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Structure, Equilibrium Conformation, and Pseudorotation in Cyclopentane. An Electron Diffraction Study[1,2]

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Abstract: Various approaches have revealed that cyclopentane molecules undergo free pseudorotation. It is shown in this study that gas-phase electron diffraction provides an alternative and sensitive measure of the pseudoradial puckering coordinate, q, but yields no direct information on the pseudorotational phase angle, ϕ. The mean and equilibrium values found, $\langle q \rangle = 0.427 \pm 0.015$ Å and $q_e = 0.438$ Å, are significantly lower than previously reported effective puckering displacements derived from thermodynamic and spectroscopic measurements, partly because of the somewhat uncertain physical significance of quantities determined from the latter types of measurement. The new values are in fair agreement, however, with recent calculations by Lifson and Warshel based on a model force field. Additional insight into the force field is also given by the measured amplitudes of vibration and the observed C–C bond length, 1.546 ± 0.0012 Å, which is 0.013 Å longer than the bond lengths in *n*-alkanes. The problem of vibrational averaging is briefly discussed.

Thermodynamic studies[4] gave the first experimental evidence that cyclopentane is puckered rather than planar. Semiquantitative calculations[5,6] relating structure and strain energy suggested, in addition, that the deformation is not static, but dynamic, with the puckering displacements progressing (pseudorotating) quite freely around the five-membered ring. Later thermodynamic studies[6–8] and energy calculations[9–11] have provided further support for this interpretation. Perhaps the most direct evidence for pseudorotation has come from a recent infrared spectroscopic study.[12] Subsequently, related five-membered ring systems have been found to undergo pseudorotation.[13,14] Cyclopentane has previously been studied by electron diffraction by both Hassel, *et al.*,[15] (visual method) and Bastiansen, *et al.*[16] While the latter work indicated that the molecule was nonplanar, no estimate was given of the degree of nonplanarity.

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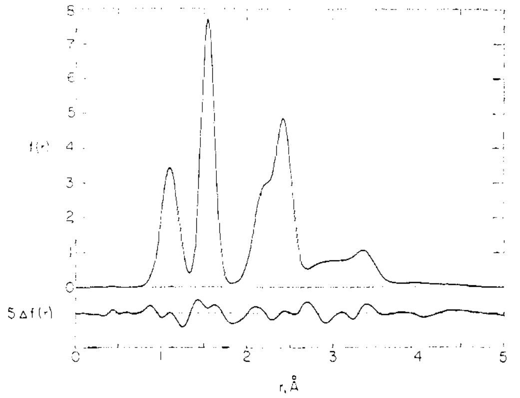

Figure 1. Experimental radial distribution function for cyclopentane; $\Delta f(r)$ represents $[f(r)_{\text{exptl}} - f(r)_{\text{calcd}}]$.

It was therefore thought worthwhile to reinvestigate the structure of this molecule to establish the amplitude of puckering involved in the pseudorotation. It also seemed desirable to investigate whether the Urey–Bradley potential energy minimization scheme of Jacob, Thompson, and Bartell[17] gives a satisfactory representation of cyclopentane.

Experimental Section

Phillips research grade cyclopentane of 99.99 mol % purity was used without further purification. Diffraction patterns were recorded on 4 × 5 in. Kodak process plates, at camera distances of 21, 11, and 6.5 cm, with 40-Kv electrons, in a diffraction apparatus[18,19] equipped with an r^3 rotating sector. The gas sample at 27 Torr was introduced into the 0.46-μA electron beam through a nickel nozzle having a throat 0.29 mm in diameter and 0.70 mm in length.

Photographic densities, measured with an automatic recording microphotometer with digital output,[20] were converted to absorbances and corrected for the radial variation of plate sensitivity.[21] Intensities were calculated from the corrected absorbances according to

$$I = A(1 + 0.05A^2)$$

as recommended by Janzen.[21] Six plates at the 21- and 6.5-cm distances and four plates at the 11-cm distance were averaged and used in the structural analysis.

Experimental intensities were leveled[22] using the analytical elastic scattering factors of Strand and Bonham[23] and the inelastic scattering factors of Heisenberg and Bewilogua.[24] Experimental leveled intensity, $I_0(s)$, and background intensity, $I_B(s)$, functions[22] for the three camera distances are available from ASIS.[2] Indices of resolution[25] were 1.035, 1.08, and 1.05 for the 21-, 11-, and 6.5-cm camera distances respectively.

Experimental and calculated molecular intensities and radial distribution functions were computed as previously described[22,25,26] with the usual corrections.[22,25–29] Radial distribution functions were calculated with $b = 0.0015$. Atomic scattering factors used in subsequent analyses were the partial wave elastic factors of Cox and Bonham[30] and the inelastic factors of Tavard.[31] Anharmonicity constants[28] were estimated[32] to be 2.0 Å^{-1} for the bonded distances and taken to be 1.0 Å^{-1} for nonbonded distances. In the calculation of the ring puckering it was assumed that the C···C nonlinear shrinkage correction was 0.002 Å.

