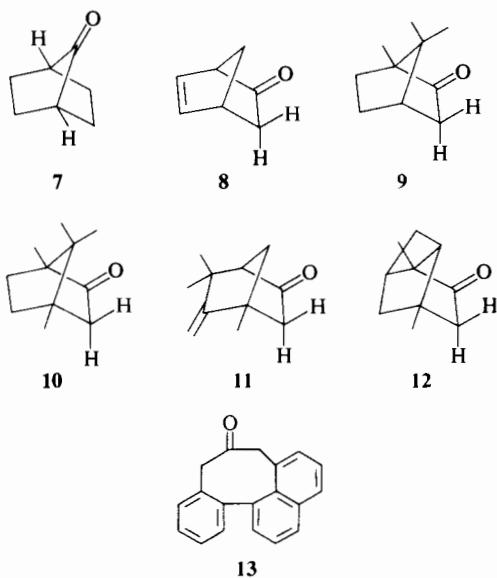


Conclusions

The suggestion that the simplest enolate anion might have non-planar geometry at carbon has not been supported. Although the electron-withdrawing effect of the carbonyl group can be shown to exist, in the absence of conformational constraint it does not overcome the conjugative interaction leading to a planar carbanion. The

required conformational constraint is found in the ketone **7** (18). The observation that the bridgehead protons of this compound undergo base-catalyzed exchange demonstrates that, as computed for the $\theta = 90^\circ$ structure, a pyramidal enolate anion has some stability. However, since the pyramidal conformation is much higher in energy than the all-planar conformation, the exchange is extremely slow.

In each of the bicyclic ketones (*e.g.*, **3**, **8–12**) for which stereoselective hydrogen exchange has been reported (10) a planar enolate anion is possible. Consequently it is valid to analyze stereoselective exchange in such compounds in terms of a kinetic model which assumes asymmetric capture of an inherently symmetrical intermediate. For stereoselective exchange of methylene protons adjacent to a carbonyl group to proceed via an asymmetric intermediate it will be necessary to employ a substrate containing diastereotopic methylene protons which cannot achieve a planar conformation in the enolate anion. Inspection of molecular models suggests that the ketone **13** may be suitable for such a study.



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1. J. W. THORPE and J. WARKENTIN. *Can. J. Chem.* **50**, 3229 (1972).
2. C. K. INGOLD and C. L. WILSON. *J. Chem. Soc.* **93** (1934).
3. S. K. HSÜ, C. K. INGOLD, and C. L. WILSON. *J. Chem. Soc.* 1778 (1935).
4. C. K. INGOLD. *Structure and mechanism in organic chemistry*, 2nd Edition. Cornell University Press, 1969, p. 829.
5. J. M. LEHN. *Top. Curr. Chem.* **15**, 311 (1970); A. RAUK, L. C. ALLEN, and K. MISLOW. *Angew. Chem. Int. Ed. Engl.* **9**, 400 (1970); J. B. LAMBERT. *Top. Stereochem.* **6**, 19 (1971); H. A. BENT. *Chem. Rev.* **61**, 275 (1961).
6. R. KUHN and H. ALBRECHT. *Chem. Ber.* **60**, 1297 (1927); R. L. SHRINER and J. H. YOUNG. *J. Am. Chem. Soc.* **52**, 3332 (1930); C. RAPPE. *Acta Chem. Scand.* **21**, 1823 (1967).
7. N. KORNBLUM, J. T. PATTON, and J. B. WOODMAN. *J. Am. Chem. Soc.* **70**, 746 (1948); G. WITTIG, F. VIDAL, and E. BOHNERT. *Chem. Ber.* **83**, 359 (1950); J. WARKENTIN and C. BARNETT. *J. Am. Chem. Soc.* **90**, 4629 (1968).
8. M. J. RONTEIX and A. MARQUET. *Tetrahedron Lett.* 5801 (1966); M. DVOLAITZKY, M. J. LUCHE, and A. MARQUET. *Compt. Rend. Ser. C.* **266**, 1797 (1968); M. J. LUCHE and A. MARQUET. *Compt. Rend. Ser. C.* **267**, 420 (1968).
9. H. LEUCHS. *Chem. Ber.* **46**, 2435 (1913); **48**, 1015 (1915).
10. A. F. THOMAS and B. WILLHALM. *Tetrahedron Lett.* 1309 (1965); J. M. JERKUNICA, S. BORČIĆ, and D. E. SUNKO. *Tetrahedron Lett.* 4465 (1965); A. F. THOMAS, R. A. SCHNEIDER, and J. MEINWALD. *J. Am. Chem. Soc.* **89**, 68 (1967); T. T. TIDWELL. *J. Am. Chem. Soc.* **92**, 1448 (1970); N. H. WERSTIUK and R. TAILLEFER. *Can. J. Chem.* **48**, 3966 (1970); G. LAMATY, A. ROQUES, and L. FONZES. *Compt. Rend. Ser. C.* **273**, 521 (1971); G. A. ABAD, S. P. JINDAL, and T. T. TIDWELL. *J. Am. Chem. Soc.* **95**, 6326 (1973).
11. R. R. FRASER, F. J. SCHUBER, and Y. Y. WIGFIELD. *J. Am. Chem. Soc.* **94**, 8795 (1972).
12. T. F. GARRARD. M.Sc. Thesis, Queen's University, Kingston, Ont. 1974.
13. D. H. CHRISTENSEN, R. N. KORTZEBORN, B. BAK, and J. J. LED. *J. Chem. Phys.* **53**, 3912 (1970).
14. W. J. HEHRE, W. A. LATHAN, R. DITCHFIELD, M. D. NEWTON, and J. A. POPLE. GAUSSIAN 70. Quantum Chemistry Program Exchange. Indiana University, Bloomington, Ind. No. 236.
15. W. J. HEHRE, R. F. STEWART, and J. A. POPLE. *J. Chem. Phys.* **51**, 2657 (1969).
16. R. DITCHFIELD, W. J. HEHRE, and J. A. POPLE. *J. Chem. Phys.* **54**, 724 (1971).
17. S. WOLFE, L. M. TEL, and I. G. CSIZMADIA. *Can. J. Chem.* **51**, 2423 (1973).
18. P. G. GASSMAN and F. V. ZALAR. *J. Am. Chem. Soc.* **88**, 3070 (1966).