

References and Notes

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Molecular Structures and Potential Functions for the Deformation of Cyclopropane, Cyclopropene, Cyclobutane, and Cyclopentadiene

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Abstract: Cyclopropane, cyclopropene, cyclobutane, and cyclopentadiene have been chosen as models to study angular deformations for higher hydrocarbons (e.g., spiro hydrocarbons). To this end, ab initio molecular orbital theory has been used to examine the structural and energetic changes accompanying distortion of an exocyclic HCH angle in these molecules. Results are compared with previous studies on methane. Although methane is confirmed to be a reasonable model in most respects, the structural variations found in C-C bonds are significantly larger than those found for the C-H bonds in methane, a result which is consistent with the difference in bond strength between C-C and C-H bonds. The structural and energetic consequences of angular deformation are usefully analyzed in terms of Walsh-Mulliken diagrams of the several highest bonding molecular orbitals. The calculated dipole moments and the HOMO energies (for cyclopropene and cyclopentadiene) are shown to be sensitive to the deformed exocyclic HCH angle.

Introduction

Molecular deformations are of particular interest to chemists because molecules with different bond angles may differ appreciably in both physical and chemical properties. In the past, attention has mainly been focused on small angular deformations which are of interest in connection with studies of molecular vibrations. Relatively little work has been carried out which deals with the potential functions and the geometric changes that are associated with highly distorted structures.

Recently, however, the angular deformation of methane has been extensively studied using ab initio orbital theory.^{1,2} The structural simplicity and inherent symmetry of methane make it an economical model for investigating angular deformation at tetracoordinate carbon for higher hydrocarbons. However, it has not yet been established whether distorted methane provides a reliable and realistic model for making detailed predictions concerning the properties of larger distorted molecules (e.g., cyclohydrocarbons, spiro hydrocarbons). In particular, it is not clear whether the greater effective nuclear charge on carbon (compared with hydrogen) can be compensated by the greater C-C (compared with C-H) bond length. The effect of differing C-C and C-H bond strengths also needs to be assessed.

In order to provide a better understanding of angular deformations in higher hydrocarbons and to learn how well methane can serve as a model for these molecules, studies of additional larger systems are desirable. In this paper, angular deformations in cyclopropane, cyclopropene, cyclobutane, and cyclopentadiene have been studied using ab initio molecular

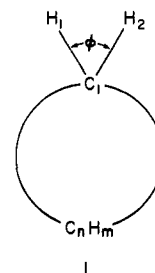
orbital theory. The structural and energetic variations are interpreted in terms of Walsh-Mulliken diagrams. Comparison is made with results obtained from the previous model studies^{1,2} of methane.

Method

Standard ab initio LCAO SCF molecular orbital calculations were carried out using a modified version of the Gaussian 70 system of programs.³ Geometry optimizations were performed with the STO-3G basis set⁴ and a gradient optimization procedure.⁵ Single calculations on optimized structures were carried out with the 4-31G basis set⁶ which is somewhat more reliable for energetic comparisons.^{6,7}

The STO-3G optimized equilibrium structures for cyclopropane, cyclopropene, and planar cyclobutane⁸ have been reported previously.^{9,10} We report here for the first time the fully optimized STO-3G structure for cyclopentadiene.

Structural and energetic variations accompanying distortion of the exocyclic HCH angle (ϕ , see **1**) have been studied by



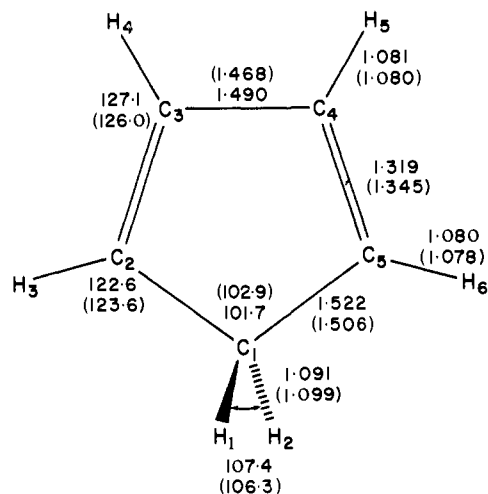


Figure 1. Theoretical (STO-3G) and experimental (in parentheses) structural parameters for cyclopentadiene.

fixing ϕ and optimizing other structural parameters. For cyclopropane and cyclopropene, all the remaining structural parameters have been optimized, whereas for cyclobutane and cyclopentadiene, only partial optimization has been carried out in the sense that the C_2-H_3 and C_3-H_5 lengths and $H_5C_3H_6$ angle for cyclobutane, and C_2-H_3 and C_3-H_4 lengths and $H_4C_3C_2$ angle for cyclopentadiene, have been held at their values in the equilibrium (undistorted) structure. Such partial optimization is desirable in terms of computational economy and is justified in the light of results for the full optimizations on distorted cyclopropane and cyclopropene structures.

