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# Pseudorotation in Cyclopentane. An Experimental Determination of the Puckering Amplitude by NMR in Oriented Solvents

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**Abstract:** Proton NMR spectra of normal cyclopentane, 1,2,2′,5,5′-pentadeuteriocyclopentane, and randomly deuterated cyclopentane in liquid crystalline solvents between −30 °C and +110 °C are reported. The spectra yield all possible distinct average dipolar interactions between the protons in the molecule. These results are compared with the predictions of five different theoretical models for the dynamic puckering deformation of cyclopentane. Although the general trend in these models is consistent with the experimental results, there is no exact agreement between the average dipolar interactions calculated from these models and those obtained experimentally. The experimental results are then subjected to a best-fit analysis in terms of Pitzer's pseudorotation model, using the modification of Adams et al., with the puckering amplitude, $q$, as a single adjustable parameter. A perfect agreement between the experimental dipolar parameters and those calculated from this model is obtained with $q = 0.463$ Å.

It is generally accepted that cyclopentane and other five-membered saturated ring molecules undergo fast pseudorotation—a puckering displacement that moves around the ring in a more or less barrier-free potential.[1] The concept of pseudorotation was first introduced by Kilpatrick, Pitzer, and Spitzer[2] to account for the inconsistency in the entropy determined by calorimetry for cyclopentane in the gas phase and the value calculated from spectroscopic data. The pseudorotation consists essentially of a linear superposition of the two (degenerate) out-of-plane normal modes for a regular pentagon (Figure 1):

$$Z_i = a\cos\left[\frac{4\pi}{5}(i-1)\right] + b\sin\left[\frac{4\pi}{5}(i-1)\right] = (2/5)^{1/2}\, q\cos\left[\frac{4\pi}{5}(i-1) - P\right] \qquad (1)$$

where $q = (5/2)^{1/2}(a^2 + b^2)^{1/2}$ and $P = tg^{-1}(b/a)$ are respectively the amplitude and phase of the pseudorotation. The two deformations are commonly referred to as the envelope ($C_s$) and half-chair or twist ($C_2$) modes. For the cyclopentane molecule there is ample experimental and theoretical evidence that the puckering energy is essentially independent of $P$.[1] Accordingly, there is a continuous transformation between the various envelope, twist, and intermediate conformations with apparently equal probability for all $P$ values. The puckering energy is however sensitive to the amplitude $q$, and since the original suggestion of the pseudorotation model several experiments[3-6] and a large number of theoretical works[7-11] were devoted to substantiate the model and determine the magnitude of $q$. Most of the theoretical work[7-9] is patterned on the semiempirical force-field method as outlined many years ago by Westheimer.[12] Only relatively recently was a quantum-mechanical ab initio calculation of cyclopentane also reported.[10] Most of the experimental studies involve infrared and microwave spectroscopy and their interpretation depends strongly on the molecular potential assumed in the analysis. An important exception is the study of Adams et al.,[5] who used the electron-diffraction method which provides a direct measure of the average interatomic distances. In this study however the amplitude $q$ was determined essentially from a single experimental parameter, i.e., the ratio between the distances of the nonbonded C···C to bonded C–C carbons.

In the present work we use a different approach to determine the puckering amplitude in cyclopentane by recording and analyzing its proton NMR spectrum in liquid crystalline solvents. The advantage of this method is that it provides data on the average dipolar interaction between all pairs of protons in the molecule, from which consistent information related to the molecular geometry can be derived.[13] The results strongly support the pseudorotational model of Kilpatrick et al. and also provide an accurate value for the puckering amplitude.

## Experimental Section

**A. Material and Sample Preparation.** As will be shown below the spectrum of normal cyclopentane in a liquid crystalline solvent is too complicated to analyze and we have therefore resorted to the use of deuterated species which gave simpler spectra and provided all the necessary parameters. The following deuterated compounds were prepared: (i) cyclopentane-*1,2,2′,5,5′*-$d_5$ (CP-$d_5$) was prepared from cyclopentanone with use of standard procedures. First the α hydrogens were substituted with deuterium by exchange with $D_2O$ to form cyclopentanone-*2,2′,5,5′*-$d_4$ (~90% deuterium enrichment). This compound was then reduced with $LiAlH_4$ to form cyclopentanol-*2,2′,5,5′*-$d_4$ from which cyclopentyl bromide and then cyclopentylmagnesium bromide were prepared. The latter compound was finally decomposed with $D_2O$ (99.7%) to yield the desired product cyclopentane-*1,2,2′,5,5′*-$d_5$. (ii) The second deuterated species that we have used was randomly deuterated cyclopentane, prepared by exchange of normal cyclopentane with deuterium gas according to the method of Miller and Inskeep.[3] Two samples were prepared in which the deuterium enrichment was respectively 80 and 90 atom %.

