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Electronic States of Organic Molecules. I. Potential Functions for the Deformation of Methane[1,2]

Kenneth B. Wiberg,* G. Barney Ellison, and John J. Wendoloski

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received May 27, 1975*

Abstract: The energy changes for four angle deformation modes of methane have been calculated using three different basis sets. A double-ζ basis set reproduced experimental results satisfactorily and gave values which agreed well with those for a larger basis set and large angular deformations. The deformation modes are related to those which are involved in the formation of several types of small ring compounds.

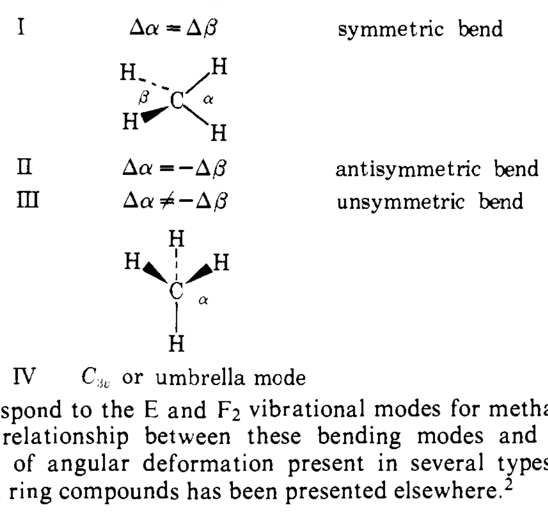
Saturated compounds which possess distorted bond angles have been of particular interest to organic chemists over the past decade. Despite the many studies which have been carried out, relatively little is known about the potential functions for bond angle bending.[3] Most of the calculations which have been carried out have concentrated on small angular deformations which are of interest in connection with studies of molecular vibrations.[4] A few calculations, however, have been carried out for the planar methane configuration.[5]

We have carried out a series of calculations on the potential functions for the deformation of methane.[2] Methane was chosen since it is a prototype for the effects which can be studied, and it is small enough to permit a detailed study of the potential surface. Most of the calculations were carried out at the minimal STO-3G[6] or double-ζ 4-31G level,[7] and a few selected points were studied using a double-ζ plus polarization (DZP) basis set.[8]

Before considering the angular deformation modes, we present a comparison of the equilibrium geometry and symmetric stretching force constants derived from the basis sets used herein with the results obtained using other basis sets (Table I). It can be seen that all basis sets give essentially the same equilibrium geometry, which is in good agreement with the experimentally determined value.[11] The STO-3G basis set gives a relatively high stretching force constant, whereas the 4-31G set gives a value close to the experimental result. The extensive summary of Meyer and Pulay[4] suggests that the 4-31G basis set should be adequate for the calculation of the relative energies of all but possibly the more highly deformed methane configurations. Although the calculated energies are still considerably higher than the Hartree–Fock limit, the relative energies do not appear to change significantly when larger basis sets are used.

Knowing that at least the 4-31G basis set gives reasonable deformation energies, we have examined the modes in Chart I. The symmetric and antisymmetric bending modes correspond to the E and F_2 vibrational modes for methane. The relationship between these bending modes and the types of angular deformation present in several types of small ring compounds has been presented elsewhere.[2]

Chart I



I $\Delta\alpha = \Delta\beta$ symmetric bend

II $\Delta\alpha = -\Delta\beta$ antisymmetric bend

III $\Delta\alpha \neq -\Delta\beta$ unsymmetric bend

IV C_{3v} or umbrella mode

Table I. Equilibrium Geometry, Energy, and Symmetric Stretching Force Constants for Methane

Basis set	r_e, Å calcd	Total energy at r_e, au	Total energy at r = 1.0936 Å	k_{str},[a] mdyn/Å	Ref
STO-3G	1.083[b]	−39.726863	−39.726489	7.37	
4-31G	1.081	−40.139766	−40.139343	5.98	
DZP			−40.190551		
6-31G*	1.084	−40.19517			9
Best MO	1.083	−40.21398		5.58	4
HF limit		−40.22			10
Exptl		−40.50		5.84	11

[a] Based on a 0.01 Å displacement from the equilibrium value. [b] The experimental harmonic r_e = 1.084 Å, whereas the experimental anharmonic r_e = 1.0936 Å.[4]