Results and Discussion

The STO-3G optimized structure for cyclopentadiene is compared with the experimental structures^{11,12} in Figure 1. Calculated structural variations accompanying bond angle distortion for cyclopropane, cyclopropene, planar cyclobutane, and cyclopentadiene are shown in Tables I-IV. All corresponding energies are presented in Table V.

The theoretical and experimental structures for cyclopentadiene are in reasonable agreement. The largest difference (0.026 Å) occurs for the $C=C$ double bonds which, characteristically of STO-3G, are underestimated by the theory.

Comparison of STO-3G and 4-31G energies (Table V) shows that the use of the larger basis set stabilizes strained structures more than the less strained ones. For instance, the energy of the cyclopropane structure with ϕ held at 50° relative

Table II. Structural Variations Accompanying Changes in the Exocyclic $H_1C_1H_2$ Angle (ϕ) for Cyclopropene

ϕ	C_1C_2	C_2C_3	C_1H_1	C_2H_3	$H_3C_2C_1$	$C_2C_1C_3$
50.0	1.471	1.291	1.141	1.076	147.5	52.1
60.0	1.469	1.290	1.121	1.076	147.1	52.1
80.0	1.473	1.286	1.102	1.076	146.4	51.8
90.0	1.477	1.284	1.096	1.075	146.0	51.5
100.0	1.483	1.281	1.091	1.075	145.6	51.2
112.5	1.493	1.277	1.087	1.075	145.0	50.6
120.0	1.500	1.275	1.085	1.075	144.7	50.3
130.0	1.511	1.271	1.083	1.075	144.2	49.8

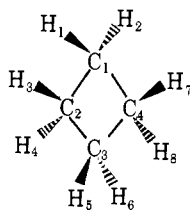
to that of the equilibrium structure (i.e., $\phi = 113.8^\circ$) is 116.2 kcal mol⁻¹ at the STO-3G level compared with 86.5 kcal mol⁻¹ if the 4-31G basis set is employed.

As can be seen from Tables I-IV, the calculated C_1-H_1 lengths increase monotonically as ϕ decreases from 130° to 60° or 50°. The elongation of the C_1-H_1 bond may be attributed to the rapid increase in the $H_1\cdots H_2$ nuclear repulsion energy and a smaller carbon 2s contribution¹³ to the C_1-H_1 bond as ϕ decreases.^{1,2} Accordingly, there is more carbon 2s contribution available for the C_1-C_2 bond and this leads to a shorter C_1-C_2 bond and a larger CCC bond angle around C_1 . The resultant longer C_2-C_3 bond lengths in both cyclopropane and cyclopropene, longer $C_2\cdots C_4$ distance in cyclobutane, and longer $C_2\cdots C_5$ distance in cyclopentadiene may be partially attributable to avoidance of the increased steric interaction caused by the shortening of the C_1-C_2 bonds. We note that the increase in the C_2-C_3 bond length is smaller in cyclopropene than in cyclopropane (for example, 0.013 vs. 0.025 Å at $\phi = 60^\circ$), which is consistent with their respective bond strengths. The smaller increase in the $C_2\cdots C_5$ distance in cyclopentadiene compared with that of the $C_2\cdots C_4$ distance in cyclobutane (0.005 vs. 0.025 Å at $\phi = 60^\circ$) similarly suggests that the cyclopentadiene nucleus is more rigid than the cyclobutane ring. The opening of $H_{34}-C_2-C_1$ ¹⁴ and $H_3-C_2-C_1$ angles, respectively, in cyclopropane and cyclopropene may also reflect attempts to relieve steric repulsions caused by shorter C_1-C_2 bond lengths. Similar observations may be made for cyclopentadiene and cyclobutane. Note that variation in ϕ causes only small changes in the C_2-H_3 bond length and the $H_3C_2H_1$.

Table I. Structural Variations Accompanying Changes in the Exocyclic $H_1C_1H_2$ Angle (ϕ) for Cyclopropane

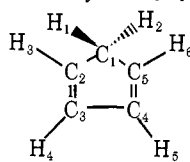
ϕ	C_1C_2	C_2C_3	C_1H_1	C_2H_3	$H_3C_2H_4$	$H_{34}C_2C_1^a$	$C_2C_1C_3$
50.0	1.459	1.534	1.140	1.084	113.2	154.5	63.4
60.0	1.468	1.527	1.116	1.083	113.5	153.1	62.7
80.0	1.482	1.516	1.094	1.082	113.8	151.4	61.5
90.0	1.488	1.512	1.088	1.081	113.9	150.9	61.1
100.0	1.494	1.508	1.084	1.081	113.9	150.5	60.6
113.8	1.502	1.502	1.081	1.081	113.8	150.0	60.0
120.0	1.506	1.500	1.078	1.081	113.8	149.9	59.7
130.0	1.514	1.496	1.078	1.080	113.7	149.7	59.2

^a The symbol H_{ij} denotes a point on the bisector of the bonds $C-H_i$ and $C-H_j$.

