p-dinitrobenzene which yields an NO_2^{2-} ion of small abundance (see below), overlooked in the previous study.[13]

(15) See, for example, J. H. Bowie, *J. Am. Chem. Soc.*, **95**, 2547 (1973).

(16) J. H. Bowie and B. J. Stapleton, unpublished results.

(17) J. H. Bowie and S. G. Hart, *Int. J. Mass Spectrom. Ion Phys.*, **13**, 319 (1974).

(18) Compare J. Seibl, *Org. Mass Spectrom.*, **2**, 1033 (1969).

(19) For recent reviews see, (a) J. G. Dillard, *Chem. Rev.*, **73**, 589 (1973); (b) J. H. Bowie, "Mass Spectrometry", Vol. 2, Specialist Reports, The Chemical Society, London, 1973, p 137; Vol. 3, 1975, p 288, (c) J. H. Bowie and B. D. Williams, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two.* (1975).

(20) The effect of charge separation is also of particular importance for doubly charged positive ions, see, for example T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **6**, 741, 749 (1972), and references cited therein.

(21) Similar plots are obtained for M^{2-} and $[M-H]^{2-}$ ions from the acids.

(22) The geometry of these compounds is similar to those of the amino acid derivatives *p*-$O_2N-C_6H_4-CO-NH-CH(R)-CO_2Me$ for which we first observed $-E/2$ spectra (see the introductory section).

(23) Bond formation reactions which precede the unimolecular decompositions of singly charged positive ions have also been noted, see, e.g., S. Meyerson and L. C. Leitch, *J. Am. Chem. Soc.*, **93**, 2244 (1971), and references cited therein.

(24) A study of molecular models indicates that bond formation between N of the *nitro* group and the carbonyl C cannot occur when n = 3.

(25) J. H. Bowie, *Org. Mass Spectrom.*, **5**, 945 (1971).

(26) J. H. Bowie and A. C. Ho, *J. Chem. Soc., Perkin Trans. 2*, 724 (1975).

(27) The Coulomb barrier must be overcome in order for the electron-capture process to occur.

(28) (a) If some dianions are produced with excess energy, then this energy must be dissipated in some way. Collision stabilization is unlikely, as these ions are thought to be formed near the entrance of the electric sector (see below). Perhaps dianions with *excess* energy are simply unstable and reform A^-. To date, no reactions of A^{2-} ions have been observed. (b) A referee has stated that we have not proven unequivocally the electron capture mechanism. We would like to stress that we propose it as a plausible mechanism, arrived at because of elimination of mechanisms involving collision gases.

(29) The defocusing unit[17] has been carefully calibrated for known metastable transitions and is correct to $\pm 0.0002E$.

(30) The $[M^{2-}]/[M^-]$ ratio is however dependent on the value of V; i.e., for *p*-nitrobenzoic acid at 2×10^{-5} Torr the ratio = 1×10^{-3} (3.6 kV), 3×10^{-4} (2.4 kV), and 1×10^{-4} (1.8 kV).

(31) This suggestion was initially made by Professor R. G. Cooks who also suggested the experiments (see below) necessary to substantiate the proposal.

(32) Unimolecular positive ion dissociations in the electric sector have been reported previously. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973, p 51. Decomposition of positive ions near the entrance to the electric sector has been described recently [R. G. Cooks, T. Ast, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, **16**, 348 (1975)].

(33) The α slit is kept wide open during this experiment, thus limiting the possibility of electron capture in the slit region.

(34) A referee has commented that this is a very simplistic explanation. He points out that any reaction involving a change in the charge of a fast ion in an electric field would give rise to a continuum in the energy or mass spectrum if all ions are transmitted. Reaction $A^- \rightarrow A^{2-}$ at the entrance and exit of the sector would appear at exactly $-E/2$ and $-E$, respectively. The observed usual value of $-0.506E$ can be ascribed to the fact that capture occurs with *high probability of product ion transmission* once the ion has entered the sector. Transmission is maximized at the interface with the field-free region, hence the observed result.

(35) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **71**, 779 (1949).

(36) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 705.

Shape and Angle Strain in Organic Intermediates. A Model Study of Alkyl Radicals, Anions, and Cations

Eluvathingal D. Jemmis,[1a] Volker Buss,[1b] Paul von R. Schleyer,*[1a] and Leland C. Allen*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received July 18, 1975*

Abstract: The Walsh-Mulliken diagrams for methyl are constructed from ab initio wave functions and are used to explain the shape and energetics of alkyl cations, radicals, and anions. Two angles, HCH and the out-of-plane CH bend, define the energy surfaces. The minimum energy conformation of the cation is always planar and that of the radical is also planar except for an HCH angle of 90°, in which case CH is bent out-of-plane by 32.4°. For the anion, HCH angles of 90, 109.47, 120, and 135° lead to minimum energy out-of-plane CH angles of 72, 63.4, 56.6, and 32.8°, respectively. It is shown that the entire energy surface can be explained solely in terms of the occupancy and hybridization of the highest occupied molecular orbital. It is expected that the shape of all alkyl intermediates will be governed by the simple rules established in this model study and it is shown that existing experimental and computational data fit this pattern.

A central goal of physical organic chemistry is detailed understanding of the relationship between structure and energy for organic intermediates. The methyl cation, radical, and anion exemplify the problems involved: Only indirect experimental information is available concerning the structures of the ionized species. Whether or not the methyl radical is planar has not been settled with certainty experimentally.[2] Inferences regarding structures are typically drawn from more stable isoelectronic molecules; e.g., CH_3^- is compared with NH_3 and $(CH_3)_3C^+$ with $(CH_3)_3B$. Chemical reactions involving intermediates also provide indirect structural information, but obviously not of a detailed character; e.g., carbenium ion reactions are inhibited at the bridgeheads of small polycyclic ring systems and from this it is inferred that carbenium ions prefer planarity.[3]

Theoretical calculations provide insights not currently accessible experimentally. In this paper, we study the effect of angle deformation on energies and electronic structure of CH_3^-, $CH_3\cdot$, and CH_3^+ as models for larger systems. Numerous ab initio calculations have already been performed on these methyl species, but these studies have been carried out for only a limited range of geometries, usually C_{3v} or D_{3h} conformations. A unique feature of the present work is that the same basis set has been applied to all three species under a considerable variety of geometrical constraints. In addition, the potential energy surfaces which have been computed are analyzed in terms of Walsh-Mulliken diagrams[4] resulting in a simple picture for the behavior of these intermediates.