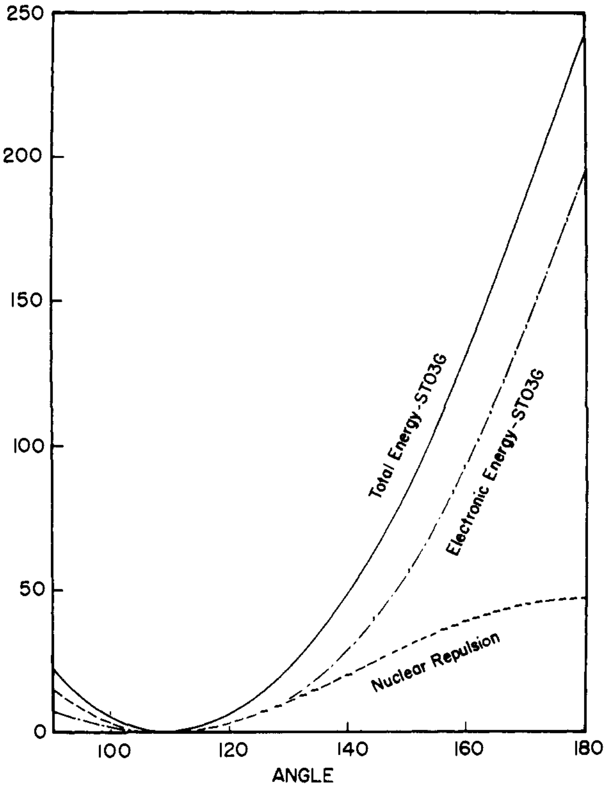


Figure 1. Effect of angle bending on the energy of methane for the symmetric mode. The electronic energies were calculated using the STO-3G basis set.

The symmetric bend, I, is the simplest to examine since the four bond lengths would be expected to remain equal. Thus, for any given angle, the energy need only be minimized with respect to the bond length. The results of calculations at the STO-3G, 4-31G, and DZP levels are shown in Table II, and the values of the nuclear repulsion, electronic energy, and total energy for r = 1.0936 Å (the observed bond length) are shown in Figure 1 for STO-3G and Figure 2 for DZP. The results for the 4-31G basis set are close to those for DZP. The force constant for small angular displacements is calculated to be 0.84 mdyn/Å (STO-3G) or 0.67 mdyn/Å (4-31G). The observed value,[11] 0.56 mdyn/Å, is in reasonable agreement with the 4-31G result. One may also note that the calculated equilibrium bond lengths and stretching force constants are essentially independent of angle from α = 90 to 130°.

The total energy of a molecule may be given by $V = T + V_1 + V_{12} + V_N$ where T is the kinetic energy, V_1 is the potential energy of the electrons in the field of the nuclei, V_{12} is the electron-electron repulsion, and V_N is the nuclear repulsion. For values of α between 90 and 130°, the sum of the electronic terms ($T + V_1 + V_{12}$) is essentially constant (Figure 3), and the nuclear repulsion is the major component of the change in the total energy.

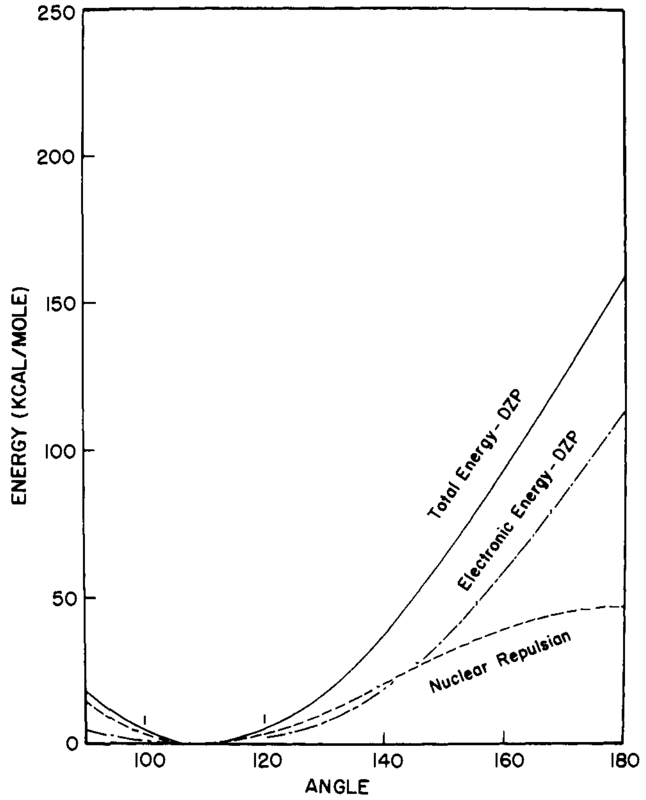


Figure 2. Effect of angle bending on the energy of methane for the symmetric mode. The electronic energies were calculated using a double ζ plus polarization (d orbitals on carbon and p orbitals on hydrogen) basis set.

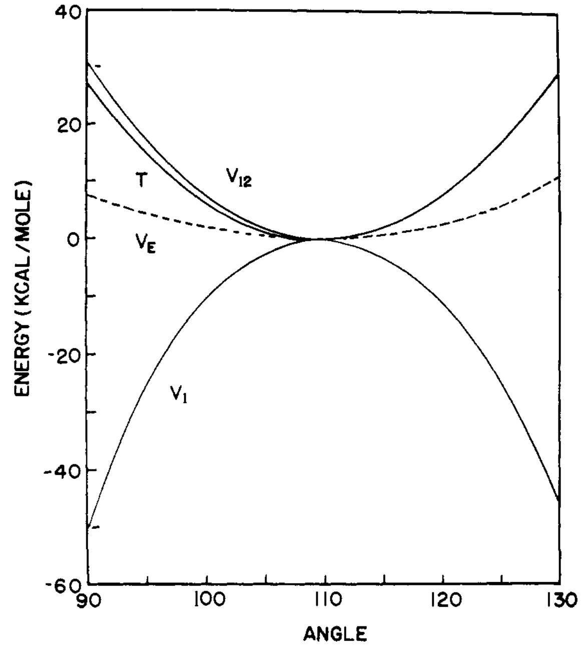


Figure 3. Components of the electronic energy for the symmetric bending mode. V_1 is the potential energy of the electrons in the field of the nuclei, T is the kinetic energy of the electrons, and V_{12} is the electron–electron repulsion. $V_E = T + V_1 + V_{12}$.

