genvector λ to constuct the best approximation to χ of Pauling's form as

$$\chi(r,\theta,\phi) \simeq \left[\epsilon \sum_a \lambda_a{}^2\right]^{-1}\left[\sum_a \lambda_a R_a(r)\right]\left[\sum_a \lambda_a Y_a(\theta,\phi)\right]$$

The fitting parameter ε turns out to be the square of the overlap between χ and the optimum orbital of the form $f(r)\ \Sigma_{l,m}\lambda_l{}^m Y_l{}^m(\theta,\phi)$.

(7) For example, in order to obtain 2s and 2p orbitals with identical radial functions Pauling used a nodeless 2s orbital which cannot be orthogonal to a 1s orbital.

(8) Other choices of $w(r)$ might be made. For example, if one wishes to correlate hybridization with a particular physical property then $w(r)$ might be chosen to weight most heavily the radial regions of importance for that property.

(9) In addition to assuming identical hybridization at all radial distances, the Pauling formulation also assumes that the axis of a bond orbital points directly at the nucleus to which the bond is formed and that hybrid orbitals on the same center are orthogonal. These assumptions provide constraints on the relative orientation of the hybrid orbitals.

(10) The valence bond orbitals were obtained by a self-consistent-field optimization of the wave function for a single perfect-pairing structure. See, D. M. Chipman, B. Kirtman, and W. E. Palke, *J. Chem. Phys.*, **65**, 2556 (1976).

(11) According to the prescription we mix normalized s, p_x, p_y, and p_z orbitals to produce two equivalent bond hybrids pointing at the hydrogen atoms (which subtend an angle of 104.45° at the oxygen) and two equivalent lone pair hybrids above and below the molecular plane. Constraints of normalization and orthogonality then uniquely determine the hybrid orbitals leading to lone pairs forming an angle of 115.42° and giving the hybridization coefficients quoted in the text.

(12) In practice we have found it difficult to follow this rapid crossover because of numerical roundoff errors. For the same reason the direction of the bonding VBO on oxygen becomes poorly determined as one enters the bonding overlap region.

Ab Initio Calculations of the Equilibrium Structure of Cyclobutane

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Abstract: The equilibrium structure of cyclobutane has been calculated by single determinant restricted Hartree–Fock theory using an extended basis set of Gaussian orbitals augmented by polarization functions. The molecule is found to be nonplanar with a degree of puckering of 0.23 Å and a barrier to planarity of 0.9 kcal mol^{-1}. Tilting of the methylene groups proves to be essential for relieving steric strain.

Cyclobutane[1] has been extensively investigated using electron diffraction[2,3], IR-Raman,[4-10] and NMR.[11] All experimental results agree that the molecule possesses a puckered structure with a small surmountable barrier to planarity. As its degree of nonplanarity is determined by a single puckering amplitude q[12] one would expect detailed experimental information on the equilibrium conformation and the inversion process. For a number of cyclobutane derivatives[13-17] microwave and far-IR studies provide these data but for the parent molecule itself the corresponding details are less accurate, owing to the fact that it has no dipole moment and hence no microwave spectrum. Furthermore, the ring puckering vibration is IR inactive and no far-IR spectrum can be expected. Although the height of the inversion barrier has been determined quite accurately,[8,9] several structural features are still not fully resolved: (a) Recent spectroscopic studies of the degree of puckering[8,11] vary considerably. (b) The amount of bond staggering of the methylene groups remains unclear. (c) The CH bond lengths found by electron diffraction[2,3] and high resolution proton resonance in a nematic solvent[11] are unexpectedly long compared with CH bond lengths of other cycloalkanes. (d) No experimental account of the difference between axial and equatorial hydrogens in puckered cyclobutane has been given.

Recent ab initio studies on cyclobutane[18-21] were rather inconclusive with regard to these questions. With a minimal basis set of Slater-type orbitals the molecule was found to be rather flat with almost no barrier to inversion.[18] A calculation employing floating spherical Gaussian orbitals was in reasonable accord with experimental structural data but gave a barrier value much too high.[19] Therefore, we would like to report a thorough ab initio study of cyclobutane using elaborate basis sets in order to get reliable predictions of the various energetic and structural features of the four-membered ring.

Quantum Mechanical Method

Our investigation is based on single determinant restricted Hartree–Fock theory.[22] A 6-31G split-valence basis set augmented by six d functions (6-31G* basis) for the description of the carbon atoms was used.[23] From previous studies it has become obvious that extended basis sets including polarization functions are sufficient to reproduce relative energies and geometries in good agreement with experiment.[23,24] Therefore, our study was essentially aimed at determining these features of planar (D_{4h}) and puckered (D_{2d}) cyclobutane at the 6-31G* level. In order to obtain an initial guess of the theoretical structures, preliminary calculations with smaller basis sets were done, namely the minimal STO-3G basis[25] and the extended 4-31G basis.[26]