Computational Aspects

The results presented here were obtained with standard single determinant LCAO-SCF-MO theory, using the GAUSSIAN-70 program[5] with the 4-31G basis set where each inner shell is represented by a four-term Gaussian expansion and each valence shell orbital is split into three and one term expansions for the inner and outer parts, respectively. For open shell cases, the unrestricted procedure of Pople and Nesbet was used.[6] A series of calculations at high symmetry conformations

Table I. Energies and Optimized Bond Lengths[a] for CH_3^+, $CH_3\cdot$, and CH_3^- at C_{3v} Symmetry and $a = b$

	$\beta = 0$ ($\alpha = 120°$)	$\beta = 13.1°$ ($\alpha = 115°$)	$\beta = 19.5°$ ($\alpha = 109.47°$)	$\beta = 23.6°$ ($\alpha = 105°$)	$\beta = 27.8°$ ($\alpha = 100°$)	$\beta = 35.3°$ ($\alpha = 90°$)
CH_3^+						
E_T	−39.175 10		−39.124 60			−39.004 30
a	1.076		1.084			1.104
$CH_3\cdot$						
E_t	−39.505 08		−39.493 20			−39.433 60
a	1.070		1.080			1.101
CH_3^-						
E_T	−39.388 80	−39.395 20	−39.400 00	−39.401 63	−39.400 74	−39.389 38
a	1.081	1.095	1.106	1.119	1.131	1.148

[a] Energies in hartree units; lengths in Å.

Table II. Energies and Optimized Bond Lengths[a] for CH_3^+, $CH_3\cdot$, and CH_3^- in Planar Conformations ($\beta = 0°$)

	$\alpha =$ 90°	105°	120°	135°	150°	180°
CH_3^+						
E_T	−39.149 40	−39.169 04	−39.175 13	−39.169 65	−39.154 30	−39.100 10
a	1.088	1.080	1.076	1.076	1.079	1.088
b	1.071	1.073	1.076	1.081	1.088	1.116
$CH_3\cdot$						
E_T	−39.479 60	−39.498 96	−39.504 98	−39.499 55	−39.484 40	−39.432 03
a	1.084	1.076	1.070	1.068	1.068	1.071
b	1.059	1.064	1.070	1.079	1.089	1.127
CH_3^-						
E_T	−39.364 13	−39.382 96	−39.388 80	−39.383 52	−39.368 75	−39.318 31
a	1.097	1.087	1.081	1 077	1.074	1.069
b	1.062	1.071	1.081	1.093	1.109	1.161

[a] Energies in hartrees, bond lengths in Å.

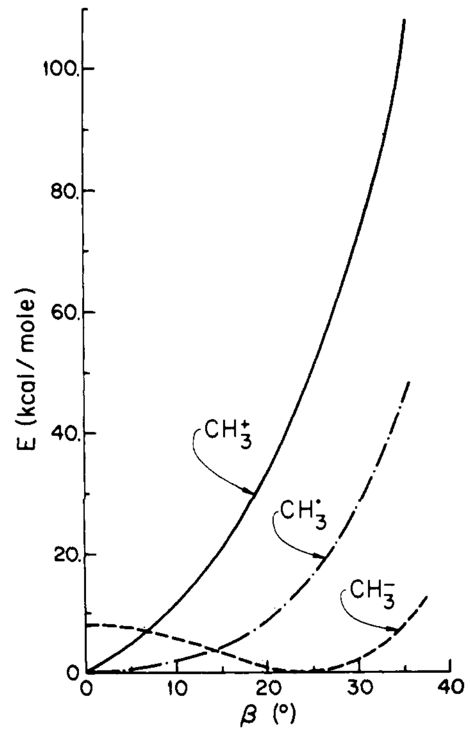


Figure 1. Total energies, E_T, vs. out-of-plane angle, β, for C_{3v}, $a = b$, conformations of CH_3^+, $CH_3\cdot$, and CH_3^-. Minimum energy conformation of each system referenced to zero energy (4-31G basis).

with optimized bond lengths were performed for CH_3^+, $CH_3\cdot$, and CH_3^- (Tables I and II). For the anion and radical a more extended geometry exploration was carried out with the C–H bond lengths optimized for each combination of α and β (Table III). In addition, β was optimized for a given value of α to give the minimum energy conformation.

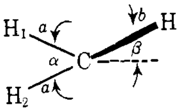


Table I and Figure 1 give results for the high symmetry, $a = b$ conformations. In this case, the angle β is the simultaneous out-of-plane deformation of the C–H bonds measured with respect to a plane perpendicular to the three-fold axis. The curves of Figure 1 closely parallel those of a similar figure given by Driessler et al.,[7] which were obtained with a considerably larger basis set that included d-polarization functions on C and p-polarization functions on H. In addition, Driessler et al calculated in situ intra- and interpair correlation energies by their Boys-localized, natural orbital expansion technique (IEPA-PNO) and they found that the correlation corrections resulted in relatively small perturbations of magnitudes and no change in curve shapes. The methyl carbanion deviates to the greatest extent. The 4-31G minimum for the C_{3v} form occurs at $\beta = 23°$ (vs. 18° with correlation), but the inversion barrier is 8 kcal/mol (vs. 1.5).[7] The high degree of agreement between these calculations and ours suggests that our results for lower symmetry conformations also give accurate relative values. The variation of one-electron energies with angle is another problem where the availability of high accuracy calculations substantiates the results obtained at 4-31G.[8]

Results and Applications

The change in total energy as a function of the out-of-plane angle β is presented in Table IV and in Figures 3 and 4. A po-

Table III. Optimized Bond Lengths for Radical and Anion[a] (Å)