Two types of liquid crystalline solvents were used in this study; bis(hexyloxy)azoxybenzene (DHAB) which has a nematic mesophase be-

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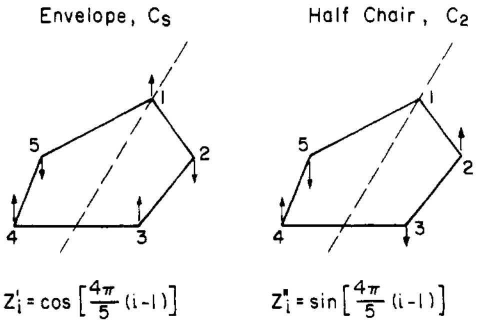

**Figure 1.** The atomic displacements for the two degenerate out-of-plane vibrations of a regular pentagon. The numbers label the atoms and the dashed lines correspond to the $C_2$ axis in the half-chair conformation and the dividing line for the symmetry plane in the envelope conformation. The arrows indicate the relative direction of displacements perpendicular to the average plane, and $Z_i'$ and $Z_i''$ are proportional to the magnitude of the displacements in the envelope and half-chair conformation, respectively.

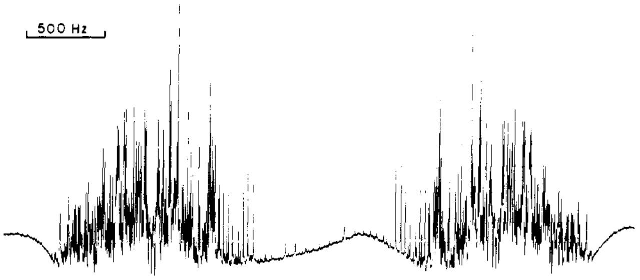

**Figure 2.** The proton NMR spectrum of a 3.5 wt % solution of normal cyclopentane in bis(hexyloxy)azoxybenzene, $t$ = 98 °C.

tween 72 °C and 130 °C, and phase V which was used to obtain spectra from room temperature down to −40 °C. The concentrations of the solutions were in the range 2–8 wt %. They were kept in sealed, degassed 5-mm sample tubes.

**B. NMR Measurements.** Proton NMR measurements were made with a Bruker WH270 NMR spectrometer at 270 MHz. The proton spectra of the deuterated species were recorded under conditions of deuterium decoupling.[14,15] For that purpose we have disabled the deuterium lock system and used it instead for introducing the deuterium-decoupling frequency. This frequency (41.45 MHz) was generated from a PTS-160 synthesizer locked to the 10 MHz standard frequency of the WH270 console and amplified by an ENI (350L) broad-band power amplifier. A Bird Electronic Co. Watt meter (Model 4314) was used to monitor the power incident on the radio-frequency coil. The maximum power used was 6 W. This was sufficient to decouple essentially all proton–deuteron dipolar interactions in the deuterated cyclopentane solutions, except that for the geminal H–D interaction the available power was just below the optimal value and a small amount of structure due to incomplete decoupling still remained in the spectrum.

## NMR Spectra of Cyclopentane in Liquid Crystalline Solvents

**A. Normal Cyclopentane.** The NMR spectrum of normal cyclopentane dissolved in bis(hexyloxy)azoxybenzene (3.5 wt % at 98 °C) is shown in Figure 2. As would be expected for a 10-spin system the spectrum is extremely rich in lines, and although its resolution is quite satisfactory it is too complex for a quantitative interpretation. Also the simulation of 10-spin spectra on the basis of trial and error would be beyond our computer capabilities. We therefore used partially deuterated cyclopentane species and studied their proton spectra in the presence of deuterium decoupling.[14,15]

As indicated in the experimental section two different types of deuterated species were used, i.e., cyclopentane randomly deuterated and cyclopentane specifically deuterated at positions 1, 2, 2′, 5, and 5′. On the basis of the assumption of fast pseudorotation, the cyclopentane spectrum in liquid crystals should exhibit five distinct dipolar (and scalar) interactions, viz, $D_{11'}$, $D_{12}$, $D_{12'}$, $D_{13}$, and $D_{13'}$ (and $J_{11'}$, $J_{12}$, $J_{12}'$, $J_{13}$, $J_{13'}$), where the numbering is as in Figure 1, and primed and unprimed numbers refer to hydrogens below and above the molecular plane. It turned out that in order to determine the magnitude and relative signs of all these coupling constants it was indeed necessary to use both types of deuterated species indicated above.