Least-squares analyses were performed upon the anharmonic radial distribution function, the molecular intensity derived from each camera distance, and the composite molecular intensity curve.[33] The effects of both random and systematic errors were included in calculated standard errors as discussed by Bartell.[34] Systematic errors in bond lengths and mean amplitudes of vibration were estimated to be 0.07 and 2.0%, respectively. The principal systematic error in the mean amplitude of vibration arises from the uncertainty in the index of resolution.

Pseudorotation Model

A comparison of the experimental radial distribution function, Figure 1, and the calculated distribution function for a planar (D_{5h} symmetry) model of cyclopentane shows the ring to be decidedly nonplanar. First, the 2.4-Å C···C nonbonded peak is closer to the C–C bonded peak than would be possible in a planar ring. Secondly, the C···H nonbonded distribution near 3.2 Å is split into two components instead of appearing as the single nearly Gaussian peak to be expected for a planar skeleton. A pseudorotation description was therefore adopted which characterized the structures of all conformations of a freely pseudorotating molecule and made possible a comparison with previous thermodynamic[6–8] and infrared[12] studies. The description was modified somewhat from one proposed earlier by Kilpatrick, *et al.*,[6] as described below.

The pseudorotational descriptive model adopted is illustrated in Figure 2. Puckering displacements are described relative to the plane of the unpuckered, D_{5h} configuration of the carbon atom skeleton. An origin is centered on the carbon atom skeleton and a z axis is defined to be perpendicular to the skeletal plane. The dotted lines are hypothetical spokes of length

$$S_0 = (r_{\text{CC}}/2) \operatorname{cosec} (2\pi/10)$$

extending from the origin to the carbon atoms (1, . . . , 5) in their reference positions. The vectors $\mathbf{S}_j$ radiating from the origin define the instantaneous atomic positions of the carbon atoms. During the pseudorotation, each carbon atom is constrained to move in its respective vertical plane. The angular separation between adjacent vertical planes is $2\pi/5$ radians.

An angular displacement of the vector $\mathbf{S}_j$ from the horizontal reference plane is defined by

$$\alpha_j = \tan^{-1} (z_j/S_0) \qquad j = 1, \ldots, 5$$

in which z_j corresponds to the hypothetical perpen-

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(34) The effects of systematic interactions implicit in eq 27 of ref 19 were not taken into account.

Table I. Molecular Distances (Å) Calculated by the C_5H_{10} Pseudorotation Model for a Puckering Amplitude q = 0.435 Å

Parameter	Pseudorotational phase angle $\phi = 0°$ (C_s symmetry)	 $\phi = 5°$	 $\phi = 9°$ (C_2 symmetry)
C–H	1.1135	1.1135	1.1135
C–C	1.5460	1.5460	1.5460
$C\cdots H$	2.2140	2.2140	2.2140
$C_1\cdots C_3$	2.4716	2.4647	2.4573
$C_1\cdots C_4$	2.4052	2.4082	2.4144
$C_2\cdots C_4$	2.4716	2.4754	2.4764
$C_2\cdots C_5$	2.4357	2.4230	2.4144
$C_3\cdots C_5$	2.4357	2.4483	2.4573
$(C\cdots C)_{av}$	2.4440	2.4439	2.4444
$C_1\cdots H_{13}$, $C_4\cdots H_7$	2.8350 (2×)[a]	2.8695, 2.8186	2.9084, 2.8188
$C_2\cdots H_{14}$, $C_3\cdots H_{14}$	2.8584 (2×)	2.8302, 2.8994	2.8188, 2.9395
$C_5\cdots H_8$, $C_5\cdots H_{10}$	3.0208 (2×)	2.9552, 3.0899	2.9084, 3.1445
$C_2\cdots H_{13}$, $C_3\cdots H_7$	3.0449 (2×)	3.1073, 2.9844	3.1565, 2.9395
$C_1\cdots H_{10}$, $C_1\cdots H_{11}$	3.2557 (2×)	3.3000, 3.1966	3.3285, 3.1445
$C_4\cdots H_8$, $C_4\cdots H_9$	3.2557 (2×)	3.2031, 3.3065	3.1565, 3.3402
$C_5\cdots H_9$, $C_5\cdots H_{11}$	3.3695 (2×)	3.3808, 3.3505	3.3861, 3.3285
$C_2\cdots H_{12}$, $C_3\cdots H_6$	3.3925 (2×)	3.3674, 3.4083	3.3402, 3.4150
$C_1\cdots H_{12}$, $C_4\cdots H_6$	3.3939 (2×)	3.3897, 3.3993	3.3861, 3.4045
$C_2\cdots H_{15}$, $C_3\cdots H_{15}$	3.4153 (2×)	3.4098, 3.4173	3.4045, 3.4150