Table III. Structural Variations Accompanying Changes in the Exocyclic $H_1C_1H_2$ Angle (ϕ) for Planar Cyclobutane

ϕ	C_1C_2	C_1H_1	C_2C_3	$C_2C_1C_4$	$H_3C_2H_4$	$C_1C_2H_3H_4$	$C_2C_4^a$
60.0	1.524	1.123	1.560	93.8	108.7	136.9	2.225
80.0	1.537	1.100	1.557	91.9	108.8	135.9	2.209
108.7 ^b	1.554	1.087	1.555	90.0	108.7	135.0	2.200
130.0	1.568	1.082	1.551	88.7	108.5	134.3	2.191

^a Not an independent structural parameter; shown only for easy comparison. ^b The optimum geometry in which $C_2-H_3 = 1.087 \text{ \AA}$, $C_3-H_5 = 1.087 \text{ \AA}$, and $H_3C_3H_6 = 108.7^\circ$.

Table IV. Structural Variations Accompanying Changes in the Exocyclic $H_1C_1H_2$ Angle (ϕ) for Cyclopentadiene

ϕ	C_1C_2	C_2C_3	C_1H_1	$C_2C_1C_5$	$C_3C_2C_1$	$H_3C_2C_1$	$C_2C_5^a$	$C_3C_4^a$
50.0	1.469	1.332	1.161	107.3	106.8	124.9	2.366	1.473
60.0	1.485	1.326	1.130	105.8	107.6	124.3	2.368	1.482
90.0	1.512	1.320	1.098	103.0	109.1	123.2	2.366	1.491
107.4	1.522	1.319	1.091	101.7	109.9	122.6	2.361	1.490
130.0	1.536	1.318	1.088	99.9	110.9	122.0	2.351	1.487

^a Not an independent structural parameter; shown only for easy comparison.

Table V. Total Energies (hartrees) and Relative Energies (kcal mol^{-1})

Molecule	ϕ	STO-3G		4-31G ^a	
		Total	Rel	Total	Rel
Cyclopropane	50.0	-115.481 00	116.2	-116.745 70	86.5
	60.0	-115.540 83	78.7	-116.787 85	60.0
	80.0	-115.621 55	28.0	-116.847 74	22.4
	90.0	-115.645 10	13.2	-116.866 31	10.8
	100.0	-115.659 38	4.3	-116.877 92	3.5
	113.8	-115.666 16	0	-116.883 50	0
	120.0	-115.664 91	0.8	-116.882 38	0.7
	130.0	-115.657 80	5.3	-116.876 13	4.6
Cyclopropene	50.0	-114.190 93	131.9	-115.486 35	97.5
	60.0	-114.262 03	87.3	-115.535 87	66.4
	80.0	-114.354 12	29.5	-115.603 47	24.0
	90.0	-114.379 87	13.4	-115.623 69	11.3
	100.0	-114.394 91	3.9	-115.636 06	3.5
	112.6	-114.401 16	0	-115.641 68	0
	120.0	-114.399 14	1.3	-115.640 31	0.9
	130.0	-114.390 51	6.7	-115.633 47	5.2
Cyclobutane	60.0	-154.166 40	67.4	-155.787 59	49.2
	80.0	-154.239 92	21.3	-155.840 28	16.1
	108.7	-154.273 87	0	-155.865 94	0
	130.0	-154.258 59	9.6	-155.852 57	8.4
	Cyclopentadiene	50.0	-190.315 54	88.8	-192.414 86
60.0		-190.362 36	59.5	-192.445 14	42.0
90.0		-190.445 72	7.2	-192.503 58	5.4
107.4		-190.457 11	0	-192.512 13	0
130.0		-190.440 52	10.4	-192.498 21	8.7

^a Energy calculated using STO-3G optimized geometry.