Table I. Abundancies of Isotopic Species, the Number of Isomers for Each Species, and the Expected $^1H\{^2D\}$ NMR Spectrum for Each Isomer in a Liquid Crystalline Solvent in Samples of Cyclopentane Enriched to Respectively 90% and 80% Deuterium with Statistical Distribution

| | species | | | | |
|---|---|---|---|---|---|
| | $C_5D_{10}$ | $C_5D_9H_1$ | $C_5D_8H_2$ | $C_5D_7H_3$ | others |
| abundancy (90%) | 34.9 | 38.7 | 19.4 | 5.7 | 1.3 |
| abundancy (80%) | 10.7 | 26.8 | 30.2 | 20.1 | 12.2 |
| no. of isomers | 1 | 1 | 5 | 8 | |
| $^1H\{^2D\}$ spectrum | | singlet | doublet | symmetric septuplet | |

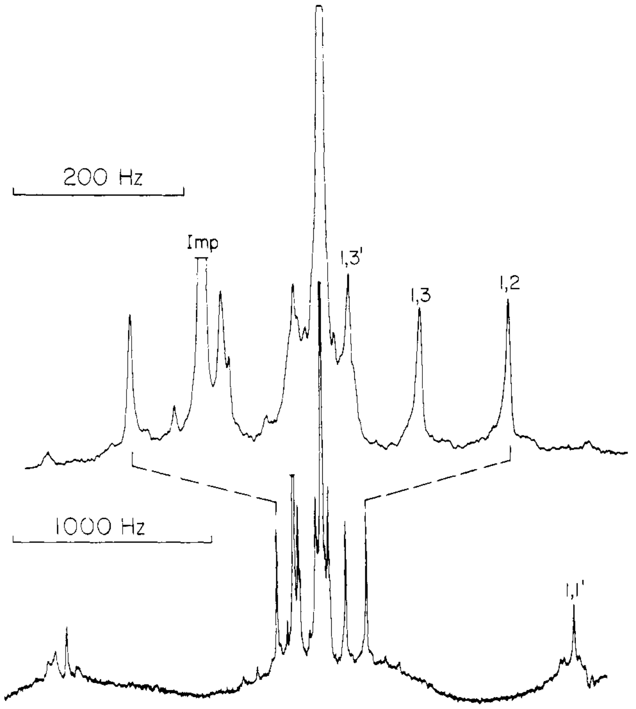

**Figure 3.** Proton NMR spectra of a 7.8 wt % solution of randomly deuterated (80 atom %) cyclopentane in bis(hexyloxy)azoxybenzene at 82 °C. The upper trace is an expanded spectrum of the central region of the lower trace. The number $i,j$ indicate the peak assignment of the $C_5H_2D_8$ species. The central peak due to $C_5HD_9$ is truncated and so is also an impurity line indicated by Imp. Several weak peaks due to more highly protonated species are also observed.

**B. Randomly Deuterated Cyclopentane.** One type of isotopic species that were employed consisted of randomly deuterated cyclopentane. Two samples were prepared with enrichment of about 80 and 90 atom % deuterium. The synthetic procedure of these species ensures (neglecting isotope effects) a statistical distribution of the deuterons among the carbon–hydrogen bonds. The relative abundancies of the various isotopic species in these samples calculated on the basis of a statistical distribution are shown in Table I. Also indicated in the table is the number of different isomers for each isotopic species and the type of spectrum expected for each species.[16] In constructing this table we neglected

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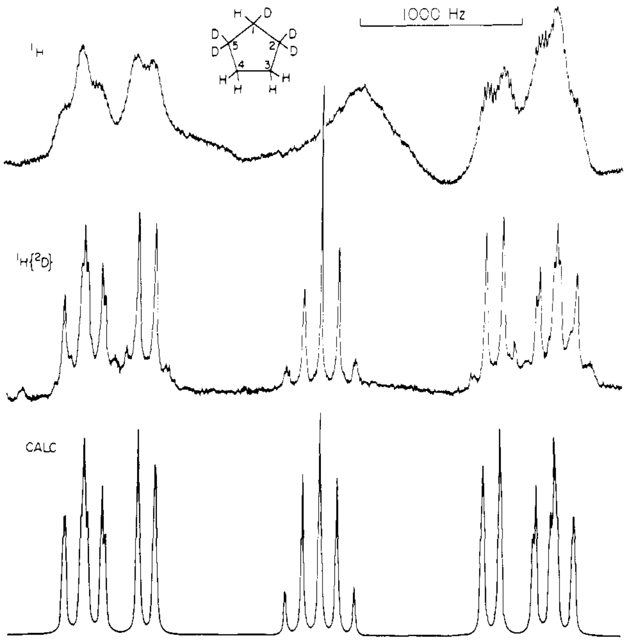