[a] The same value was calculated for both distances.

dicular displacement

$$z_j = \sqrt{2/5}q \cos [2(2\pi j/5 + \phi)]$$

associated with an e_2'' symmetry coordinate. The displacements, then, are characterized by two independent parameters, q and ϕ, the pseudoradial puckering amplitude and pseudorotational phase angle, respectively. In the model of Kilpatrick, *et al.*,[6] z_j corresponds to the actual perpendicular displacement of carbon atom j from the reference planar configuration. In Kilpatrick's displacements, the Eckart conditions are satisfied, but unfortunately, the individual C–C bond lengths in the molecule are much more strongly dependent on both q and ϕ than seems physically reasonable. A scheme to circumvent the problem of nonconstant bond lengths was devised for the present investigation. Atomic displacements are constrained to the vertical planes of the Kilpatrick model, but the actual displacement amplitudes are described in terms of the angles α_j rather than the distances z_j. The vectors $\mathbf{S}_j$ are then varied in length, as q and ϕ vary, in order to preserve all C–C bond lengths. That is, for any given q and ϕ, the individual α_j are unambiguously specified, as are the five angles between adjacent $\mathbf{S}_j$'s. These five angles relate the $\mathbf{S}_j$ to the individual r_{CC} and give five simultaneous equations for $|\mathbf{S}_j|$ which must be satisfied if the C–C bonds are to remain invariant. A solution yields trajectories of carbon atoms which, for a given q, are nearly parabolic instead of linear as in the model of Kilpatrick, *et al.* It is notable, however, that the actual distance traveled by atom j from the reference configuration is equal (within 0.3%) to the perpendicular displacement z_j in the Kilpatrick, *et al.*, model.

Although the present scheme rigorously preserves the C–C bond lengths, it does not satisfy the Eckart conditions exactly.[35] The center of mass of the molecule rotates about the defined z axis, in a pseudorotational cycle, with a radius of 0.0236 Å for q = 0.435 Å. This has no influence on the diffraction analysis, but shows the need for a minor correction to

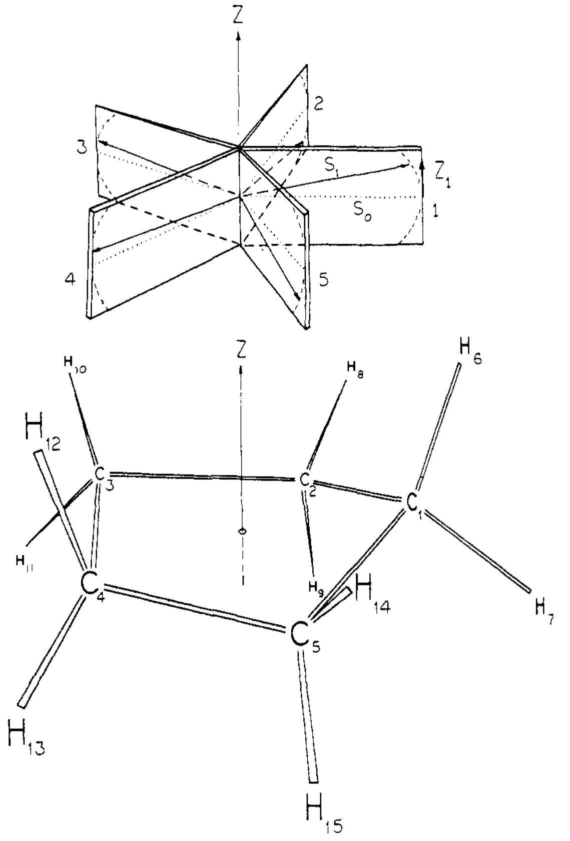

Figure 2. Molecular model and pseudorotational displacement parameters for cyclopentane. One of the ten equivalent C_s conformers is shown (that with ϕ = 108°).

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$$q_{cor} = q - [M/(2m_0q)]\delta^2$$

where q is defined as in the text, q_{cor} is the displacement appropriate for dynamical problems, M is the molecular weight, m_0 is the reduced mass for the puckering mode, and δ is the radius with which the center of mass wobbles about the z axis defined for the present pseudorotation model. The correction is only about four parts per thousand in q for cyclopentane and will be neglected in the text.