As methane is distorted moving the hydrogens nearer each other, the potential energy of the electrons decreases

Table II. Change in Energy with Angle for the Symmetric Bending Mode

	STO-3G				4-31G				DZP
Angle	Rel energy at r = 1.0936 Å, kcal/mol	r_e, Å	Rel energy at r_e, kcal/mol	k_{str}, mdyn/Å	Rel energy at r = 1.0936 Å, kcal/mol	r_e, Å	Rel energy at r_e, kcal/mol	k_{str}, mdyn/Å	Rel energy at r = 1.0936 Å, kcal/mol
90	21.95	1.086	22.06	7.25	17.49	1.084	17.35	5.84	16.92
95	11.94	1.085	12.00	7.37					
100	5.05	1.084	5.07	7.38	4.06	1.082	3.83	5.95	
105	1.12	1.083	1.12	7.38					
109.47	0.00[a]	1.083	0.00[b]	7 37	0.00[c]	1.081	0.00[d]	5.98	0.00[e]
115	1.67[f]	1.083	1.67	7.38					
120	6.12	1.084	6.03	7.38	4.83[g]	1.082	4.60	5.94	
130	22.50	1.086	22.62	7.35					
140	49.38	1.090	49.53	7.31	39.05	1.089	39.02	5.66	37.68
160	132.83	1.103	133.00	6.37	101.85	1.100	101.80	5.17	
180	240.60	1.071	240.00	6.48	168.30	1.081	168.03	5.60	159.92

[a] The calculated total energy was −39.726 489. [b] The calculated total energy was −39.726 863. [c] The calculated total energy was −40.139 343. [d] The calculated total energy was −40.139 766. [e] The calculated total energy was −40.190 551. [f] The bending force constant derived from these values is 0.84 mdyn/Å. [g] The bending force constant derived from these values is 0.67 mdyn/Å.

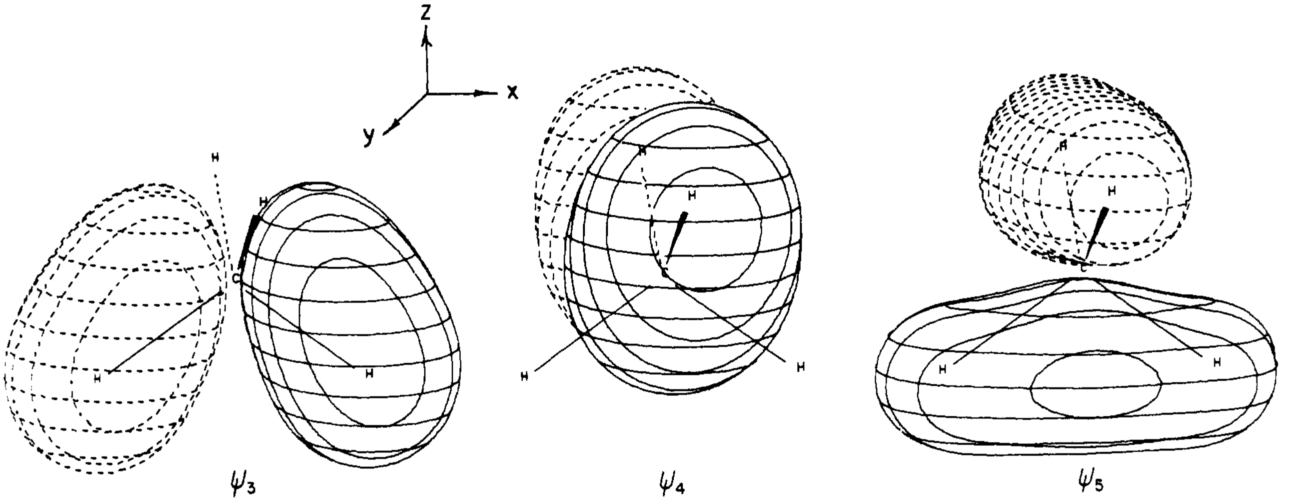


Figure 4. Highest occupied molecular orbitals for tetrahedral methane. In ψ_3 two hydrogens AO's mix with the carbon $2p_x$ orbital, in ψ_4 the AO's of the other two hydrogens mix with the carbon $2p_y$ orbital, and in ψ_5, all four hydrogen AO's mix with the carbon $2p_z$ orbital.

since the electrons see a greater effective internuclear field. As required by the virial theorem, the change in the kinetic energy of the electron is $-\frac{1}{2}$ the change in potential energy. At the same time, the distortion brings the electrons closer together on the average leading to an increase in V_{12}. In the present case, the changes in T and V_{12} are approximately equal (Figure 3), leading to an essentially constant sum for the electronic terms as the angles are deformed.[12] Under these conditions, the nuclear repulsion term dominates and determines the geometry.