**Figure 4.** Proton NMR spectra of cyclopentane-*1,2,2′,5,5′-d*$_5$ in a liquid crystalline solvent. The upper trace corresponds to a 5.2 wt % solution in bis(hexyloxy)azoxybenzene at 84 °C, in the absence of deuterium decoupling. The middle trace is of the same solution but under conditions of deuterium decoupling. The lower trace is a simulated spectrum calculated with the following parameters: $D_{11'}$ = 1730 Hz; $D_{12}$ = −305 Hz; $D_{12'}$ = −5 Hz; $D_{13}$ = −150 Hz; $D_{13'}$ = −59 Hz; $J_{11'}$ = −12.8 Hz; $J_{12}$ = +8.0 Hz; $J_{12'}$ = +6.3 Hz; $J_{13}$ = $J_{13'}$ = 0; $1/T_2$ = 6 Hz; and a chemical shift difference between proton 1 and 3, 3′, 4, and 4′ of 7.5 Hz.

isotope effects on the chemical shift so that all hydrogens are assumed to be equivalent. Thus for the samples of 80% and 90% deuteration we would expect a proton spectrum (with deuterium decoupling) consisting of a major central peak due to the $C_5D_9H_1$ species and five symmetrically positioned doublets due to the $C_5D_8H_2$ molecules. In addition there will be many peaks due to the triply and more highly protonated species. Our main interest lies in the doubly protonated species since the doublet splittings exhibited by them are directly proportional to the corresponding average proton–proton dipolar interaction.

In Figure 3 are shown experimental traces of $^1$H{$^2$D} NMR spectra of 80% perdeuterated cyclopentane sample. The central peak and four out of the five expected doublets are clearly observed as well as several peaks due to the more highly protonated species. Clearly the fifth (missing) doublet is hidden under the broad base of the central peak. It will be shown below that one of the dipolar interactions is indeed extremely small, much too small to be observable in the presence of a large signal such as that due to the $C_5D_9H_1$ molecules. A more severe problem is however that of the assignment, since on the basis of the type of spectra shown in Figure 3 alone it is not possible to identify the observed peaks with particular $C_5D_8H_2$ isotopic isomers. The only exception is the outermost doublet which can readily be attributed to the $C_5D_8H_2$-*1,1′-h*$_2$ species. As may be seen these peaks have half the integrated intensity relative to the peaks of the other doublets, as would be expected for the (1,1′) species on the basis of statistical distribution of isomers. Other essential information that is lacking in these spectra is the relative signs of the interactions.

**C. 1,2,2′,5,5′-Pentadeuteriocyclopentane (CP-*d*$_5$).** To overcome these limitations and to obtain a definite assignment as well as the relative signs of the five possible dipolar interactions in cyclopentane, we have studied the proton NMR spectrum of 1,2,2′,5,5′-pentadeuteriocyclopentane (CP-d$_5$). Figure 4 shows a typical spectrum of this compound in bis(hexyloxy)azoxybenzene. The upper and middle traces correspond to spectra recorded in the absence and presence of deuterium decoupling. In the following we discuss only the middle trace. It consists of a symmetric pair of outer bands, each with five well-resolved lines, and a central symmetric quintuplet centered almost at the midpoint of the outer bands. The spectrum can readily be understood[16] in terms of an (A′A″A‴A⁗)A spin system where the primed A's correspond to the 3, 3′, 4, and 4′ hydrogens and the unprimed A corresponds to hydrogen number 1. Since the coupling parameters ($D_{13}$ and $D_{13'}$) between A and the group A′A″A‴A⁗ are small compared to the major coupling within this group ($D_{11'}$) it is possible to identify, to a very good approximation, the various peaks in the spectrum with these two groups of nuclei. In fact the center quintuplet corresponds predominantly to transitions of proton 1 while the outer bands correspond to transitions within the group of four protons. The five peaks of the quintuplet correspond to the five $M$ values of the group of four nuclei, and their splitting, in first order, is equal to $D_{13} + D_{13'}$. The center of the quintuplet is slightly removed from the midpoint of the outer bands due to a small isotope shift (0.0278 ppm) of the geminal deuteron on the resonance frequency of proton number 1. Note that the outer peaks of the quintuplet exhibit some structure. This is due to incomplete decoupling of the geminal H–D dipolar interaction. We were unable to completely eliminate this structure because of lack of decoupling power, but the structure could be removed separately on the right- and left-hand sides of the spectrum by a slight increase or decrease in the decoupling frequency from its optimal center value.[14,15]

As indicated the outer bands correspond to transitions within the group of the protons 3, 3′, 4, and 4′. In fact to first order this part of the spectrum consists of a superposition of two identical subspectra of the type A′A″A‴A⁗ with $C_{2v}$ symmetry and coupling parameters $D_{11'}$, $D_{12}$, $D_{12'}$ and $J_{11'}$, $J_{12}$, and $J_{12'}$. The two subspectra are shifted respectively to the right and left of the spectrum midpoint by $\pm{}^1/_2$ $(D_{13} + D_{13'})$.