Table VI. Calculated HOMO and LUMO Energies for Cyclopropene and Cyclopentadiene (eV)

Molecule	ϕ	STO-3G		4-31G	
		HOMO	LUMO	HOMO	LUMO
Cyclopropene	50.0	-5.75	8.98	-7.53	4.82
	60.0	-6.60	8.84	-8.16	4.82
	80.0	-7.76	8.76	-9.05	4.86
	90.0	-8.10	8.76	-9.32	4.90
	100.0	-8.31	8.83	-9.51	4.94
	112.5	-8.45	8.95	-9.64	5.01
	120.0	-8.47	9.03	-9.68	5.05
	130.0	-8.47	9.15	-9.72	5.10
Cyclopentadiene	50.0	-6.62	7.58	-8.19	4.00
	60.0	-6.83	7.28	-8.31	3.89
	90.0	-7.08	7.11	-8.45	3.89
	107.4	-7.07	7.25	-8.45	4.01
	130.0	-7.01	7.52	-8.45	4.19

angle of cyclopropene, and the C₂-H₃ length in cyclopropene. This provides some justification for the simplifying assumptions (vide supra) in the optimizations for cyclobutane and cyclopentadiene. One of the simplifications in our cyclobutane optimizations was the assumed constancy of the H₅C₃H₆ bond angle. When this constraint is relaxed for the $\phi = 60^\circ$ structure, the H₅C₃H₆ angle changes by only 0.1° and the total energy is unaltered. This provides further support for our optimization model.

It is worth pointing out here that whereas the changes in C₁-H₁ accompanying changes in ϕ are similar to those predicted from the model studies^{1,2} on methane, the changes in the C₁-C₂ bond lengths are about twice the predicted quantity. The greater variation in the C-C bond compared with C-H is consistent with its much weaker bond strength (82 vs. 99 kcal mol⁻¹)¹⁵ and much smaller stretching force constant (4.57 vs. 5.84 mdyn Å⁻¹).¹⁶

Shown in Table VI are the calculated energies for the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for cyclopropene and cyclopentadiene. The HOMO energies show little variation for ϕ in the range 90–130° but increase sharply when ϕ is less than 90°. The LUMO energies, on the other hand, are usually lowered as ϕ decreases, although they are less sensitive to the change in the angle. The destabilization of HOMO levels and stabilization of LUMO levels is related to the C=C bond lengths (Tables II and IV): the HOMO levels are bonding across C=C and are destabilized when the bond length is increased while the LUMO levels are antibonding across C=C and show the opposite behavior. The correlation is less pronounced for cyclopentadiene than for cyclopropene.

The relationship between strain and ultraviolet absorption maxima is of chemical interest. In the past, attention has mainly been focused on strain within the ring. A correlation between the ring-size and the UV absorption maxima for several ring compounds indicated that increasing ring strain shifts the absorption maximum bathochromically.¹⁷ Here, we call attention to the additional strain effect caused by the deformation of an exocyclic angle. On the basis of our results, we predict that exocyclic bond angle distortion in strained systems such as spiro hydrocarbons should also lead to a shift to longer wavelengths for the $\pi \rightarrow \pi^*$ transition. Of course, other effects (e.g., spiroconjugation) would also contribute to the resultant excitation energy. The point we wish to stress here is that in explaining¹⁸ an observed bathochromic or hypsochromic shift for a $\pi \rightarrow \pi^*$ transition band, the effect of exocyclic (or spiro) bond angle distortion should not be overlooked, particularly if rings of different sizes are involved in the comparison.¹⁹

Calculated and experimental dipole moments are shown in Table VII. Agreement with the magnitudes of the two exper-

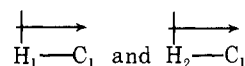
Table VII. Calculated and Experimental Dipole Moments (D)^a

Molecule	ϕ	Calcd		Exptl ^b
		STO-3G	4-31G	
Cyclopropene	50.0	1.00	0.58	
	60.0	0.63	0.38	
	80.0	0.19	0.14	
	90.0	0.08	0.08	
	100.0	0.02	0.04	
	113.8	0	0	0
	120.0	0.00	-0.02	
	130.0	0.02	-0.05	
Cyclopropene	50.0	0.17	-0.46	
	60.0	-0.17	-0.58	
	80.0	-0.53	-0.66	
	90.0	-0.59	-0.65	
	100.0	-0.59	-0.62	
	112.6	-0.55	-0.56	[0.46]
	120.0	-0.50	-0.53	
	130.0	-0.44	-0.49	
Cyclobutane	60.0	0.47	0.31	
	80.0	0.11	0.12	
	108.7	0	0	
	130.0	0.05	0.07	
Cyclopentadiene	50.0	2.00	1.79	
	60.0	1.34	1.26	
	90.0	0.45	0.52	
	107.4	0.34	0.36	[0.45]
	130.0	0.37	0.26	

^a The positive sign is defined such that the negative end of the dipole moment is within the ring and vice versa. ^b Reference 19.

imental values²⁰ is good (<0.1 D). There is a point of conflict, however, concerning the direction of the dipole moment of cyclopropene for which the earlier ab initio calculations^{9,10,21} have challenged the experimental assignment of Benson and Flygare.²²

The general conclusion from Table VII is that pinching down an exocyclic methylene angle will produce a dipole moment in a direction from the deformed methylene group towards the ring. This may be explained in terms of an increase in the vector sum ($2 \mu_{HC} \cos \phi/2$) of the



bond dipoles (μ_{HC}) as ϕ (i.e., H₁C₁H₂) decreases, and in addition, an increase in the individual μ_{HC} 's as the C-H bonds lengthen.