However, as α increases from 130 to 180°, the electronic energy begins to increase rapidly. The increase in electronic energy is easily understood if one examines the bonding molecular orbitals. The lowest energy MO (−300 eV) involves essentially only the carbon 1s orbital. The second (−25 eV) utilizes the carbon 2s orbital and the hydrogen 1s orbitals. Since the s function is nondirectional, this MO is relatively unaffected by bond angle deformation. The remaining three bonding MO's are degenerate in methane and utilize the carbon 2p orbitals and the hydrogen 1s orbitals (Figure 4).[13]

When α is increased, the hydrogens move in the direction of the xy plane leading to poorer overlap of the four hydrogens with the p_z orbital in ψ_5 and an increase in energy for this MO. At the same time, this leads to a better overlap of a pair of hydrogens with the p_x and p_y orbitals in ψ_3 and ψ_4, respectively, and a decrease in energy for these MO's. A decrease in α from the tetrahedral value leads to the opposite changes in energy. Since the changes in energy for ψ_5 and for ψ_3 and ψ_4 are in opposite directions, the net change in energy is relatively small.

When α is increased over 130°, the energy of ψ_3 and ψ_4 decreases only slightly since little more can be done to improve the overlap between the corresponding carbon 2p and the hydrogen orbitals. However, the energy of ψ_5 increases rapidly and when α = 180°, ψ_5 represents a nonbonding MO (Figure 5). The calculated relative energy for α = 180° using the STO-3G basis set is quite high (240 kcal/mol). The use of the more flexible 4-31G basis set led to a marked reduction in relative energy to 168 kcal/mol.

An interesting feature of both calculations is the change in calculated equilibrium bond length and force constant with angle. For α between 120 and 160°, the bond length increases significantly, and the force constant decreases. This is expected since the bonding between the carbon and the hydrogens becomes poorer as the angle increases. However, when α = 180°, the calculated equilibrium bond length decreases, and the force constant increases. For this angle, ψ_5 is nonbonding as indicated above and will have two electrons. This leads to a relatively large charge transfer from hydrogen to carbon between 160 and 180°.[14] The resultant large increase in Coulombic attraction appears to

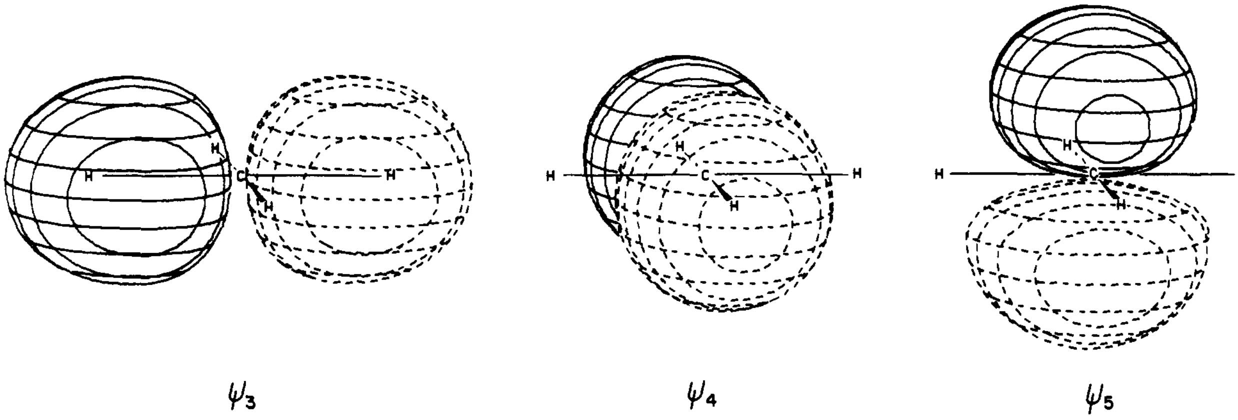
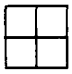


Figure 5. Highest occupied molecular orbitals for planar methane. The MO's correspond to those in Figure 4.

be responsible for the change in bond length and force constant.

The energy of ψ_5 might be improved by providing a mechanism for C–H bonding. The C–H bonding could be provided using either a $d_{x^2-y^2}$ orbital at carbon which has the appropriate symmetry for bonding with the hydrogens or $2p_z$ orbitals at the hydrogens which may bond with the carbon $2p_z$ orbital. The use of the DZP basis set did lead to a small further decrease in the relative energy of planar methane. There was no significant contribution from the 3d orbital, and the main contribution arose from the hydrogen $2p_z$ orbital.[15]

Although the relative energy of planar methane is sufficiently high to make it impractical to reach this geometry, distortions with α up to 140° have experimentally accessible energies. If the results may reasonably be extrapolated to compounds having carbon–carbon bonds, compounds such as 1 may be reasonable synthetic goals.[16]



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The results for the antisymmetric bending mode are given in Table III. Here, there are three structural variables, α, r_1 for the C–H bonds forming the angle α, and r_2 for the C–H bonds forming the angle β. The change in β must be equal and opposite to the change in α. The equilibrium values of r_1 and r_2 were determined using the STO-3G basis set. It may be noted that the relative energies at a fixed C–H bond length of 1.0936 Å are essentially the same as those obtained using the equilibrium bond lengths. Similarly, the calculated dipole moments were similar.