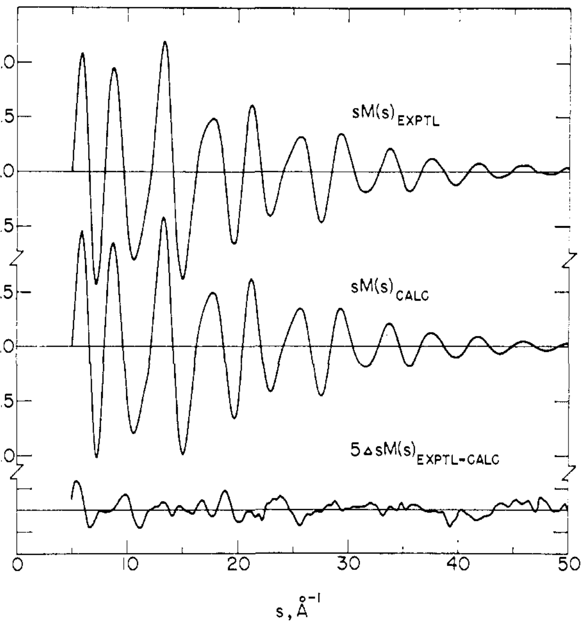

Figure 3. Comparison of experimental and calculated molecular intensity functions for cyclopentane; $\Delta sM(s)$ represents $[sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}]$.

the displacement coordinates in treatments of dynamical properties.

The hydrogen atoms (6, ..., 15), Figure 2, were constrained to follow the motion of the carbon atoms in order to preserve local C_{2v} symmetry at each methylene group. All CCH valency angles were assumed to be equal.

Results

Intramolecular distances (excepting H···H distances) calculated by the pseudorotation model for a puckering amplitude, $q = 0.435$ Å, at three different pseudorotational phase angles are given in Table I. Included in Table II are the CCC valency angles and torsional angles β^i for these conformations as well as the sums

$$^1/_2\sum_{i=1}^{5}(\theta^i - \theta^0)^2$$

and

$$^1/_2\sum_{i=1}^{5}[1 + \cos(3\beta^i)]$$

where θ^i and θ^0 are the instantaneous and reference CCC angles for each of these conformations.

Table II. Valency and Torsional Angles[a] Calculated by the C_5H_{10} Pseudorotation Model for a Puckering Amplitude $q = 0.435$ Å

Parameter	Pseudorotational phase angle $\phi = 0°$ (C_s symmetry)	 $\phi = 5°$	 $\phi = 9°$ (C_2 symmetry)
$\angle C_2\text{–}C_1\text{–}C_5$	103.947	103.191	102.676
$\angle C_1\text{–}C_2\text{–}C_3$	106.134	105.714	105.257
$\angle C_2\text{–}C_3\text{–}C_4$	106.134	106.373	106.432
$\angle C_3\text{–}C_4\text{–}C_5$	103.947	104.709	105.257
$\angle C_4\text{–}C_5\text{–}C_1$	102.134	102.309	102.676
$^1/_2\sum_{i=1}^{5}(\theta^i - \theta^0)^{2\,b}$	68.572	68.567	68.553
$\angle C_5\text{–}(C_1\text{–}C_2)\text{–}C_3$	25.012	30.572	34.342
$\angle C_1\text{–}(C_2\text{–}C_3)\text{–}C_4$	0.0	7.398	13.164
$\angle C_2\text{–}(C_3\text{–}C_4)\text{–}C_5$	25.012	18.669	13.164
$\angle C_3\text{–}(C_4\text{–}C_5)\text{–}C_1$	40.265	37.433	34.342
$\angle C_4\text{–}(C_5\text{–}C_1)\text{–}C_2$	40.265	41.888	42.290
$^1/_2\sum_{i=1}^{5}[1 + \cos(3\beta^i)]^c$	2.74625	2.74629	2.74632

[a] Angles are in degrees, with the absolute values of torsional angles reported. [b] θ^i corresponds to the CCC valency angles, with the reference CCC valency angle, θ^0, taken to be tetrahedral. The corresponding sum for a planar ring is 5.40. Note that a revised reference θ^0 cannot influence the ϕ dependence of the sum since $\Sigma\theta^i$ is independent of ϕ. [c] β^i corresponds to the C–(C–C)–C torsional angles.

The composite experimental reduced molecular intensity, $sM(s)$

$$sM(s) = s\{[I_0(s)/I_B(s)] - 1\}$$

and its calculated counterpart computed using the parameters given in Table I (but including H···H distances) for the $\phi = 0°$ model are compared in Figure 3. The experimental radial distribution function is shown in Figure 1 and is compared with the distribution function calculated using the parameters of the same $\phi = 0°$ (C_s) model. Equally excellent fits were obtained using the parameters given for the $\phi = 5$ and $9°$ (C_2) models, indicating that the experimental diffraction intensities are independent of the phase angle of puckering. However, the experimental diffraction intensities are sufficiently sensitive to the puckering displacement that the mean value, $\langle q \rangle$, may be determined from the radial distribution function by comparing the mean C–C bonded and C···C nonbonded distances. The CCH valency angle is derived from the mean C···H nonbonded distance at 2.2 Å, while the spectrum of long C···H nonbonded distances centered around 3.2 Å checks the consistency of the model and the derived parameters. The converged set of structural parameters and their estimated standard errors are given in Table III. It may be noted that the spectrum of C···H nonbonded distances computed using the pseudorotation model allows the broad asymmetric, composite peak centered near 3.2 Å to be well fitted with a single value for the amplitude of vibration assigned to each component C···H distance.