Comparison of STO-3G and 4-31G dipole moments shows that the numerical values for small deformations are quite similar with best agreement for optimum geometries. Surprisingly, for highly distorted structures such as $\phi = 50^\circ$ or 60° quite different results are obtained in which case we believe that the 4-31G values are more reliable. However, although there are some numerical differences between STO-3G and 4-31G, the columnwise trends in Table VII are the same for both basis sets.

In Figure 2, we have plotted the 4-31G total energies vs. the deformed angles, referenced to zero for the appropriate optimum structures. The calculated results for methane (C_{2v}) in which bond angles about C₁ are given the same values as in the corresponding cyclohydrocarbon structure are also included in Figure 2. The potential functions for the four cyclohydrocarbons are rather similar in shape and can approximately overlap one another; i.e., the energy required for angular distortion ($\Delta\phi$) does not differ greatly among this set of molecules. This suggests that the angular deformation primarily affects the bonding nature between C₁ and its nearest-neighbor atoms

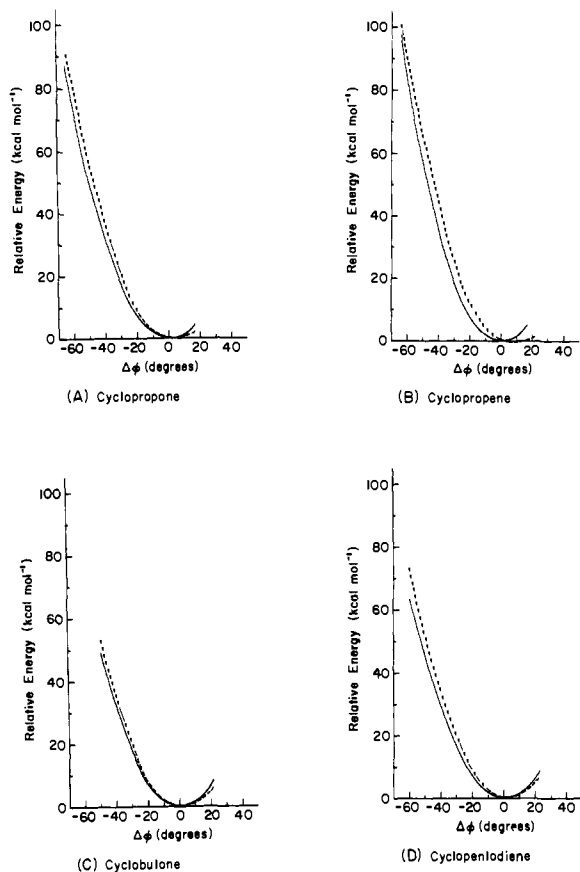


Figure 2. Comparison of 4-31G potential functions for angular deformations ($\Delta\phi$) in (i) cyclohydrocarbons (—) and (ii) methane (---). The angles about C_1 in (ii) are taken to be the same as the corresponding cyclohydrocarbon values. Relative energies and angular deformations are referenced to zero for the appropriate optimum structure.

and other perturbations can be equally well adjusted. By comparing potential functions of cyclohydrocarbons with the corresponding methane potential functions as shown in Figures 2A–D, we find that the curves in each case are also rather close to each other: the difference between two curves is usually less than 5 kcal mol^{-1} . We therefore suggest that provided the appropriate bond angles are known from other sources, methane is a reasonably good model for predicting angular deformation energies for higher hydrocarbons.

The breakdown of the total energy (E_T) into nuclear repulsion (E_N) and electron attraction (E_e) components is shown in Figure 3. E_N and E_e usually operate in different directions and the most stable equilibrium geometry results from the best balance of these two opposite forces. It is interesting to note that whereas in cyclobutane and cyclopentadiene the minima in E_T and E_N are close to one another, a result which had been noted^{1,23} in previous calculations on distorted methane, this is definitely not the case for cyclopropane and cyclopropene.