	α =							
	90°		109.47°		120°		135°	
β, deg	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
				Anion				
0	1.0966	1.0625	1.0850	1.0737	1.0811	1.0811	1.0768	1.0932
10	1.0973	1.0623	1.0858	1.0749	1.0812	1.0813	1.0761	1.0932
20	1.1002	1.0681	1.0881	1.0783	1.0831	1.0845	1.0776	1.0957
30	1.1054	1.0745	1.0918	1.0839	1.0863	1.0896	1.0802	1.1001
40	1.1107	1.0842	1.0969	1.0917	1.0905	1.0965	1.0830	1.1057
50	1.1187	1.0952	1.1023	1.1009	1.0956	1.1053	1.0868	1.1128
60	1.1241	1.1067	1.1084	1.1113	1.1010	1.1144	1.0909	1.1021
70	1.1331	1.1198	1.1148	1.1226	1.1074	1.1263	1.0952	1.0952
80	1.1369	1.1324	1.1205	1.1348	1.1132	1.1381	1.0995	1.0995
90	1.1484	1.1484	1.1260	1.1479	1.1185	1.1509	1.1033	1.1033
				Radical				
0	1.0838	1.0588	1.0733	1.0654	1.0703	1.0703	1.0680	1.0786
10	1.0838	1.0575	1.0736	1.0659	1.0695	1.0696	1.0680	1.0786
20	1.0847	1.0608	1.0784	1.0676	1.0712	1.0721	1.0686	1.0799
30	1.0864	1.0625	1.0759	1.0702	1.0724	1.0746	1.0696	1.0822
40	1.0882	1.0672	1.0777	1.0738	1.0740	1.0780	1.0709	1.0853
50	1.0903	1.0706	1.0795	1.0781	1.0752	1.0819	1.0724	1.0894
60	1.0925	1.0765	1.0815	1.0834	1.0777	1.0876	1.0739	1.0945
70	1.0945	1.0829	1.0836	1.0901	1.0793	1.0939	1.0755	1.1005
80	1.0978	1.0912	1.0858	1.0983	1.0815	1.1022	1.0770	1.1077
90	1.1011	1.1006	1.0879	1.1084	1.0831	1.1122	1.0784	1.1161

[a] In-plane C–H bond length is *a*, C–H bond length associated with out-of-plane bend (angle β) is *b*.

Table IV. Total and Relative Energies for Each Combination of α and β for Radical and Anion

	Total energy E_T, hartrees, α =				Rel energies, kcal, α =			
β, degr	90°	109.47°	120°	135°	90°	109.47°	120°	135°
			Anion					
0	−39.364 13	−39.385 96	−39.388 80	−39.383 52	23.31	9.31	7.49	10.84
10	−39.365 42	−39.386 72	−39.389 27	−39.383 63	22.19	8.83	7.23	10.77
20	−39.369 16	−39.388 87	−39.390 60	−39.383 90	19.85	7.48	6.39	10.60
30	−39.374 84	−39.392 04	−39.392 48	−39.384 14	16.29	5.49	5.21	10.45
40	−39.381 60	−39.395 64	−39.394 45	−39.384 04	12.04	3.23	3.98	10.51
50	−39.388 32	−39.398 86	−39.395 88	−39.393 22	7.83	1.21	3.08	11.03
60	−39.393 66	−39.400 79	−39.396 05	−39.381 21	4.47	0.00	2.97	12.28
70	−39.396 37	−39.400 48	−39.394 21	−39.377 55	2.77	0.21	4.21	14.58
80	−39.395 22	−39.397 04	−39.389 66	−39.371 79	3.44	2.36	6.99	18.20
90	−39.389 38	−39.389 73	−39.381 77	−39.363 55	7.16	6.94	11.93	23.34
			Radical					
0	−39.479 60	−39.502 06	−39.504 98	−39.499 55	15.95	1.83	0.00	3.40
10	−39.479 93	−39.502 07	−39.504 82	−39.499 23	15.74	1.82	0.09	3.60
20	−39.480 73	−39.501 94	−39.504 26	−39.498 18	15.24	1.90	0.45	4.26
30	−39.481 33	−39.501 24	−39.502 97	−39.496 24	14.84	2.34	1.26	5.48
40	−39.480 92	−39.499 39	−39.500 48	−39.493 12	15.12	3.50	2.82	7.43
50	−39.478 56	−39.495 72	−39.496 29	−39.488 54	16.59	5.80	5.45	10.30
60	−39.473 40	−39.489 61	−39.489 91	−39.482 21	19.84	9.62	9.46	14.28
70	−39.464 65	−39.480 50	−39.480 92	−39.473 90	25.34	15.32	15.10	19.49
80	−39.451 59	−39.467 94	−39.469 01	−39.463 48	33.59	23.22	22.57	26.00
90	−39.433 60	−39.451 66	−39.454 06	−39.450 98	44.74	33.42	31.95	33.87

tential energy surface (Figures 5 and 6) for both anion and the radical is constructed from the data. Relative energies of the anion and the radical are tabulated in Table IV. The variation of inversion barrier with α is shown by Figure 7 and β vs. α by Figure 8. Values for these latter figures are given in Table V.

As can be seen from Figures 1 and 2, there is an especially strong tendency toward planarity and equal angles between bonds in the cation. The chemical implications of its relatively simple behavior have already been discussed by us previously.[9] There are two other features of the planar conformations shown in Figure 2 that are worth noting. First, the energy cost for angle deformation in CH_3^+ is only slightly higher than that for $CH_3\cdot$ or CH_3^-. Second, Figure 2 is almost exactly symmetrical around 120°; thus the energy cost for increasing α by a given number of degrees is almost identical with that for decreasing the angle by the same amount.