As indicated in Figure 1 the equilibrium structure of the D_{4h} form was evaluated by optimizing the CC bond length, the CH bond length, and the HCH bond angle. In the puckered D_{2d} form axial and equatorial hydrogens were distinguished, thus giving two different CH bonds to be calculated. The degree of nonplanarity was determined by the puckering amplitude q.[27] An additional sixth degree of freedom arose from the fact that because of ring puckering the local C_{2v} symmetry of a C–CH_2–C fragment is relieved: the methylene groups tilt, which is quantitatively described by the tilting angle τ depicted in Figure 1.[28] The structure optimizations were done using an improved version of the complementary Davidon–Fletcher–Powell method.[29]

Results and Discussions

Table I presents the RHF energies of the two cyclobutane forms obtained with the STO-3G, 4-31G, and 6-31G* basis sets. Also listed are theoretical and experimental barrier heights. Table II gives the computed structural data of planar and puckered cyclobutane. The latter are compared with the results of two experimental studies.

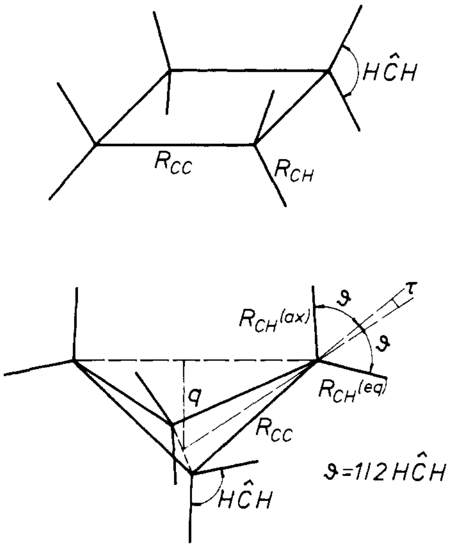

Figure 1. Structural parameters of planar (D_{4h}) and puckered (D_{2d}) cyclobutane.

Table I. Total Energies (hartrees) and Barrier Height (kcal mol^{-1}) of Cyclobutane

Method	Planar form (D_{4h})	Puckered form (D_{2d})	Barrier height
STO-3G	−154.27387	−154.27389	0.01
4-31G	−155.86617	−155.86681	0.40
6-31G*	−156.09574	−156.09718	0.90
IR, Raman[a]			1.14
IR[b]			1.44
Raman[c]			1.48
Near IR[d]			1.28

[a] Reference 4. [b] Reference 8. [c] Reference 9. [d] Reference 7.

The calculated bond lengths and bond angles are in good accordance with the observed data. The 6-31G* value of the CC bond length resembles closely the electron diffraction result[3] while the CH bond lengths seem to be somewhat short. Studies on other small hydrocarbons indicate that theory tends to underestimate CH bonds by 0.01 Å.[30] A value of 1.095 Å would parallel the electron diffraction result but not the NMR bond length which is longer by 0.02 Å.[11] The axial and equatorial CH distances are found to be similar with each of the three basis sets, which is in line with the observation that only one CH peak occurs in the radial distribution curve of the electron diffraction spectrum.

The necessity for polarization functions in an ab initio study of cyclobutane becomes obvious when comparing the calculated barrier heights (Table I) and puckering amplitudes (Table II). As found recently by Wright and Salem[18] the minimal basis is insufficient to take account of the puckering of the four-membered ring. The lack of flexibility in the STO-3G basis leads to an overestimation of bond angle strain and hence to a significant destabilization of nonplanar cyclobutane. With the more flexible extended 4-31G basis the double minimum shape of the cyclobutane potential is established but the barrier to planarity is rather small. The best results are obtained with polarization functions in the basis. Puckering amplitude as well as tilting angle are close to the corresponding NMR results of Meiboom and Snyder.[11] The larger electron diffraction value of q (0.34 Å) is based on an estimate as the diagonal distance in the carbon ring could not be precisely deducted from measurement.[3] In addition, it was assumed that the methylene tilting angle is zero. Unfortunately, all recent IR and Raman investigations[7-10] are based on the electron diffraction geometry and, therefore, make the very same assumption with regard to τ. Their puckering amplitudes are all in the neighborhood of 0.34 Å with error limits varying from less than ±0.01 Å[7,9] to as much as ±0.05 Å.[8] On the other hand, vibrational studies seem to be quite accurate in determining the barrier to ring inversion. The 6-31G* barrier of 0.90 kcal mol^{-1} has to be compared with a spectroscopic value of ca. 1.4 kcal mol^{-1} taken from the three recent IR-Raman investigations.[7-9] This comparison indicates that a q value of 0.23 Å is somewhat low. A further improvement of the basis may increase q.[31]