The relationship between the calculated total energy and the $H_1C_1H_2$ angle, ϕ , can be well described in terms of the occupied molecular orbitals. The lowest three molecular orbitals in cyclopropane as well as cyclopropene involve only the carbon 1s orbitals, and the next three utilize essentially the hydrogen 1s orbitals and the carbon 2s orbitals. These six lowest molecular orbitals are relatively unaffected by bond angle deformation because the s function is nondirectional. This leaves six bonding molecular orbitals in cyclopropane and five in cyclopropene which are likely to be important in the bond angle deformation process. Similar arguments applied to cyclobutane and cyclopentadiene show that for each of these

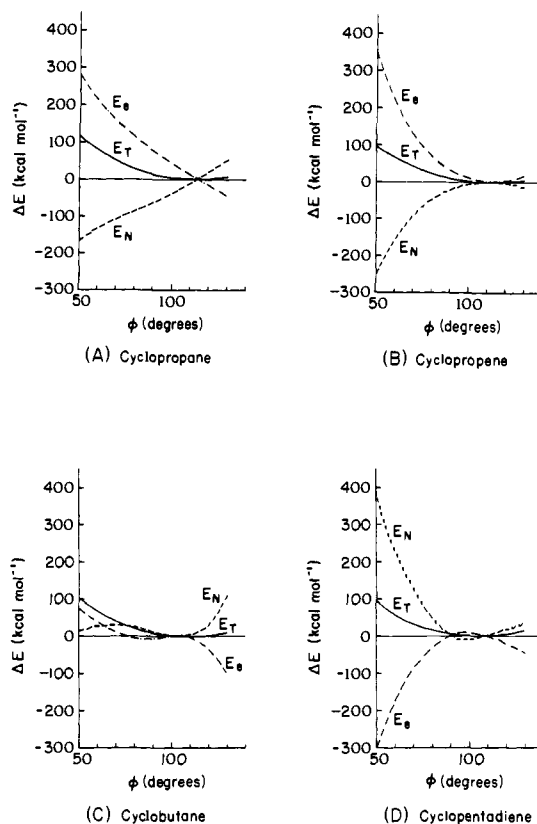


Figure 3. Breakdown of total STO-3G energy, E_T (—), into its components E_N , the total nuclear repulsion energy (---), and E_e , the total electronic energy (— · —). All values referenced to zero for the appropriate optimum $H_1C_1H_2$ (ϕ).

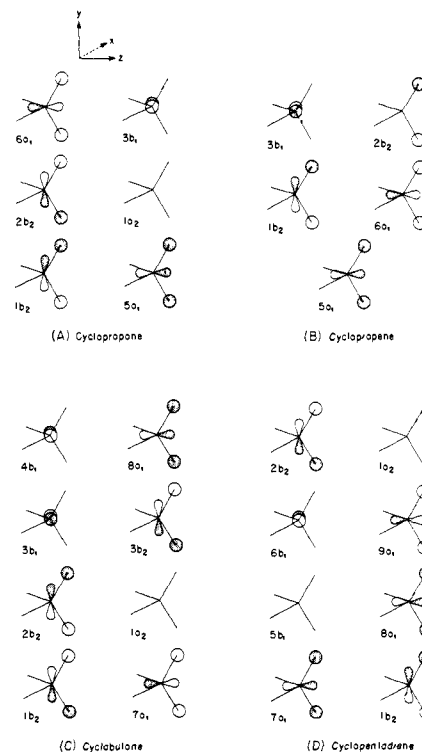


Figure 4. Schematic representation of the portion around C_1 of the several highest occupied molecular orbitals. See Figure 5 for ordering of the molecular orbitals.

molecules, the eight highest occupied orbitals need to be considered.