Table III tabulates the bond length variations with changes in α and β for the anion and radical. In general the bond length changes are moderate and follow intuitively expected trends: For fixed β, bond lengths show little variation with α. For fixed α, bond lengths increase by approximately 5% as the third

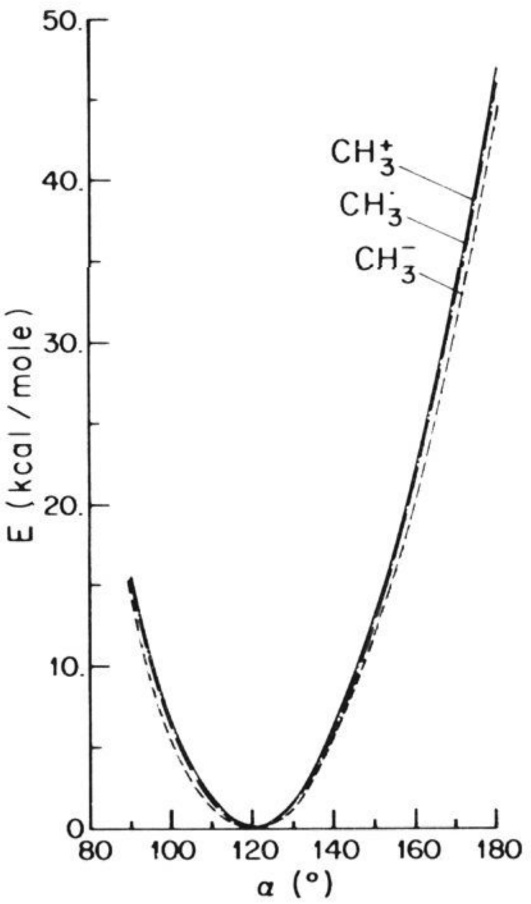


Figure 2. Total energies, E_T, vs. HCH angle, α, for planar ($\beta = 0°$) conformations of CH_3^+, $CH_3\cdot$, and CH_3^-. Minimum energy conformation of each system referenced to zero energy.

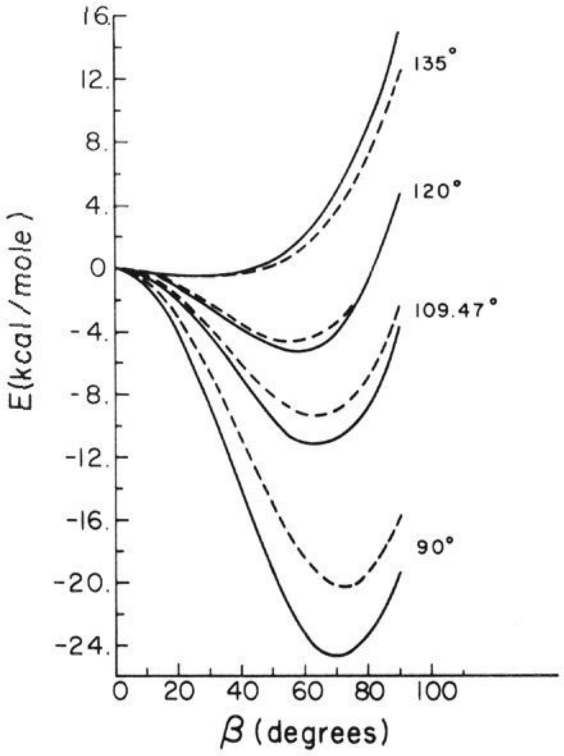


Figure 3. Energy vs. out-of-plane angle, β, for the methyl anion. E_T, referenced to zero for the planar conformation (- - -). $\Sigma\epsilon_i$, sum of the highest three one-electron energies (—). Calculations shown for four specified HCH angles, α.

hydrogen moves from in-plane to perpendicular. Bond length change is roughly twice as great in the anion as in the radical.

The most important results come from the variation of energy with angles α and β for the anion and radical. For example, the anion with $\alpha = \beta = 90°$ is only as energetically unfavorable as the one with $\alpha = 109.47°$ and $\beta = 20°$ even though the former is highly strained from a conventional point of view. The situation is completely different in the radical; here there is a strong tendency toward planarity. Only very small values of α (90°) can make it nonplanar. As α decreases for the anion, the inversion barrier increases continuously while the rate of increase of β decreases. Thus for a small change in α (at small α) the inversion barrier will still increase with little variation in optimum geometry.

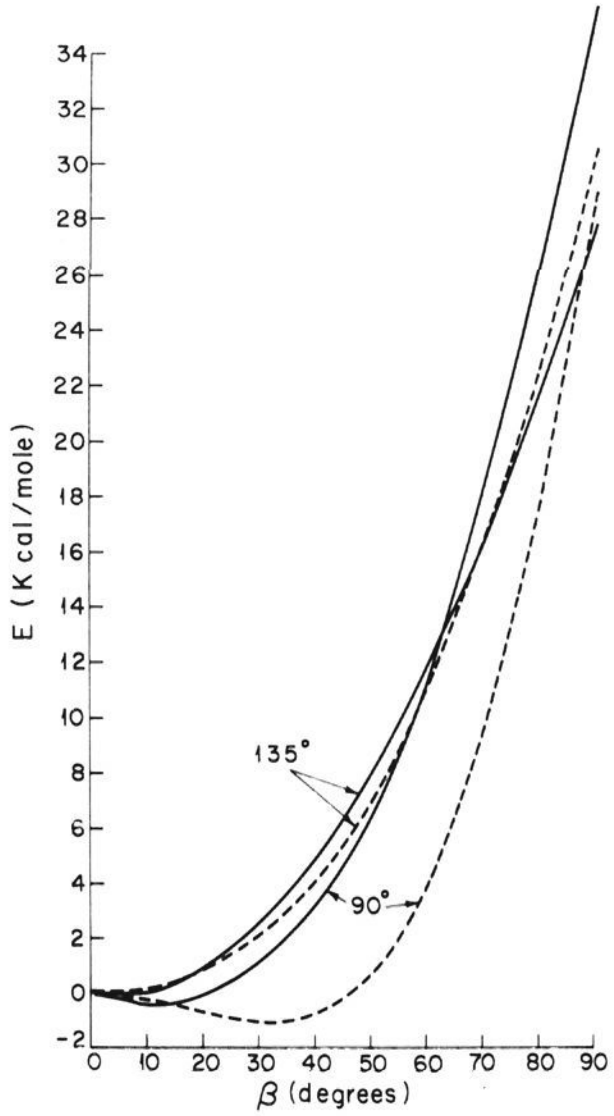


Figure 4. Energy vs. out-of-plane angle, β, for the methyl radical. E_T, referenced to zero for the planar conformation (- - -). $\Sigma\epsilon_i$, sum of the highest three one-electron energies (—). Calculations shown for the two extreme values of HCH angle, α.