Table III. Structural Parameters[a] and Estimated Standard Errors[b] for C_5H_{10}

Parameter	r_g	l_g
C–H	$1.113_5 \pm 0.001_5$	$0.081_5 \pm 0.002_1$
C–C	$1.546 \pm 0.001_2$	$0.053_5 \pm 0.001_1$
$(C\cdots H)_{\text{short}}$	$2.214 \pm 0.002_1$	0.110 ± 0.003
$(C\cdots C)_{\text{mean}}$	$2.444 \pm 0.001_5$	$0.071_5 \pm 0.001_6$
$(C\cdots H)_{\text{long}}{}^c$		0.113 ± 0.004
$\langle q \rangle^d$	$0.42_7 \pm 0.01_5$	
$\angle$CCH = 111.7 ± 0.2[e]		

[a] Distances and amplitudes in Å, angle in degrees. [b] The effects of both random and systematic errors[19,34] were included in calculated standard errors. [c] Internuclear distances constrained to be the same as those given in Table I. [d] Derived assuming a C···C shrinkage of 0.002 Å. [e] Not corrected for shrinkage effects.

A matrix of correlation coefficients based on the least-squares fit of the composite molecular intensity using a diagonal weight matrix

$$W(s) = 1 - \exp[-0.00828(s - 2.827)^2]$$

is given in Table IV.

Table IV. Matrix of Correlation Coefficients[a] for C_5H_{10}

	r(C–H)	r(C–C)	r(C···H)^b	r(C···C)	l(C–H)	l(C–C)	l(C···H)^b	l(C···C)	l(C···H)^c	R
$\sigma^0(\theta_i)^d$	0.63	0.23	1.19	0.57	0.66	0.36	0.99	0.60	3.01	0.004
r(C–H)	1.0	0.03	−0.09	−0.01	0.02	0.09	0.09	0.10	−0.00	0.20
r(C–C)		1.0	−0.12	−0.07	0.12	−0.00	0.05	0.03	0.00	0.04
r(C···H)^b			1.0	0.48	−0.18	−0.30	−0.23	−0.12	−0.08	−0.42
r(C···C)				1.0	−0.03	−0.04	−0.20	−0.06	−0.16	−0.05
l(C–H)					1.0	0.23	0.15	0.18	0.02	0.38
l(C–C)						1.0	0.25	0.32	0.04	0.70
l(C···H)^b							1.0	0.57	−0.04	0.37
l(C···C)								1.0	−0.06	0.46
l(C···H)^c									1.0	0.05
R^e										1.0

[a] Based on 149 intensity values interpolated from 328 experimentally observed data points. Matrix elements are given by $\rho_{ij} = (B^{-1})_{ij}/[(B^{-1})_{ii}(B^{-1})_{jj}]^{1/2}$, where the notation corresponds to that of O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957). [b] Short nonbonded distance. [c] Long nonbonded distance. [d] Standard deviation from zero-order error matrix, ref 19; distances in thousandths of an ångström unit. [e] Index of resolution.

Conformational Energy Calculations. Conformational energy calculations were carried out as previously discribed,[17] using the modified Urey–Bradley potential energy function of Jacob, Thompson, and Bartell, composed of quadratic terms for bond stretches and bond angle bends, a threefold cosine function for rotations about C–C bonds, and anharmonic analytical functions for pairwise nonbonded interactions between all nonbonded pairs. The C–C and C–H bond lengths and CCH angles were varied freely to achieve minimum potential energy. The CCC valency angles and torsional angles about C–C bonds were calculated using the described pseudorotation model, for various fixed values of the amplitude and phase angle of puckering.

Calculated potential energies for a given puckering displacement, q, were found to be the same for any phase angle of puckering to within 3 cal/mol. However, the present calculations show that the simplified, universal hydrocarbon potential function proposed by Jacob, *et al.*, in their investigation of acyclic alkanes[17] does not give a quantitative representation of the cyclopentane force field. It yielded the rather low equilibrium puckering displacement of $q_e = 0.33$ Å, in comparison with the present experimental value of 0.44 Å. Nevertheless, it did yield satisfactory values for the other structure parameters. Bond lengths computed by forcing the puckering amplitude to have its experimental value, $q_e = 0.44$ Å, were 0.017 Å longer for C–C and 0.002 Å longer for C–H than the analogously calculated ethane values.[17] The corresponding experimental quantities[20] are 0.012 ± 0.002 and 0.002 ± 0.002 Å.