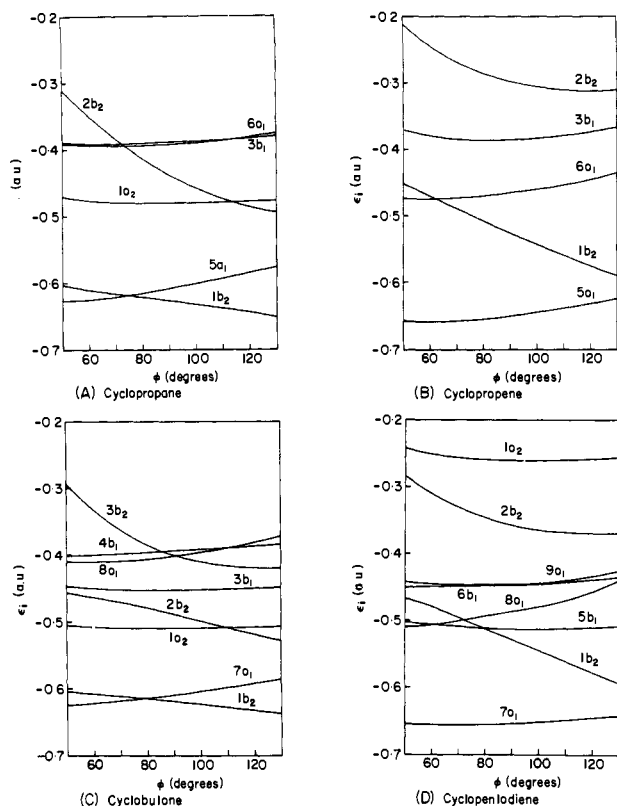


Figure 5. Walsh-Mulliken diagrams showing variation in orbital energies (ϵ_i) with the exocyclic $H_1C_1H_2$ angle (STO-3G).

The portion of these orbitals around C_1 is schematically depicted in Figure 4. In Figure 5, we have constructed Walsh-Mulliken diagrams²⁴ showing the variation in energy of these orbitals with ϕ . Finally, Figure 6 demonstrates that the changes with ϕ of the total energy and of the sums of the one-electron energies of the orbitals considered parallel one another and produce minima in close proximity.²⁵ This result supports the use of the Walsh-Mulliken diagram approach as an analysis technique.

It is useful to discuss the Walsh-Mulliken diagrams collectively since most features are common to all four molecules. Under C_{2v} symmetry, the orbitals can be classified as a_1 , a_2 , b_1 , or b_2 as shown in Figure 4 and we consider each type of orbital in turn.

The a_1 orbitals all show bonding interactions between the $1s$ orbitals at H_1 and H_2 and the $2p_z$ orbital at C_1 . The bonding decreases as ϕ increases leading to an increased energy with increasing ϕ (Figure 5).

The a_2 orbitals are antisymmetric with respect to the yz and xz planes and hence have no components in the vicinity of C_1 (unless higher angular functions are included in the basis set). Not surprisingly, the energies of the a_2 orbitals are relatively insensitive to changes in ϕ .

For the b_1 orbitals, the $H_1C_1H_2$ plane is a nodal plane. Again, these orbitals are expected, and found (Figure 5), to show little variation with ϕ .

Finally, the b_2 orbitals show positive overlap of the $1s$ orbitals at H_1 and H_2 with the $2p_y$ orbital at C_1 . This overlap increases with ϕ ; hence the energies of the b_2 orbitals decrease with increasing ϕ . Equally, the antibonding interaction between the $1s$ orbitals at H_1 and H_2 decreases with increasing ϕ leading to the same energetic behavior. The much larger slope of b_2 orbitals than a_1 orbitals is consistent with the observation that the C_1-H_1 bond shortens as ϕ increases.

Thus the optimum $H_1C_1H_2$ angle is largely determined by the balance between the a_1 orbitals (favoring small angles) and

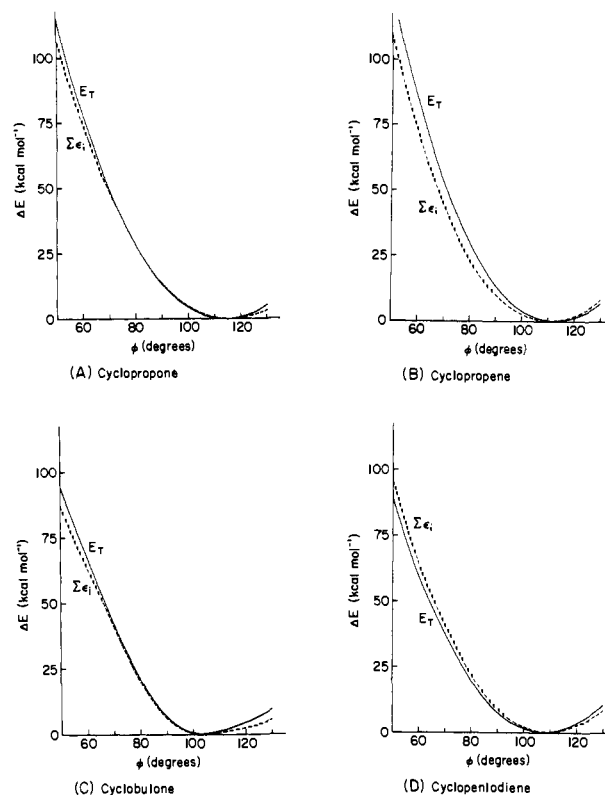


Figure 6. Variation in total energy E_T (—) and sum of several (see text) highest one-electron energies (---) with ϕ .

the b_2 orbitals (favoring large angles). The a_2 and b_1 orbitals are of little importance in this regard.