To obtain the dipolar parameters we compared the experimental spectrum with simulated spectra calculated with various values for the $D_{ij}$'s and with $J_{ij}$ values as determined in isotropic solvents[19] ($J_{11'}$ = −12.8 Hz; $J_{12}$ = +8.0 Hz; $J_{12'}$ = +6.3 Hz; and $J_{13}$ = $J_{13'}$ = 0). This analysis yielded directly values for $D_{11'}$, $D_{12}$, and $D_{12'}$ as well as the sum $D_{13} + D_{13'}$. The simulated spectra were however insensitive to a change in the ratio between $D_{13}$ and $D_{13'}$. As implied from the above discussion the ratio between $D_{13}$ and $D_{13'}$ affects the spectrum only in higher order and it is apparently too small to be of any significance. By comparing the results for CP-*d*$_5$ with those obtained for the doubly protonated species (Figure 3) it was possible to assign the peaks of the (1,2′) species and to identify the two inner doublets with the (1,3) and (1,3′) species. It was, however, not possible to tell which doublet corresponds to one or the other of these species. The final assignment of these peaks was done on the basis of comparison with model calculations on various cyclopentane conformations. In all these calculations the ratio $D_{13}/D_{13'}$ was found to lie in the range 3–4. On this basis we assign the peaks due to the (1,3) and (1,3′) species as shown in Figure 3.

A final comment concerning the interaction $D_{12'}$ is in order. The analysis of the CP-*d*$_5$ spectra showed this interaction to be the smallest of all five $D_{ij}$'s. In fact it corresponds to the splitting which was not resolved in the spectra of the randomly deuterated species. However, even in the CP-*d*$_5$ case this parameter could only be determined in extremely well resolved spectra. Such spectra were obtained in solutions prepared in bis(hexyloxy)azoxybenzene but not in the low-temperature solvent phase V. In the latter solvent the lines were too broad to allow an accurate determination of $D_{12'}$.

The interpretation of the spectra also provided information on the relative signs of the $D_{ij}$'s and the $J_{ij}$'s. In practice $J_{11'}$ did not affect the spectrum but $J_{12}$ and $J_{12'}$ did. This allowed us to determine not only the relative signs of the $D_{ij}$'s but also their absolute signs. In particular it turned out that $D_{11'}$ is positive in

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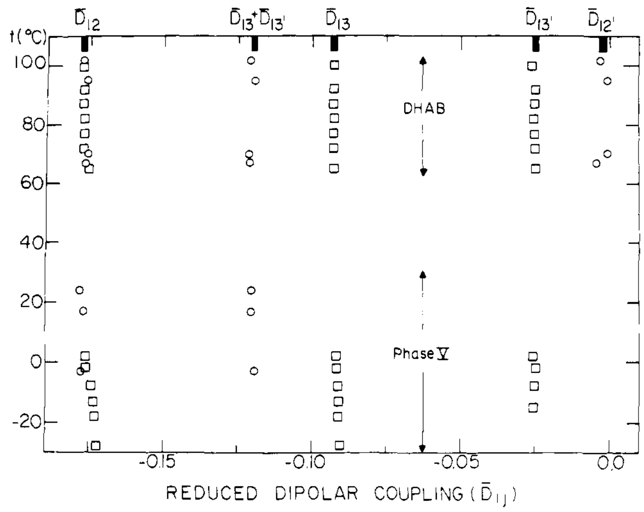

**Figure 5.** Reduced dipolar coupling parameters $\bar{D}_{ij} = D_{ij}/D_{11'}$ for the various solutions studied as a function of temperature. The results above 60 °C correspond to bis(hexyloxy)azoxybenzene (DHAB) as solvent, while the results below 30 °C correspond to phase V. In both solvents the squares represent results obtained from the $C_5H_2D_8$ species in the randomly deuterated cyclopentane, while the circles represent results from cyclopentane-*1,2,2′,5,5′-d*$_5$. The bars at the top of the figure represent the limiting values of the $\bar{D}_{ij}$'s used for the conformational analysis of cyclopentane.

all the spectra analyzed. This implies that in the liquid crystals used in the present study the cyclopentane molecules prefer the orientation in which their molecular planes lie parallel to the direction of the director. The same behavior was found in similar liquid crystalline solvents for other cycloalkane molecules, e.g., cyclopropane,[20a] cyclobutane,[20b] cyclohexane,[14] and cyclooctane.[18]