The low calculated value of q_e turns out to be of value in diagnosing the nature of the imperfections of the published Urey–Bradley model force field.[17] Such a force field necessarily contains a large number of parameters (various quadratic constants, reference bond lengths and angles, and, most speculative of all, parameters characterizing the nonbonded potential functions). In the exploratory work of Jacob, *et al.*,[17] parameters were not optimized or adjusted to fit a large body of data, but most studies in the literature using modified valence force fields attempt an optimization of parameters. In adjusting these to fit a small number of observable structures, energies, and vibrational frequencies, a fairly large ambiguity results, particularly since the fields commonly chosen neglect various interaction constants, absorbing their effects into other constants.[17,36] Of particular interest for the present force field is the observation that model calculations for the similar C–CH_2–C groups in the linear molecule, *n*-pentane, and in the cyclic molecule, cyclopentane, exhibit contrasting deficiencies. For the former molecule the calculated C–CH_2–C angle is too *small*, whereas, for the latter molecule, it is too *large* (*i.e.*, the five-membered ring is insufficiently distorted from planarity). If both molecules are to be represented by the same universal force field parameters, the difficulty cannot lie in the reference bond angles (selected for simplicity as 109° 28′ in ref 17), since the discrepancies are in opposite directions. The difficulty may lie partly in the quadratic bending constants, since the combined valence and nonbonded angular restoring forces were recognized by Jacob, *et al.*,[17] as being somewhat too large on the basis of spectroscopic force fields.[37] This would make CCC angles tend too strongly to seek their reference values. Probably of at least as great importance, however, is the fact that a shallower, less "hard" nonbonded repulsion for C···C and/or C···H interactions would have facilitated larger deformations of the C–CH_2–C groups from their reference tetrahedral structures. This is one of the more direct pieces of evidence that the 6–12 potential originally adopted for C···C for want of better information,[38] and expected to be too hard at short C···C distances, is indeed too hard.

Discussion

The 1.546-Å C–C bond in cyclopentane is appreciably longer than that in ethane, 1.534 Å,[20] and in higher *n*-alkanes, 1.533 Å.[39,40] This lengthening is undoubtedly ascribable in part to the classical atom–atom nonbonded repulsions between carbons, as predicted semiquantitatively by the Urey–Bradley model field, since the mean C···C distance of 2.444 Å in cyclo-

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(36) L. S. Bartell and K. Kuchitsu, *J. Chem. Phys.*, 37, 691 (1962).

(37) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(38) L. S. Bartell, *J. Chem. Phys.*, 32, 827 (1960).

(39) It is also appreciably longer than the value 1.537 ± 0.002 Å reported by K. Tanner and A. Weber, *J. Mol. Spectrosc.*, **10**, 381 (1963), in a Raman study of C_5H_{10} and C_5D_{10}, based on the assumption of D_{5h} symmetry. If, however, the ring puckering is taken into account, a mean CC bond about 0.01 Å longer is required to reproduce the observed moments of inertia.

(40) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959).

pentane is substantially shorter than the average value of 2.545 Å in the *n*-hydrocarbons. It is also attributable, in part, to the distinctly different bond–bond repulsion[41,42] encountered during eclipsing (small ϕ) that is now considered to account for the rotational barrier.[41] This repulsion is not built into the Urey–Bradley model field of Jacob, *et al*, but is roughly incorporated into EHMO calculations[43] which, as shown by Dallinga and Ros,[44] predict slightly long bonds for cyclopentane. Of some interest is the fact that, as the puckering phase rotates around the ring, the most completely eclipsed bonds are associated with the longest C···C interactions (strongest bond–bond with weakest atom–atom respulsions) and *vice versa.* Consequently, there are compensating stresses at all phase angles, and all C–C bonds tend to be similarly elongated.

An inspection of the spectrum of nonbonded distances for a given puckering amplitude, as given in Table I, shows that the individual nonbonded distances vary with the pseudorotational phase angle but that the envelope of the distribution function does not. Accordingly, it is not possible to establish by electron diffraction whether the molecule is undergoing dynamic pseudorotation or whether it exists in a single static conformation. Nevertheless, this fact and the following quantities, computed according to the pseudorotation model, provide insight into the pseudorotational potential energy function. As shown in Table III, the sums

$$^1/_2\sum_{i=1}^{5}(\theta^i - \theta^0)^2$$

and

$$^1/_2\sum_{i=1}^{5}[1 + \cos(3\beta^i)]$$

over CCC valency angles and torsional angles, which are associated closely with the potential energy of bending and internal rotation about C–C bonds, are nearly independent of ϕ (to within 0.3 and 0.025 part per thousand, respectively). Similarly, since the spectrum of nonbonded distances in the molecule is virtually independent of ϕ as noted above, it is apparent that the nonbonded contribution to the potential energy is also nearly independent of ϕ. These results suggest why potential energy calculations[5–11] employing significantly different force fields all yielded potential energies essentially independent of the pseudorotational phase angle. These findings support the contention of Lifson and Warshel[11] that "the existence of an equal potential path is more due to the geometry of cyclopentane than to the exact nature of the intermolecular forces."