In summary, we have shown here that in many respects, methane may serve as a useful model for studying angular deformation in higher hydrocarbons. However, variations arising from the differences (in particular, the bond strengths) between C-C and C-H bonds should be noted. The distorted cyclohydrocarbons provide a better (though more expensive) theoretical model than methane for studying spiro hydrocarbons. We find that the structural and energetic changes accompanying angular distortion can be usefully analyzed using Walsh-Mulliken diagrams of the several highest occupied molecular orbitals. We note finally the important point that the dipole moment (even of cyclopropane) and the HOMO and LUMO energies are sensitive functions of the deformed methylene angle.

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Raman Spectrum and Torsional Potential Function for Vinylcyclopropane

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Abstract: A series of six lines in the low-frequency Raman spectrum of vinylcyclopropane has been observed and assigned to the ($\Delta v = 2$) overtones of the vinyl torsional oscillation. The temperature dependence of the intensities of two pairs of Raman bands indicated the presence of two conformers with an enthalpy difference, $\Delta H = 500 \pm 50 \text{ cm}^{-1}$. The observed torsional transitions, the ΔH , and the relative intensities of the pairs of bands used in the temperature dependence study are all fitted to a potential function of the form $V(\phi) = \sum_{i=1}^4 (V_i/2) (1 - \cos i\phi)$ having minima for the trans conformer ($\phi = 0^\circ$) and two equal energy gauche conformers; the gauche species are found to be the less stable. The potential constants are found to be (in cm^{-1}) $V_1 = 279 \pm 60$; $V_2 = 699 \pm 60$; $V_3 = 782 \pm 32$; and $V_4 = -199 \pm 35$.

Introduction

The solution to the conformational behavior of vinylcyclopropane has remained an elusive one, despite many empirical and theoretical examinations of both the parent molecule and some of its derivatives. Both types of investigation have confirmed that an s-trans structure best represents the ground state or most abundant form of this molecule. Furthermore, both types of investigation have indicated the presence of an appreciable amount of a less stable conformer existing in thermal equilibrium with the s-trans species. However, the only common ground among the published reports is concurrence on the lower energy s-trans conformer; the nature of the other less stable species has been a matter of much confusion.

Nuclear magnetic resonance studies on vinylcyclopropane and many of its cyclopropyl-substituted derivatives have been interpreted in terms of both twofold and threefold torsional potential functions (the former having energy minima for trans and cis conformers, the latter having minima for trans and/or cis and two symmetry related gauche conformers). Lüttke and de Meijere¹ have concluded that their data for the parent molecule are best interpreted in terms of a twofold potential function (trans/cis) with the trans conformer more stable by $385 \pm 70 \text{ cm}^{-1}$ ($4.60 \pm 0.84 \text{ kJ mol}^{-1}$). On the other hand, several independent studies²⁻⁴ have decided upon a threefold potential function (trans/gauche) with the trans species more stable by $278 \pm 48 \text{ cm}^{-1}$ ($3.32 \pm 0.57 \text{ kJ mol}^{-1}$).

De Meijere and Lüttke⁵ have examined gaseous vinylcyclopropane by the electron diffraction method and deduced a

trans/gauche equilibrium, the trans species more stable by $385 \pm 70 \text{ cm}^{-1}$ ($4.60 \pm 0.84 \text{ kJ mol}^{-1}$) and a gauche dihedral angle $110^\circ < \phi < 120^\circ$.

Hehre⁶ has performed an ab initio investigation of vinylcyclopropane using both the STO-3G and the 4-31G minimal basis sets. Both basis sets confirm the trans geometry as representing the molecular ground state. The STO-3G basis predicts the additional presence of both a cis and a gauche conformation, the gauche having the lower energy of the two. On the other hand, use of the 4-31G basis predicts greater definition of the gauche conformer at the expense of the cis conformer. Both basis sets predict a gauche dihedral angle of $\sim 114^\circ$, in good agreement with the electron diffraction work of de Meijere and Lüttke.⁵

Codding and Schwendeman⁷ examined the microwave spectrum of vinylcyclopropane and were able to extract definitive information about the ground state trans geometry; they were not, however, able to extract any information on the nature of the less stable conformational isomer. By examining the relative intensities of torsional satellites, these authors were able to deduce a fundamental torsional frequency of $\sim 125 \text{ cm}^{-1}$ with the suggestion that the barrier hindering interconversion to another rotamer should be at least 625 cm^{-1} (7.48 kJ mol^{-1}).

In order to determine the nature of the conformational equilibrium in vinylcyclopropane we have undertaken the observation and analysis of the low-frequency torsional mode in this molecule.

Experimental Section

The sample was purchased from Aldrich Chemical Co. (stated: 99% purity) and used without further purification. After a thorough de-

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