Let us first examine the results obtained with r_{CH} = 1.0936 Å. The bending force constant is calculated to be 0.82 mdyn/Å using the STO-3G basis set and 0.67 mdyn/Å using the 4-31G basis set. The experimental value is 0.51. The derivative of the dipole moment with respect to the internal coordinate is calculated to be 0.330 (STO-3G) or 0.460 (4-31G), and the experimental value is 0.339.[11] The double-ζ basis set gives the better agreement with the experimental force constants, and the calculated dipole moment derivatives bracket the observed value.

The equilibrium bond lengths change in the expected direction with bond angle deformation. An increase in angle leads to a larger carbon 2s contribution to the C–H bond and a shorter bond length. Correspondingly, a decrease in angle leads to an increase in bond length.

Although the antisymmetric bending mode is of interest with regard to the vibrational spectrum of methane, it has little bearing on the equilibrium geometry of compounds having bond angle distortion. Thus, we have examined the unsymmetric bending mode. The results are summarized in Table IV. Here, for any value of α, one must minimize the energy with respect to β, r_1, and r_2. The equilibrium values are given in the table.

Let us first examine the case where α = 90°. Again, since the carbon 2s orbital is nondirectional, the MO involving it and the four hydrogens is not strongly affected by changes in angles. One might expect the energies of the MO's which utilize the carbon 2p orbitals to be minimized if one hydrogen were placed at each of the p_x and p_y orbitals and two at the p_z orbital. This predicts that when α = 90°, the minimum electronic energy will be found when β = 180°. This is the case.[2] However, the nuclear repulsion is at a maximum when β = 180°, and the increase in nuclear repulsion is much greater than the decrease in electronic energy. The nuclear repulsion is at a minimum when β = 106°, and the total energy is at a minimum at 114°. In all cases, the equilibrium geometry is determined largely by nuclear repulsion and not by the electronic energy.

The change in equilibrium bond lengths with changing angles occurs in the expected direction, with the smaller angles giving the larger p character and the longer bonds. Again, the relative energies are the same for a fixed C–H bond length and for the equilibrium bond lengths. The 4-31G basis set leads to smaller deformation energies than the STO-3G set, as was found for the other deformation modes.

The results for α = 90° are in good accord with experimental observations on cyclobutane. Here, the H–C–H angle is found to be 111 ± 1°, the C–H bond length is 1.090 Å, and the C–C bond length is 1.548 Å.[17] Thus, the C–H bond length is shorter than normal (1.094 Å), and the C–C bond is longer than normal (1.540 Å). The distortion energy for one carbon is found to be 7.1 kcal/mol.

In deriving a strain energy for planar cyclobutane from this value, one might be tempted to multiply it by four, giving a value close to the observed strain energy for cyclobutane. However, if one considers the deformation energy to result largely from nuclear repulsion, then there are only two 1–3 repulsions in cyclobutane leading to a deformation energy of 2 × 7.1 = 14 kcal/ml.[18] To this must be added the torsional strain resulting from the eclipsed methylene groups (~12 kcal/mol or 4 × the torsional strain in ethane) giving a total strain of 26 kcal/mol, which is close to the experimental value.[19]

It may be noted that the distortion energy for the unsymmetric bending mode is less than half that for the symmetric bending mode. Thus, when two angles at a carbon are constrained, as in the spiroalkanes, one would expect the distortion energy at the central carbon to be more than twice that in the corresponding cycloalkane. Unfortunately,

Table III. Change in Energy with Angle for the Antisymmetric Bending Mode

Angle		STO-3G								4-31G	
		Rel energy at r = 1.0936 Å, kcal/mol	μ at r = 1.0936 Å	Equil. bond lengths		Rel energy at r_e, kcal/mol	Force constants, mdyn/Å		μ at r_e	Rel energy at r = 1.0936 Å, kcal/mol	μ at 1.0936 Å
α	β			r_1	r_2		f_1	f_2			
109.4712	109.4712	0.00	0.00	1.083	1.083	0.00	(7.37)[c]		0.00	0.00	0.00
104.4712	114.4712	0.89	0.0318	1.085	1.082	0.89	7.55	7.53	0.0344	0.73	0.0616
99.4712	119.4712	3.56	0.0662	1.087	1.080	3.56	7.56	7.51	0.0710	2.92	0.1250
94.4712	124.4712	8.05[a]	0.1058	1.089	1.079	8.03	7.21	7.49	0.1122	6.58	0.1917

[a] The bending force constant derived from these values is 0.82 mdyn/Å. [b] The bending force constant derived from these values is 0.67 mdyn/Å. [c] This is the force constant for the symmetric stretching mode. It differs from the following values because of the interaction between the stretching of pairs of CH bonds.