Finally, it is instructive to compare values of the pseudoradial coordinate q, the ring puckering displacement, as inferred by various approaches including thermodynamic, spectroscopic, model force field, and electron diffraction methods.[45] These are listed in Table V. In the case of the model force fields, the reported torsional angles have been converted into the corresponding "equilibrium" displacement, q_e, associated with minimum potential energy.

Table V. Ring Puckering Displacement, q, Found by Various Methods

Method	Value, Å
Thermodynamic	$q_{\text{eff}} = 0.48^a$
Spectroscopic	$q_0 = 0.479^b$
Model force field	$q_e = 0.49^c$
	$q_e = 0.42_7{}^d$
Electron diffraction	$\langle q \rangle = 0.42_7{}^e$
	$q_e \approx 0.43_8$

[a] Pitzer and Donath, ref 9, effective displacement. [b] Durig and Wertz, ref 12, from effective pseudorotational moment of inertia, $m_0q_0^2$, for observed e_2'' transitions in combination bands. [c] Hendrickson, ref 10. [d] Lifson and Warshel, ref 11. [e] This investigation, at room temperature. The symbol $\langle q \rangle$ represents the thermal average puckering displacement and q_e represents the equilibrium (minimum potential energy) displacement.

In view of the appreciable differences between the displacements found by different methods, the influence of puckering anharmonicity was considered. The electron diffraction value corresponds to a mean value, $\langle q \rangle$, averaged over the vibrating ensemble. It should be smaller than the minimum energy value, q_e, by virtue of the asymmetry of $V(q)$ about $q = q_e$. It may be shown[28,46] that

$$q_e \approx \langle q \rangle - (3/2)al_q^2$$

where a is the Morse-like asymmetry constant

$$a = -(1/3)[(\partial^3V(q)/\partial q^3)/(\partial^2V(q)/\partial q^2)]_{\text{equil}}$$

and l_q^2 is the mean square pseudoradial amplitude of vibration given by[47]

$$l_q^2 = (h/8\pi^2\mu_q\nu_q)\coth(h\nu_q/2kT)$$

If the observed[9] pseudoradial frequency of 283 cm^{-1} and reduced mass[6] of 28.1 amu are used with an estimated[9] value for a of -2 Å^{-1}, an equilibrium puckering

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(41) O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, 49, 2592 (1968).

(42) H. J. Monkhorst, *Chem. Phys. Lett.*, 4, 119 (1969).

(43) R. Hoffmann, *J. Chem Phys.*, **39**, 1397 (1963).

(44) G. Dallinga and P. Ros, *Recl. Trav. Chim. Pays-Bas*, **87**, 906 (1968).

(45) It is fair to note that the puckering displacement q is defined only in terms of the model of pseudorotation with which the experimental data are fitted. For infinitesimal displacments from D_{5h} there is no ambiguity, but anharmonic effects over and above those of $V(q)$ itself (discussed in the subsequent text) cloud the precise meaning of q. The electron diffraction observable, from which q is inferred, is essentially the ratio of the nonbonded to the bonded CC distances, and the dependency of the ratio on q is of the form

$$\frac{\langle r(\text{C}\cdots\text{C})\rangle}{\langle r(\text{C–C})\rangle} = \left[\frac{r(\text{C}\cdots\text{C})}{r(\text{C–C})}\right]_{D_{5h}} - K_2q^2 + \ldots$$

where K_2 and higher coefficients are derivable from considerations of geometry if the pseudorotation model is specified. Most inferences of q_e from model force fields are based, as is the present diffraction analysis, on the constraint that C–C bonds around the ring are uniform in length. It is important to determine whether the inference of q is so model dependent that q has scant fundamental significance. A full answer to this question has not been given, but the following observation is useful. If the Pitzer model of linear displacement trajectories is adopted, the individual bond lengths for $q = 0.435$ Å become, for a C_2 conformer, say, 1.5014, 1.5326 (twice), and 1.5817 Å (twice) for a mean length of 1.5460 Å. This quite variable, probably excessively variable, set leads, nevertheless, to a mean nonbonded distance of 2.4401 Å in comparison with the value of 2.4440 yielded by the present uniform C–C model for the same value of q. This difference is comparable to errors in current experiments. The analog of the ratio $\langle r(\text{C}\cdots\text{C})\rangle/\langle r(\text{C–C})\rangle$ as a function of q for the molecule tetrahydrofuran[13] was also found to be very insensitive to depatures of the pseudorotational reference structure from D_{5h} symmetry. Therefore, since it is useful to express the puckering deformation in terms of one parameter, it appears that the parameter q is a reasonably satisfactory one and that it may be understood to be expressed operationally in terms of the above expanson of $\langle r(\text{C}\cdots\text{C})\rangle/\langle r(\text{C–C})\rangle$ as a function of q under the constraint of uniform C–C bond lengths.