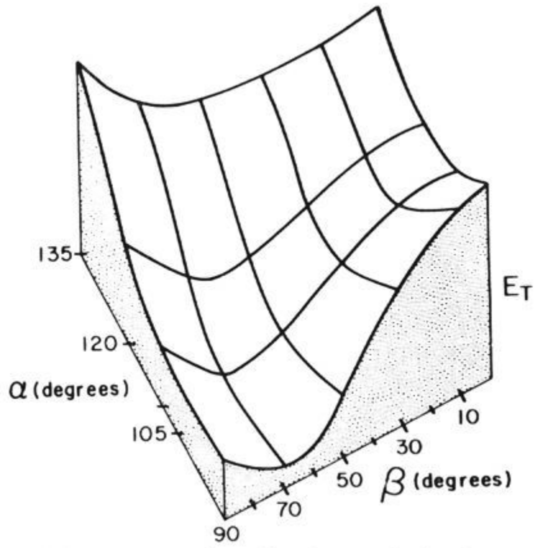


Figure 5. *Potential energy surface for the methyl anion.*

Table V. Inversion Barriers and Minimum Energy Geometry and Corresponding Total Energies

α, deg	β, deg	E_T, hartrees	a, Å	b, Å	Inversion barrier
		Anion			
90	72.0	−39.396 50	1.138	1.124	20.31
109.47	63.4	−39.400 99	1.112	1.116	9.43
120	56.6	−39.396 18	1.099	1.112	4.58
135	32.8	−39.384 16	1.081	1.102	0.40
		Radical			
90	32.4	−39.481 36	1.087	1.064	1.10

Available experimental and calculated data are consistent with the model results. High accuracy methyl anion calculations yield an inversion barrier between 0.90[10] and 2.8[11]

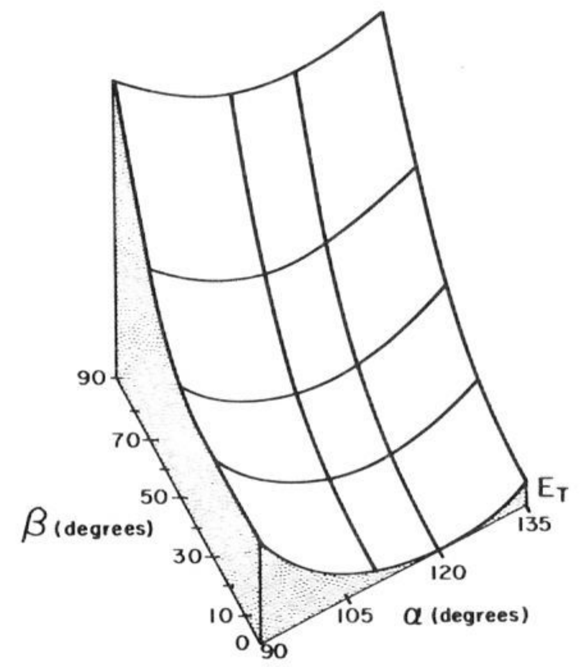


Figure 6. Potential energy surface for methyl radical.

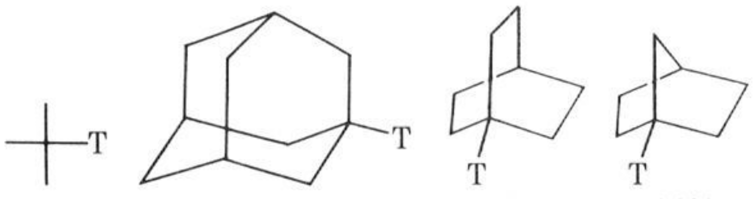
kcal/mol while experimental measurements suggest it to be slightly larger than ammonia.[12] The cyclopropyl anion is found to be nonplanar with an inversion barrier high enough to retain stereochemistry in reactions.[13] Its value is estimated to be approximately 21 kcal/mol[14]. The inversion barrier of vinyl anion has been estimated as 25–35 kcal/mol from kinetic data on the dehydrobromination of 1,2-dibromoethylenes.[15] Williams and Streitwieser[16] have calculated it to be 34 kcal/mol, close to the 39 kcal/mol obtained in previous calculations by Lehn et al.[17] (one can assume that this is the inversion barrier obtained by reducing α to 0°). Analogous results are found for aziridines.[18]

It has been pointed out that "planar" cyclopropyl possesses a pseudo-π system[19] and cyclopropyl anion has been shown to be antiaromatic just as cyclopropenyl anion is antiaromatic.[14] The 31 kcal/mol greater inversion barrier of cyclopropenyl anion relative to that of cyclopropyl anion has been attributed to a higher antiaromaticity of the former. While this is largely true, there is also a contribution from the fact that as the CCC angle decreases (standard C=C bond length assumed) the inversion barrier increases with little change in the out-of-plane CH angle.

The greatest amount of structural information is available for alkyl free radicals, particularly from the study of the ESR spectra.[20] Experiment[21] and theory[22] show the methyl radical to be planar (or very nearly so) with a shallow potential energy surface. As angle α is decreased, the radical is found to favor a bent geometry. Thus, cyclopropyl radical[23] and 7-nonbornyl radical[24] are found to be bent from ESR spectra. The bent nature of cyclopropyl radical has also been claimed in reactions leading to products which predominantly retain their configurations[25] and this is supported by the calculations on cyclopropyl[26] and vinyl[22,26,27] radicals.