**D. Temperature Dependence and Summary of the Coupling Constants.** We have measured the dipolar couplings in the randomly deuterated and the CP-$d_5$ samples dissolved in two liquid crystalline solvents over an overall wide temperature range. The results are summarized in Figure 5. In this figure we plot the "reduced dipolar coupling parameters" defined as $\bar{D}_{ij} = D_{ij}/D_{11'}$ (thus $\bar{D}_{11'} = 1$ for all spectra). The high-temperature spectra (60–110 °C) correspond to bis(hexyloxy)azoxybenzene (DHAB) as solvent, while the spectra below 30 °C correspond to solutions in phase V. For both solvents the squares represent the results from the randomly deuterated species while the circles represent those from the CP-$d_5$ samples. Two main features in this figure must be emphasized. First we note that where comparable the results for CP-$d_5$ and those for the randomly deuterated species are practically identical. This indicates that there is apparently no isotope effect on the $D_{ij}$s and thus they most probably also apply to normal cyclopentane. The second observation is the essentially complete lack of temperature dependence of the $\bar{D}_{ij}$'s. The only exceptions are the results for $D_{12}$ between −10 °C and −20 °C which are slightly smaller compared to the corresponding high-temperature values. This lack of temperature dependence is particularly important for the analysis to be presented in the next section, because it permits us to consider just a single average conformation for the cyclopentane molecule with axial symmetry. It is possible that this assumption breaks down at lower temperatures. We therefore take for the analysis the high-temperature limits of the $\bar{D}_{ij}$'s indicated by the bar at the top of Figure 5. These are: $\bar{D}_{11'} = +1.0$ (by definition); $\bar{D}_{12} = -0.178$; $\bar{D}_{12'} = -0.002$; $\bar{D}_{13} = -0.093$; $\bar{D}_{13'} = -0.026$.

## Comparison of the Experimental $\bar{D}_{ij}$'s with Theoretical Computations of the Pseudorotation Model

In this section we discuss the dipolar interactions derived in the previous section in terms of the pseudorotation of cyclopentane by comparing them with calculated values from various theoretical models. Before reviewing these models, some comments concerning the experimental results are in order.

As noted before since only five distinct proton–proton couplings are observed the pseudorotation process must be fast compared to the intramolecular dipolar interactions, thus setting a lower limit[21] to the pseudorotation rate of $10^8$ s$^{-1}$. Most probably it is several orders of magnitude higher than this limit. The direct dipolar interaction, $D_{ij}$, between a pair of nuclei $i$ and $j$ is given in terms of the molecular geometry by

$$D_{ij} = (-2 \times 5^{-1/2})K[C_{3z^2-r^2}\langle[z_{ij}^2 - (\tfrac{1}{2}) \times (x_{ij}^2 + y_{ij}^2)]/r_{ij}^5\rangle + C_{x^2-y^2}3^{1/2}(\tfrac{1}{2})\langle(x_{ij}^2 - y_{ij}^2)/r_{ij}^5\rangle + C_{xz}3^{1/2}\langle x_{ij}z_{ij}/r_{ij}^5\rangle + C_{yz}3^{1/2}\langle y_{ij}z_{ij}/r_{ij}^5\rangle + C_{xy}3^{1/2}\langle x_{ij}y_{j}/r_{ij}^5\rangle] \quad (2)$$

where $x_{ij'}$, $y_{ij'}$, and $z_{ij}$ are relative coordinates of the proton in an arbitrary coordinate system, $r_{ij} = (x_{ij}^2 + y_{ij}^2 + z_{ij}^2)^{1/2}$, $K$ is a constant depending on the magnetic moment of the interacting nuclei, and the $C$'s are the motional constants. This equation applies to a rigid conformation and the angular brackets indicate averaging over the internal molecular motions, i.e., vibrations. In its derivation it was assumed that the potentials for the molecular reorientation and for the internal vibrations are separable. When the observed species consist of a number of rapidly interconverting conformations the resulting $D_{ij}$'s will be the weighted average over all conformations, so that for each conformer a set of nuclear coordinates and a set of motional constants need to be specified in order to calculate its $D_{ij}$'s, which are then averaged over all conformers. However, if the molecular reorientation potential is independent of the conformation, it is sufficient to consider[23,24] just one set of motional constants, according to the average symmetry of the molecule, and one set of the average geometrical parameters. On the basis of the temperature dependence, or rather temperature independence, of the $D_{ij}$'s as presented in Figure 5 it may be concluded that this latter limiting case applies to cyclopentane. The justification is as follows: If the potentials for reorientation and pseudorotation are inseparable each conformer must be specified by its geometrical parameters and by several motional constants, each being temperature dependent. The normalized $\bar{D}_{ij}$'s would then depend on essentially an infinite number of motional constants and there is no reason whatsoever that the $\bar{D}_{ij}$'s would be temperature independent unless fortuitously all motional constants for all conformations have exactly the same temperature dependence—a very unlikely situation. On the other hand, if the cyclopentane is considered as a single "conformer" with an average structure of $D_{5h}$ symmetry, the equations for the $D_{ij}$'s reduce to