Table IV. Change in Energy with Angle for the Unsymmetric Bending Mode

Angle		STO-3G								4-31G	
		Rel energy at r = 1.0936 Å, kcal/mol	μ at r = 1.0936 Å	Equil. bond lengths		Rel energy at r_e, kcal/mol	Force constants, mdyn/Å		μ at r_e	Rel energy at r = 1.0936 Å, kcal/mol	μ at 1.0936 Å
α	β			r_1	r_2		f_1	f_2			
90	113.74	8.91	0.1157	1.089	1.080	8.91	7.42	7.65	0.1204	7.11	0.1655
95	112.64	4.81	0.0760	1.087	1.080	4.81	7.45	7.62	0.0800	3.87	0.1185
100	111.54	2.00	0.0442	1.085	1.081	2.02	7.50	7.62	0.0470	1.63	0.0748
105	110.46	0.44	0.0187	1.084	1.082	0.44	7.52	7.58	0.0201	0.36	0.0343
109.47	109.47	0.00	0.0000	1.083	1.083	0.00	(7.37)[a]		0.0000	0.00	0.0000
115	108.27	0.65	0.0192	1.082	1.084	0.65	7.55	7.54	0.0209	0.53	0.0404
120	107.15	2.30	0.0346	1.082	1.085	2.31	7.61	7.46	0.0378	1.89	0.0765
125	106.02	4.92	0.0494	1.081	1.086	4.94	7.66	7.38	0.0539	4.04	0.1133
130	104.90	8.47	0.0648	1.081	1.087	8.49	7.70	7.30	0.0705	6.96	0.1525

[a] Force constant for symmetric stretching mode. As a result of the interaction between C–H stretches, the apparent force constants when the hydrogens are taken as pairs are different.

Table V. Change in Energy with Angle for the C_{3v} Bending Mode

	STO-3G							4-31G						
	Rel energy r = 1.0936 Å, kcal/mol	Equil. bond lengths		Rel energy at r_e, kcal/mol	Force constants, mdyn/Å			Rel energy r = 1.0936 Å, kcal/mol	Equil. bond lengths		Rel energy at r_e, kcal/mol	Force constants, mdyn/Å		
Angle		r_1	r_2		f_1	f_2	μ, D		r_1	r_2		f_1	f_2	μ, D
90	35.70	1.114	1.080	35.45	6.40	7.42	0.472	29.07	1.133	1.077	28.50	4.43	5.93	0.664
95	20.40	1.103	1.080	20.31	6.82	7.44	0.287							
100	9.02	1.094	1.081	8.99	7.14	7.46	0.153	7.39	1.101	1.077	7.31	5.17	6.01	0.247
105	2.07	1.087	1.082	2.07	7.41	7.46	0.060							
109.47	0.00	1.083	1.083	0.00	(7.37)[a]		0.000	0.00	1.081	1.081	0.00	(5.98)[a]		0.000
115	3.38	1.079	1.085	3.38	7.77	7.41	0.060							
120	12.72	1.075	1.087	12.71	7.91	7.33	0.117	10.40	1.067	1.087	10.32	6.46	5.73	0.178
125	28.84	1.072	1.091	28.80	8.03	7.23	0.188							
130	52.88	1.069	1.096	52.75	8.17	7.09	0.284	42.77	1.058	1.105	42.27	6.89	5.35	0.341

[a] Force constant for symmetric stretching mode. As a result of the interaction between C–H stretches, the apparent force constants when the hydrogens are taken as groups of 1 and 3 are slightly different.

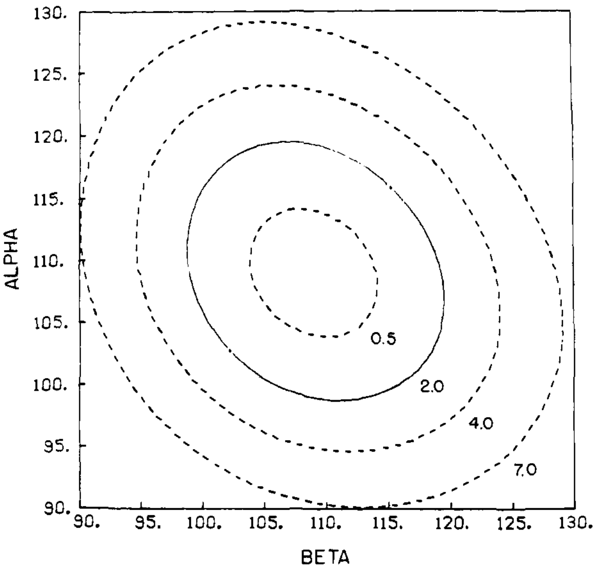


Figure 6. Relative energy contours for bending deformations of methane which preserve C_{2v} symmetry. The energies are in kcal/mol. The solid line at 2.0 kcal/mol corresponds to the zero-point energy of the bending vibrations of methane.

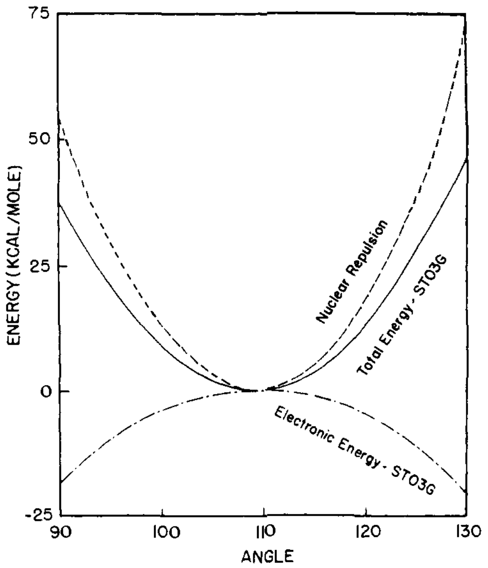


Figure 7. Effect of angle bending on the energy of methane for the C_{3v} or umbrella mode. The curves are for the STO-3G basis set. The results for the 4-31G set have the same shape, but somewhat lower total energy and electronic energy.

the strain energy of [3.3]spiroheptane is not known, so it cannot be compared with cyclobutane. However, [2.2]spiropentane is known to have 8 kcal/mol greater strain energy than two cyclopropanes.[19] It can be seen that the results are in reasonable accord with experimental data.