The puckering of cyclobutane is generally understood as a balance between ring strain and torsional strain: the former tends to keep the carbon ring planar, the latter tries to avoid eclipsing of adjacent methylene groups. The calculated geometry of the D_{2d} form clearly shows that torsional strain can be further diminished by tilting of the methylene groups in such a way that axial hydrogen atoms in the 1,3-position come closer together. The dihedral angle between an axial and an equatorial CH bond is increased from 17.2° ($\tau = 0°$) to 24.7° ($\tau = 4.4°$). This change is accompanied by a decrease of the 1,3-hydrogen-hydrogen distance from 3.01 to 2.88 Å, thus leaving the axial hydrogens still in the attractive range of the van der Waals potential. A tilting of the CH_2 groups in the opposite direction would destabilize the puckered form by reducing the ae-hydrogen, hydrogen dihedral angle and, therefore, increasing torsional strain. The amount of tilting is limited by increased CCH bond angle strain and 1,3 interactions. Therefore, four factors determine the degree of puckering of cyclobutane, namely ring strain, torsional strain, angle strain in the CH_2 groups, and 1,3-hydrogen-hydrogen interactions. The inversion of the ring has to be seen as a synchronized movement of the ring frame and the four methylene groups with q and τ being zero for the planar form and becoming negative for the inverted form.

Table II. Theoretical and Experimental Structural Parameters of Cyclobutane

Method	R_{CC}, Å	R_{CH}(ax), Å	R_{CH}(eq), Å	∠HCH, deg	q, Å	τ, deg
			Planar Form			
STO-3G	1.554	1.087		108.7		
4-31G	1.556	1.081		108.2		
6-31G*	1.549	1.084		107.9		
			Puckered Form			
STO-3G	1.553	1.086	1.086	108.8	0.125	2.1
4-31G	1.554	1.082	1.080	108.5	0.205	3.8
6-31G*	1.547	1.085	1.084	108.3	0.234	4.4
ED[a]	1.548 ± 0.003	1.092 ± 0.01		110	0.34	
NMR[b]	(1.548)[c]	1.133		108.1	0.26	4

[a] Reference 3. [b] Reference 11. [c] Taken from ref 3.

Conclusion

It has been shown that single determinant RHF theory using an extended basis set with polarization functions is sufficient to describe the equilibrium geometry and barrier to inversion of cyclobutane. Theoretical and experimental data are found to be in good agreement. The quantum mechanical calculations verify a significant coupling between ring puckering and methylene group tilting which was first found by Meiboom and Snyder.[11] It seems that this effect plays an important role in puckered ring systems with comparative strain.

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(27) The puckering amplitude q is equal to the distance between the two CC diagonals in the cyclobutane ring, i.e., twice the internal coordinate Z used in vibrational studies (ref 8). If α is taken to be the CCC angle, θ the angle between the two ring planes C(4)C(1)C(2) and C(2)C(3)C(4), and $\omega = \frac{1}{2}(180 - \theta)$, then the amplitude q can be calculated from $q = R_{CC} \cos(\alpha/2) \sin \omega$.
(28) The tilting angle is defined as the angle between the CCC bisector and the HCH bisector.
(29) D. Cremer, to be published.
(30) D. Cremer, to be published.
(31) Recent studies indicate that electron correlation plays a certain role in stabilizing the puckered form (D. Cremer, to be published).

Proton Shift Additivity and Substituent Interaction Parameters

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Abstract: The 4-substituted acetophenone family is characterized and its shifts are correlated with those of nine families of 1,4-disubstituted benzenes reported previously. Then a simple mathematical model is derived to account for the proton magnetic resonance shifts within families of 1,4-disubstituted benzenes. The model suggests that the substituents interact by σ-bond polarization. The polarization model rationalizes shift additivity and is consistent with the qualitative relationship between the number of valence electrons on a substituent and its capacity to induce shifts.

In a recent study the internal and meta proton shifts were correlated for nine families of 1,4-disubstituted benzenes.[1] The equations of correlation were used to predict shifts with an error of less than 3%, a marked improvement over the empirical equations of Diehl[2] or Dailey.[3] It was shown that the shift additivity concept of Diehl[2] could be applied to the internal shift equations and that 1,4-interactions, induced ring currents, and other effects[4] might be implicit contributors to the internal shift.

The study of a tenth family, the 4-substituted acetophenones, seems to complement our earlier work and has provided an opportunity to examine the equations of internal shift correlation in greater detail. It will be shown that 1,4 interactions can be written explicitly and may be used to assess the nature of substituent effects.

Results and Discussion

The proton shifts of the 4-substituted acetophenones are given in Table I. The equations of internal shift correlation relating the acetophenone family to previous data sets[1] are given in Table II and the coefficients of correlation are quite high. The relative magnitudes of the internal shifts suggest that the $COCH_3$ group provides a magnetic environment similar to the other α-carbonyl containing functions, placing it between the COOH and $COOCH_3$ groups in the spectrochemical series suggested by our earlier study.[1]

If one examines the relative magnitudes of the slope and intercept values for the equations of internal shift correlation in Table II of this and our earlier study,[1] he will note that the slope values range near unity. He might also observe that the coefficients of correlation are highest when the intercept values are small. Those two facts can be used to understand how the internal chemical shift incorporates basic information about substituent effects and chemical bonding in the 1,4-disubstituted benzenes.

The general equation internal shift correlation is

$$\Delta_{Z,R} = m_{R,S}\Delta_{Z,S} + b_{R,S} \quad (1)$$

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