$$D_{ij} = (-2/5^{1/2})KC_{3Z^2-r^2}\langle[Z_{ij}^2 - \tfrac{1}{2}(X_{ij}^2 + Y_{ij}^2)]/r_{ij}^5\rangle \quad (3)$$

where $Z$ is taken to be parallel to the average $C_5$ axis and the angular brackets now indicate averaging over the pseudorotation pathway. It is clear that since the $D_{ij}$'s depend only on one motional constant the reduced dipolar couplings, $\bar{D}_{ij}$, will depend only on the average geometrical parameter $\langle[Z_{ij}^2 - {}^1/_2(X_{ij}^2 + Y_{ij}^2)]/r_{ij}^5\rangle$ and would be independent of temperature unless the pseudorotation amplitude is temperature dependent in the region investigated—this does not seem to be the case.

In the rest of this section we consider several theoretical models proposed for the pseudorotation. For each model we compute the averages in the angular brackets in eq 3 over the pseudorotation pathway and the corresponding $\bar{D}_{ij}$'s. These are then compared with the experimental values derived in the previous section. The theoretical models which we consider include those of Hendrickson,[7] Lifson and Warshel,[9] Adams et al.,[5] Cremer and Pople,[10] and Lugar.[11] In all these references sufficient raw data are given from which the coordinates of the various atoms for several discrete

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**Table II.** Normalized Dipolar Interactions ($\overline{D}_{1,1'} = 1$) and Average Puckering Amplitude for the Various Models Considered in the Present Work[a]

| method | $d$, Å | $h$, Å | $R = h/d$ | $\overline{D}_{12}$ | $\overline{D}_{13}$ | $\overline{D}_{12'}$ | $\overline{D}_{13'}$ | $\langle q \rangle$, Å |
|---|---|---|---|---|---|---|---|---|
| planar | 1.540 | 1.090 | 0.708 | −0.2380 | −0.0562 | 0.0159 | −0.0178 | 0 |
| Hendrickson | 1.533 | 1.108 | 0.723 | −0.1897 | −0.0905 | 0.0008 | −0.0234 | 0.428 |
| Lifson and Warshel | 1.528 | 1.106 | 0.724 | −0.1945 | −0.0871 | 0.0022 | −0.0228 | 0.406 |
| Lugar | 1.528 | 1.104 | 0.723 | −0.1788 | −0.1015 | −0.0024 | −0.0218 | 0.476 |
| Cremer and Pople | 1.540 | 1.090 | 0.708 | −0.1941 | −0.0773 | 0.0024 | −0.0251 | 0.373 |
| Adams et al. | 1.546 | 1.114 | 0.720 | −0.1918 | −0.0869 | 0.0015 | −0.0230 | 0.416 |
| this work | 1.546 | 1.098 | 0.710 | −0.1775 | −0.0933 | −0.0027 | −0.0244 | 0.463 |
| exptl (NMR) | | | | −0.1775 | −0.0931 | −0.0020 | −0.0255 | |

[a] The carbon–carbon and carbon–hydrogen bond distances used in the computations are also given. For all models the angle of HCH is 109°47′.

points or continuously along the the pseudorotation pathway can be computed. The procedure we have used to transform the raw data into atomic coordinates $x_i$, $y_i$, $z_i$ is described in Appendix A. However, for eq 3 to apply we must transform these coordinates which correspond to an arbitrary coordinate system into a system that corresponds to the average geometry of the cyclopentane molecule such that the $X$ and $Y$ axes lie in the "mean plane" of the molecule about which the puckering takes place and the $Z$ direction coincides with its "average" $C_5$ axis. Cremer and Pople[25] have outlined an analytical method for transforming the positional coordinates $x_i$, $y_i$, $z_i$ from an arbitrary system to that of the "mean plane". We refer to the original paper for a discussion of the method and to Appendix A for the detailed procedure used by us to determine the atomic position coordinates in this system. Once these coordinates are determined for a particular pseudorotation state, its $D_{ij}$'s are calculated. The procedure is then repeated for different states along the pseudorotation pathway. In addition, for each state of the pseudorotation pathway, the parameters $q$ (and $P$) which represent the amplitude (and phase) of the puckering are also determined (using eq A23 and A24). The final average dipolar interactions are obtained by averaging the $D_{ij}$'s over the whole range of the $P$'s. In practice we have found that the amplitudes $q$ for a given model were independent of the phase $P$. It is thus meaningful to refer to an average puckering amplitude $\langle q \rangle$ obtained by averaging the $q$'s over the whole pseudorotation pathway of a given model.