The increased destabilization with increased nonplanarity shown by the potential energy surface of Figure 4 is illustrated by the rates of decomposition of the following series of compounds:[28]

T = CO-C-C-t-Bu



Rel rate 1 0.4 0.05 0.000

If one of the angles is made smaller than 120°, the radical prefers to be nonplanar. Recently the ESR spectra of bicyclo[2.1.1]hex-5-yl radical[29] has been reported. The observed hyperfine splitting constants are interpreted as a C–H bent approximately by 30° with a corresponding CCC angle of ≃90°. The increased bending of the C–H at the radical is evident from the hyperfine splitting constants for the following radicals.[30]

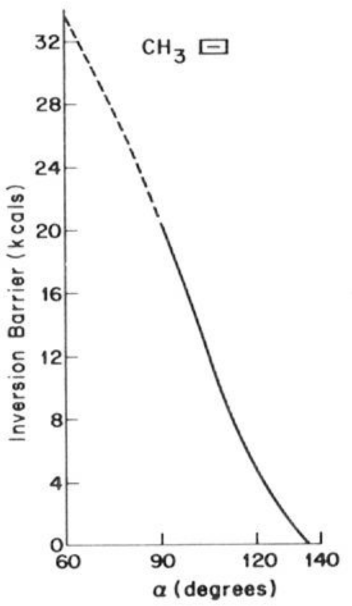


Figure 7. Inversion barrier of methyl anion vs. HCH angle, α. Dashed line indicates extrapolated values.

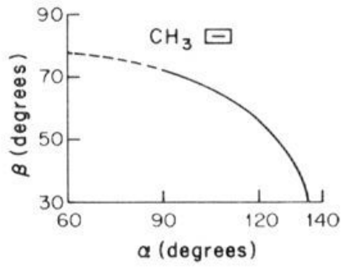
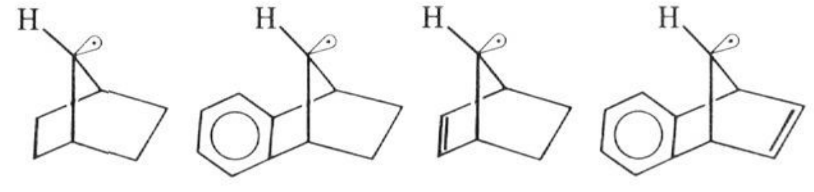


Figure 8. HCH angle, α, vs. energy optimized out-of-plane angle, β. Dashed line indicates extrapolated values.



a_H 16.78 12.70 10.87 8.27

We earlier investigated the suggestion[31] that the 7-norbornyl cation might have a nonplanar carbonium center due to angle strain ($\beta \approx 95°$).[32] When C_{2v} symmetry was imposed on the *carbon skeleton*, no deviation from planarity was found by calculation.[9,32] However, when this constraint is relaxed, the ion at the MINDO level distorts to C_s symmetry with a nonplanar cationic center.[33] Even though symmetry permits planarity, in accord with the Nyholm–Gillespie hypothesis,[34] other electronic interactions overweigh the normal geometrical preference.

Analysis

The principal orbital changes with angle which result as the geometry of the three species is varied occur in the highest three molecular orbitals and Walsh–Mulliken diagrams are constructed using only these orbital energies. For the radical and anion, these are shown with fixed β and variable α as Figure 9 and in Figure 10 with fixed α and variable β. Validation of this choice and demonstraton that the Walsh–Mulliken diagram approach can be a successful analysis technique is given in Figures 3 and 4. These figures show that energy changes with angle for E_T and the sums of the highest three one-electron energies parallel one another[35] and, in particular, produce nearly the same minima (the corresponding plot for the cation also shows a parallelism between E_T and the sum[9]). The overall pattern of levels remains the same for all three species and this

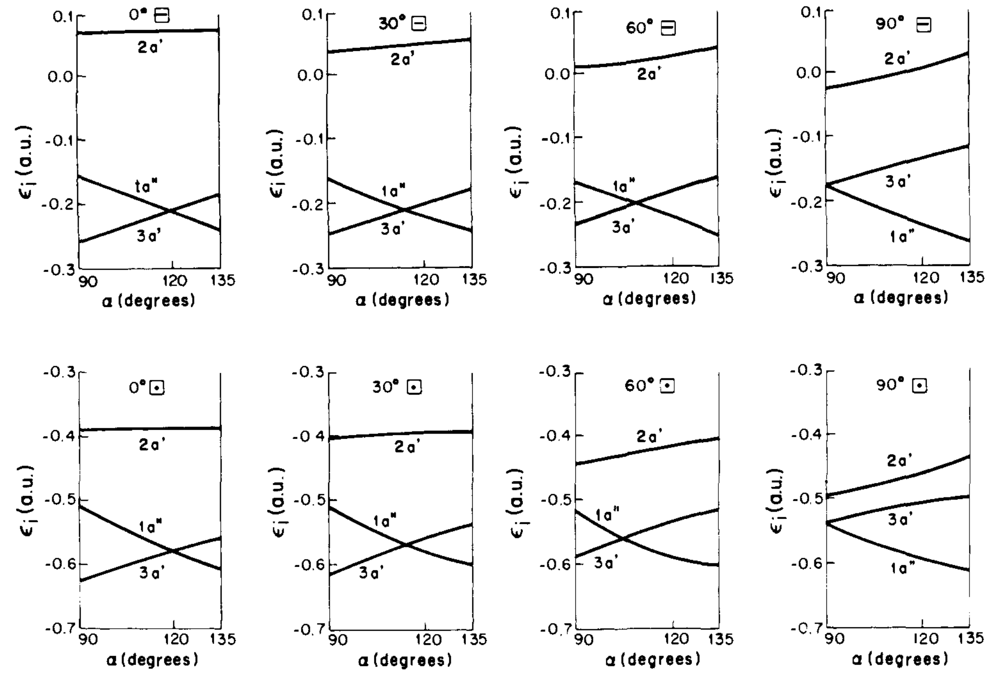


Figure 9. Walsh-Mulliken diagrams for methyl anion and radical with fixed β and variable α.