All of the relative energy data for the C_{2v} deformation modes of methane for $r_{CH} = 1.0936$ Å may be summarized by the expression

$$\begin{aligned}\bar{V} = -0.5446 \times 10^{-4}(\Delta\alpha^3 + \Delta\beta^3) + 0.1172 \\ \times 10^{-4}(\Delta\alpha\Delta\beta^2 + \Delta\beta\Delta\alpha^2) + 0.1843 \\ \times 10^{-1}(\Delta\alpha^2 + \Delta\beta^2) + 0.7612 \times 10^{-2}(\Delta\alpha\Delta\beta)\end{aligned}$$

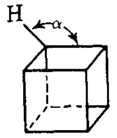
The root mean square error in fitting 20 sets of data was 0.004 kcal/mol. A contour diagram showing the change in energy with angle is shown as Figure 6. The solid line is drawn at 2 kcal/mol which corresponds approximately to the zero-point energy for a bending mode.

The remaining deformation mode which preserves some symmetry is the C_{3v} or umbrella mode (IV). In this case, the geometry may be specified using a single angle, α, and two bond lengths, r_1 and r_2. The results of calculations of the equilibrium geometry and the distortion energy are given in Table V. The change in the electronic energy and nuclear repulsion with angle is shown in Figure 7.

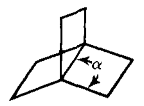
The electronic energy for this deformation mode is a maximum at the tetrahedral geometry and surprisingly decreases when α goes toward either 90 or 130°. Again, there is a delicate balance between the stabilizing term V_1 and the destabilizing terms T and V_{12}. In this case, V_1 predominates. The nuclear repulsion is at a minimum at the tetrahedral geometry and determines the geometry.

The changes in bond lengths are in accord with expectations based on hybridization arguments. The unique bond, r_2, gains s character as α approaches 90°, and as a result its length decreases. Correspondingly, the increased p character in the other three bonds leads to an increase in the bond length. There is a surprisingly large difference in the equilibrium bond lengths calculated using the STO-3G and 4-31G basis sets. Presumably, the latter are more reliable, although there are no experimental data with which they may be compared. The calculated stretching force constants also change as would be expected on the basis of the change in s character.

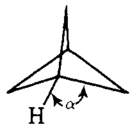
Let us examine some compounds which are formed via a C_{3v} distortion: cubane (**2**), [2.2.2]propellane (**3**), and bicyclo[1.1.1]pentane (**4**):



2



3



4

In cubane, $\alpha = 125.3°$, and in accord with the observation that the distortion energy is mainly a repulsive term, it can be seen that there are 12 cross-ring repulsions. The calculated distortion energy includes three of them, and so the angle distortion part should be on the order of four times the distortion energy for methane (25.0) or 100 kcal/mol. In addition, there are three internal cross-ring repulsions and twelve C–C bonds with eclipsed conformations. The inclusion of these terms will bring the estimated energy close to the observed value of 157 kcal/mol.[20]

In the [2.2.2]propellane, $\alpha = 90°$ at each of the bridgehead positions giving a deformation energy of 2 × 35.7 or 71 kcal/mol. This includes all of the cross-ring repulsion terms. To this must be added the torsional strain for the three eclipsed CH_2–CH_2 bonds, or about 9 kcal/mol, giving a total of 80 kcal/mol. This appears reasonable in view of the observed strain energy of the [3.2.1]propellane.[21]

Finally, in bicyclo[1.1.1]pentane, $\alpha = 126.7°$ at the bridgehead,[22] giving a calculated deformation energy of 29 kcal/mol. This accounts for all of the interaction between the three nonbridgehead atoms. There must be added the interaction between the bridgehead atoms, which can be approximated by one C_{2v} distortion with $\alpha = 73.3°$ (the C–C–C angle at the methylene group[22]) or about 25 kcal/mol giving as the sum 54 kcal/mol. There are no important torsional interactions, but the H–H nonbonded interactions at the methylene groups will probably raise the value somewhat. The estimate seems reasonable, although the experimental value is not as yet known.[23]

In summary, the 4-31G basis set gives a reasonable account of the deformational modes of methane, both with regard to energies and changes in bond lengths. The calculated deformation energies and bond lengths correlate satisfactorily with the experimental results for cycloalkanes.

The results lead one to treat compounds containing four-membered rings in a different fashion than other cycloalkanes. A more detailed treatment for these compounds must separate local effects of bond angle deformation from the 1–3 repulsive part and must address the problem of torsional interactions.

References and Notes

(1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-72-2239. The calculations were performed using POLYATOM-II and GAUSSIAN-70 and the CDC 6600 and 7600 computers at the Brookhaven National Laboratory. The programs were obtained from the Quantum Chemistry Program Exchange.