(46) L. S. Bartell, *J. Chem. Phys.*, **38**, 1827 (1963).

(47) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier, Amsterdam, 1968, p 89.

deformation, $q_e = 0.438$ Å, is calculated from the observed mean value, $\langle q \rangle = 0.427$ Å, taking the temperature to be that of the diffraction nozzle, 298°K. In comparsions with puckering values calculated from model force fields ("molecular mechanics"), the quantity q_e corresponding to minimum potential energy is the appropriate parameter to consider.

The earlier thermodynamic, model force field, and spectroscopic puckering displacements of 0.48 Å were in remarkable accord with each other and seemed to settle the matter. It now appears, however, that the physically significant mean and equilibrium displacements, $\langle q \rangle$ and q_e, are appreciably smaller than the effective displacements determined previously. The revised puckering is also somewhat less than that found in the D ring of steroids thus far investigated by X-ray diffraction,[48] the five-membered ring in this case being *trans*-fused to the chair form of a six-membered ring. Supporting the revised values are new infrared measurements by Hirakawa[49] and electron diffraction studies by Kuchitsu.[50] In the infrared work, a systematic, anharmonic trend was noted which led to the extrapolated value of $q_e = 0.45$ Å, in satisfactory agreement with both electron diffraction values and with the newer model force field calculations of Lifson and Warshel. The improved experimental values and physical interpretation should be helpful in establishing better model force fields for conformational calculations.

Acknowledgment. We are indebted to the Michigan Computing Center for a generous allowance of computing time, and to Professor Kuchitsu for making available his infrared and diffraction results prior to publication.

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(48) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron Lett.*, 1383 (1967); C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 24, 13 (1968).

(49) H. Kambara, A. Hirakawa, M. Tsuboi, and K. Kuchitsu, in preparation.

(50) Y. Morino, K. Kuchitsu, and H. Kambara, in preparation.

Application of Simple Theoretical Methods to the Solution of Chemical Problems. III. Hyperconjugation *vs.* 1–3 Conjugation as the Mechanism for Electron Spin Delocalization to β Fluorines[1]

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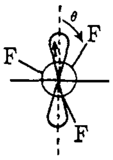
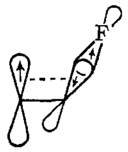
Abstract: The dependence of the β-fluorine hyperfine splitting constant (hfsc) on the dihedral angle, θ, is studied. The experimental nitrogen and fluorine hfsc's for a series of *t*-butylperfluoroalkyl nitroxides were determined, and it was found that the fluorine hfsc decreases as θ increases. INDO calculations on CF_3-NO-CF_3 showed a maximum fluorine hfsc at $\theta = 0°$. It is concluded that 1–3 conjugation between the p_z orbital on nitrogen and the p orbital of fluorine which is perpendicular to the plane formed by N, C, and F is not a significant mechanism of spin delocalization, but that the results are interpretable in terms of hyperconjugation.

The effect of geometry on the magnitude of epr hyperfine splitting constants (hfsc's) must be considered in evaluating the relative importance of the various possible spin delocalization mechanisms. For α and β hydrogens these mechanisms have been quite well established[2,3] and for more distant hydrogens certain empirical rules have been developed.[4]

In this paper we direct our attention to fluorine hfsc's with particular emphasis on the dependence of the β-fluorine hfsc upon the dihedral angle, θ, between the C–F bond and the π system containing the unpaired electron. This subject is of importance because there are two major mechanisms which have been proposed to account for the interaction between the β fluorines and an unpaired electron. The first is hyperconjugation, by which we mean the interaction of the electron on atom 1 with the electrons in the C_2–F σ bond so as to produce an excess of α spin at the fluorine nucleus. This mechanism, which is analogous to that proposed for β-hydrogen hyperfine interactions, would result in a maximum coupling constant at $\theta = 0°$. These β-hydro-





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[2] (a) H. M. McConnell, *J. Chem. Phys.*, 28, 1188 (1958); (b) H. S. Jarrett, *ibid.*, 25, 1289 (1956); (c) R. Bersohn, *ibid.*, 24, 1066 (1956); (d) S. I. Weissman, *ibid.*, 25, 890 (1956).

[3] C. Heller and H. M. McConnell, *ibid.*, 32, 1535 (1960).

[4] (a) G. A. Russell and G. R. Underwood, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; (b) G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 3.