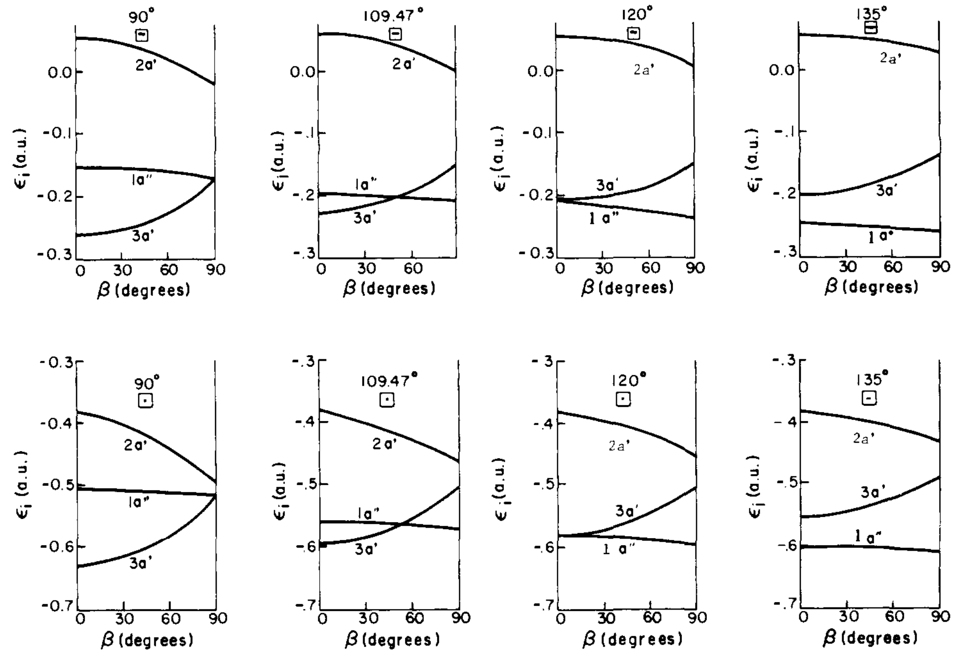
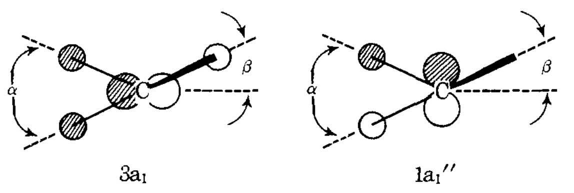


Figure 10. Walsh-Mulliken diagrams for methyl anion and radical with fixed α and variable β.

topological similarity is the second general property of Walsh-Mulliken diagrams which make them a useful method of analysis.

Consider the second and third highest orbitals in the Walsh-Mulliken diagrams of Figures 9 and 10. These two orbitals are the degenerate pair (e) for the high symmetry planar system, $\alpha = 120°$, $\beta = 0°$, but are split for all other angles. At a general point they are $3a_1$ and $1a_1''$ shown schematically below. For fixed β variable α (Figure 9), the energy changes of these orbitals will clearly be opposed leaving the highest orbital (2a'' at a general point) as the sole determinant of shape and energetics. For fixed α variable β (Figure 10), 1a'' shows little change because CH is a nodal plane. The energy of $3a_1$ on the other hand will increase (destabilization) because of the decreasing C_{2p} and H_{1s} overlap. This produces planarity when the 2a'' is unoccupied (cation) and planarity for most α when 2a'' is single occupied. The highest orbital, 2a'', is the carbon 2p perpendicular to the plane of the $3a_1$, $1a_1''$ orbital schematics when $\alpha = 120°$, $\beta = 0°$. At other angles there is s, p hybridization. For fixed α variable β (Figure 10), its energy decreases (stabilization) because there is an increase in the s admixture. For fixed β variable α (Figure 9), its energy increases as α increases (destabilization) because the s orbital is mixing less.



With two electrons in 2a'' the anion is stabilized much more than the radical by bending and hence the observed pattern of minimum values of β. As α decreases the rate of decrease of energy of 2a'' increases resulting in larger values of β. For the radical, 2a'' becomes low enough to yield a bent stable structure at $\alpha = 90°$. In the cation, this MO is vacant. The two highest occupied orbitals are then the $3a_1$ and $1a_1''$. Since the carbon AO's in both of these MO's are in the plane, the cation is planar ($\beta = 0°$) for all α. Walsh-Mulliken diagrams for CH_3^+ have not been given since they are adequately represented by the $3a'$ and $1a_1''$ curves of either CH_3^- or $CH_3\cdot$ in Figures 9 and 10.

In addition to the energy vs. angle discussion above, the origin of the relatively larger change in bond length with β compared to the change with α is readily apparent from the Walsh-Mulliken diagrams. The average of ϵ vs. α in Figure 9 is flatter than the average of ϵ vs. β in Figure 10.

Decomposition of the total energy into components V_{nn}, V_{ee}, V_{ne}, and T sometimes has been found to be a helpful technique. Investigation of energy components as a function of angles α and β showed that those for the anion change by greater amounts than those of the radical and that V_{nn} dominates the behavior of cations. But the Walsh-Mulliken diagrams themselves appear to offer the simplest unified picture for all three species. Noqualitatively different or additional information is obtainable from the energy components and therefore further discussion of them is not included.

Summary

Potential energy surfaces for the methyl species were constructed and the relative energy differences were used to systematize the experimental and theoretical data available on large structural fragments having similar angular strain. Thus, the inversion barrier of cyclopropyl radical and anion as well as the vinyl radical and anion fall in the expected range and it is predicted that a classical nonplanar secondary carbonium ion will never be observed. The rate of decomposition of polycyclic peresters depends on the relative stability of the tertiary radical that is produced and experimental values follow the potential energy surface of the model.

The observation that radicals prefer bent structure if one of the bond angles is restricted to a small value may be inferred from the changes of hyperfine splitting constants of several 7-norbornyl radicals in which the bridge CCC angle is decreased continuously.

The shape of the curve for variation of the HCH angle α vs. the out-of-plane angle β of the third hydrogen was calculated for the anion and it was found that for small values of α, β tends to be a constant. Thus the nonplanarity at the carbonium center on cyclopropyl and cyclobutyl anions is not expected to differ greatly.

A contribution from angle bending to the increased inversion barrier of cyclopropenyl anion compared to the cyclopropyl anion was shown in addition to the already established increased antiaromaticity of the former.