(2) A brief account of this investigation has been presented: K. B. Wiberg and G. B. Ellison, *Tetrahedron*, **30**, 1573 (1974).

(3) Cf. J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

(4) W. Meyer and P. Pulay, *J. Chem. Phys.*, **56**, 2109 (1972), have presented the force constants for methane calculated using a variety of basis sets. References to earlier literature may be found therein.

(5) H. J. Monkhorst, *Chem. Commun.*, 1111 (1968); P. v. R. Schleyer, Collins, Dill, Apeloig, and J. A. Pople, in press.

(6) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

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(12) Similar results would be expected for other AH_4 species. However, with NH_3 and other compounds having a lone pair and missing an atomic center at one vertex of the tetrahedron, the results will be quite different.

(13) The figures were drawn using the computer program developed by W. L. Jorgensen (cf. W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973). We thank Dr. Jorgensen for making the program available to us. It was modified by J. W. to accept STO-3G and 4-31G wave functions and to run on a PDP-11/45 minicomputer.

(14) The C–H overlap population decreases from 0.381 at 109.5° to 0.352 at 160° and 0.312 at 180°. Similarly, the hydrogen charge drops from 0.848 to 109.5° to 0.777 at 160° and 0.638 at 180° ($r = 1.0936$ Å, 4-31G).

(15) A similar observation has been made by J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969), in their study of the relative energies of pyramidal and planar ammonia.

(16) This molecule will, of course, not be planar. In one reasonable conformation, a plane could be passed through the central carbon and the four methylene groups. Two of the CH groups would lie above this plane and two would lie below it. An angle $\alpha \approx 140°$ would appear reasonable for such a conformation.

(17) L. Wolloe, Thesis, University of Oslo, 1965. The HCH angle is not well determined by electron-diffraction data, but in cyclobutyl chloride it is 111 ± 1° [H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **44**, 865 (1966)].

(18) Cyclobutane and polycyclic compounds containing cyclobutane rings are unique in that there are fewer 1–3 interactions than C–C–C bond angles. Thus, cyclobutane has four C–C–C angles but only two 1–3 interactions, whereas cyclopentane has five C–C–C angles and five 1–3 interactions. It is not unreasonable to relate 1–3 hydrogen interactions and 1–3 carbon interactions despite the obviously larger nuclear charge of carbon. Much of the nuclear charge is shielded by the electrons and so the effective charge is only slightly greater than that of hydrogen. This is compensated by the greater C–C bond length. The similarity of 1–3 interactions for a given angle is shown by the observation that the C–C–C angle in propane is only slightly larger than tetrahedral.

(19) K. B. Wiberg, "Determination of Organic Structures by Physical Methods", Vol. III, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N.Y., 1971.

(20) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966).

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(22) J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 1614 (1970).

(23) The strain energy has been estimated as 51 kcal/mol based on MO calculations: M. D. Newton in "Modern Theoretical Chemistry", Vol. II, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1976.

Mechanisms of Photochemical Reactions in Solution. LXXVII.[1] Energy Wastage and Exciplex Formation in the Quenching of a Ketone Triplet by Sterically Hindered Alkenes

Amitava Gupta and George S. Hammond*

Contribution from the Division of Natural Sciences, University of California, Santa Cruz, California 95064.

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Abstract: The interactions of acetophenone, a familiar triplet photosensitizer, with the cis and trans isomers of 2,2-dimethyl-3-hexene (**1**), 4,4-dimethyl-2-pentene (**2**), and 3,4-dimethyl-2-pentene (**3**) have been studied. All the alkenes are reactive quenchers of the excited sensitizer molecules. However, the quantum yields for isomerization of *trans*-**1**, *trans*-**2**, and both isomers of **3** are very low. Since little or no oxetane formation is observed in any case, we conclude that quenching results mostly in energy wastage by nonradiative decay with the four alkenes which do not isomerize efficiently. *cis*-Piperylene was allowed to compete with *cis*-**1** for sensitizer triplets. The results indicate that the alkene and acetophenone triplets form an exciplex which can be quenched by piperylene. Competition between *trans*-**3** and *cis*-piperylene at high concentration of the alkene indicates that there is a quenching reaction which is kinetically second order with respect to the alkene.

The interaction of the triplet states of ketones with alkenes leads to energy transfer and energy wasting steps in which both molecules revert to their single ground states.[2-4] Such bimolecular reactions are often discussed by reference to mechanistic models involving the intermediate formation of triplet exciplexes.

Singlet exciplexes are obviously formed when fluorescence quenching is accompanied by new, red-shifted emission[6] so extension to many fast fluorescence-quenching interactions even when no new emitting species is formed seems reasonable.[7-12] This kind of speculation is fortified by the fact that seemingly modest variation of structure of quencher and quenchee produces new classes of fluorescent exciplexes.[13-15] In fact, Caldwell and Smith present kinetic evidence that quenchable precursors to [2 + 2] cycloaddition are the fluorescent exciplexes formed from 9-cyanophenanthrene and various electron rich olefins.

Further extension of the exciplex model to molecular reactions of triplet states is often made,[2,3,16-26] albeit with less confidence. Although the binding energy of triplet exci-