Insofar as the model is correct, any two trivalent alkyl species can be compared as their relative stabilities by knowing bond angles and vice versa. Thus some highly strained intermediates in a conventional sense will not be as unstable as their "moderately strained" companions, e.g., $\alpha = \beta = 90°$ vs. $\alpha = 109°$, $\beta = 20°$ for the anion. Another interesting point that may be kept in mind when analyzing new experiments is shown in Figure 2. The energy increase on bond angle bending for a planar system is much the same for cation, radical, and anion and a displacement which increases α has almost exactly the same energy cost as one which decreases it.

Acknowledgment. This work was supported by National Science Foundation Grant GP-25167 and by the Molecular Biology Section of the NSF, Grant BMS 73-06999. Part of the computer calculations were carried out at the University of Munich during the tenure of a fellowship awarded by the von Humboldt Foundation (to P.v.R.S.). We thank the Leibniz Rechenzentrum for technical assistance and for computer time.

References and Notes

(1) (a) Universität Erlangen-Nürnberg, Institut fur Organische Chemie, D-8520 Erlangen, West Germany. (b) An earlier, somewhat more limited study, using a minimal basis of Hartree–Fock AO's [J. L. Whitten, *J. Chem. Phys.*, **44**, 309 (1966)] is contained in the Ph.D. thesis of V. Buss, Princeton University, 1970.
(2) T. Koenig, T. Balle, and W. Snell, *J. Am. Chem. Soc.*, **97**, 662 (1975), and references cited therein.
(3) R. C. Fort and P. v. R. Schleyer, *Adv. Alicyclic Chem.*, **1**, 283 (1966); R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189 (1971); R. C. Fort in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., (Wiley, New York, N.Y:, 1973, Chapter 32, p 1783 ff.
(4) (a) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301 (1953); *Prog. Stereochem.*, **1**, 1 (1954); (b) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942); *J. Am. Chem. Soc.*, **77**, 887 (1955); (c) L. C. Allen, *Theor. Chim. Acta*, **24**, 117 (1972); R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).
(5) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., No. 236. The parameters for the 4-31G basis set are given in R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(6) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954). This procedure is a built-in feature of GAUSSIAN 70 and both solutions yield the same energy dependence on angle and were averaged in constructing the Walsh–Mulliken diagrams.
(7) F. Driessler, R. Ahlrichs, W. Staemmler and W. Kutzelnigg, *Theor. Chim. Acta*, **30**, 315 (1973), and references cited therein.
(8) The theorem of T. Kato, *J. Phys. Soc. Jpn.*, **14**, 382 (1959); *Commun. Pure Appl. Math.*, **12**, 403 (1959), proves that the positive ϵ values frequently observed for anions result from basis set inadequacies but the dependence of ϵ's on angle for methyl anion is qualitatively the same for basis sets showing positive ϵ values[19,22] as those with negative ϵ's.[7]
(9) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, **7**, 253 (1972).
(10) R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1235 (1975). These wave functions include extensive correlation and are the best reported to date. A. J. Duke, *Chem. Phys. Lett.*, **21**, 275 (1973), obtained a lower CH_3^- energy at the SCF level with a barrier of 1.7 kcal/mol.
(11) R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **56**, 4337 (1972).
(12) L. Andrews, *J. Chem Phys.*, **47**, 4834 (1967).
(13) J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968).
(14) D. T. Clark and D. R. Armstrong, *Chem. Commun.*, 850 (1969).
(15) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).
(16) J. E. Williams, Jr., and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).
(17) J. M. Lehn, B. Munsch, and P. Millie, *Theor. Chim. Acta*, **18**, 143 (1970).
(18) A. Rank, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).
(19) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969).
(20) R. O. C. Norman, *Chem. Br.*, **66**, (1970).
(21) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967); G. Herzberg, *Proc. R. Soc. London, Ser. A*, **262**, 294 (1961); T. Koenig, T. Balle, and W. Snell, *J. Am. Chem. Soc.*, **97**, 662 (1975).
(22) R. E. Kari and I. G. Csizmadia, *Int. J. Quantum Chem.*, **6**, 401 (1972); P. Millé and G. Berthier, *Int. J. Quantum Chem.*, **2**, 67 (1968).
(23) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3940 (1969).
(24) P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Am. Chem. Soc.*, **92**, 1434 (1970).
(25) (a) J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969); (b) M. J. S. Dewar and I. M. Harris, *J. Am. Chem. Soc.*, **91**, 3652 (1969).
(26) M. J. S. Dewar and M. Shanshal, *J. Am. Chem. Soc.*, **91**, 3654 (1969).
(27) K. Morokuma, L. Pedersen, and M. Karplus, *J. Chem. Phys.*, **48**, 4801 (1968).
(28) (a) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Am. Chem. Soc.*, **90**, 5266 (1968); (b) R. C. Fort and R. E. Franklin, *ibid.*, **90**, 5267 (1968).
(29) M. Matsunaga and T. Kawamura, *J. Am. Chem. Soc.*, **97**, 3519 (1975).
(30) R. Kawamura, Y. Sugiyama, M. Matsunaga, and R. Yonezawa, *J. Am. Chem. Soc.*, **97**; 162 (1975).
(31) P. G, Gassman, J. M. Hornback, and J. L. Marshall, *J. Am. Chem. Soc.*, **90**, 1265 (1968); F. B. Miles *ibid.*, **90**, 1265 (1968).
(32) (a) J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 1037 (1969); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).
(33) MINDO/2: M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971); MINDO/3: W. L. Jorgensen, private communication. Also see R. Hoffman, P. D. Mollière, and E. Heilbronner, *J. Am. Chem. Soc.*, **95**, 4860 (1973).
(34) R. J. Gillespie, *Angew. Chem.*, **79**, 885 (1967).
(35) Qualitatively the same curves are obtained if the core orbitals are included in $\Sigma\epsilon_i$, however, as discussed in S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966), it is conceptually and numerically more satisfactory to include the core sum with the Coulomb and exchange terms in partitioning the total energy.