It should be pointed out that in order to obtain the average $D_{ij}$'s (and $\langle q \rangle$) it is not necessary to consider all the pseudorotation states. A more economical computation is to consider a limited range of $P$'s, including a single envelope form corresponding to $P = 0$, a single half-chain form, $P = 18°$, and several intermediate states corresponding to $0 < P < 18°$. The average $D_{ij}$'s are then obtained by double averaging: first within each state we average over all similarly related protons, e.g.,

$$D_{11'} = \tfrac{1}{5}(D_{11'} + D_{22'} + \ldots + D_{55'})$$
$$D_{12} = \tfrac{1}{10}(D_{12} + D_{23} + \ldots + D_{1'2'} + D_{2'3'} + \ldots) \qquad \text{etc.}$$

and then perform the average over the various states. In practice the second average turned out to be redundant, since for all $P$ values we found essentially the same $D_{ij}$'s when averaged over similarly related protons. One final remark concerns the C–C and C–H bond lengths ($d$ and $h$, respectively). In our calculations they were assumed to be constant and were taken as in the original work (if specified). The angles HCH were assumed constant and equal to the tetrahedral angle 109.47°.

In Table II are summarized the reduced dipolar interactions and puckering amplitudes calculated for the various theoretical models considered. For comparison the expected $\bar{D}_{ij}$'s for a planar structure are also included. Clearly the results for the planar structure are completely inconsistent with the experimental results and all theoretical models improve the agreement considerably. But on closer examination it may be seen that while the agreement of the $\bar{D}_{12'}$ and $\bar{D}_{13'}$ is reasonable for all models the calculated values of the stronger interactions, $\bar{D}_{12}$ and $\bar{D}_{13}$, do not fit the experimental results as well. We have also checked the sensitivity of the calculated $\bar{D}_{ij}$'s to the assumed value of the HCH angle and to the bond length ratio $h/d$. The results of this check are shown diagramatically in Figure 6. In this figure the experimental results of the $\bar{D}_{ij}$'s are indicated by bars at the bottom and by dashed lines along the figure. The values calculated for the various models are shown as rectangles. The width of each dashed rectangle gives the range of variation of the corresponding $\bar{D}_{ij}$ as the HCH angle is varied between 107.5° and 111.5°, keeping the $h/d$ ratio constant as shown in Table II, while the widths of the dotted rectangles give the range of variation obtained by varying $h/d$ between 0.700 and 0.730, keeping the HCH angle equal to 109°47′. Note that none of the theoretical models fits the experimental NMR results even by varying the molecular geometrical parameters over quite large ranges.

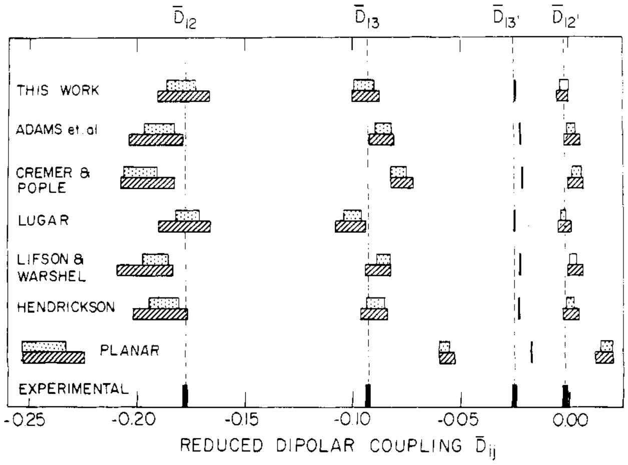

**Figure 6.** Comparison of the experimental and calculated $\bar{D}_{ij}$'s for cyclopentane and variation in the latter with small changes in the geometrical parameters. The experimental results are indicated by the bars at the bottom of the figure and by the dashed vertical lines. The calculated values are represented by the rectangles. The width of the dashed rectangles gives the range of variation of the corresponding $\bar{D}_{ij}$ as the HCH angle is varied between 107.5° and 111.5°, keeping $h/d$ constant as shown in Table II. The width of the dotted rectangles gives the corresponding range obtained by varying $h/d$ between 0.700 and 0.730, keeping the HCH angle at 109.47°.

We have therefore attempted a best-fit analysis of our experimental results to the original pseudorotational model of Kilpatrick, Pitzer, and Spitzer[2] as modified by Adams et al.,[5] taking the puckering amplitude $q$ as a single adjustable parameter. The calculations are described in detail in Appendix B, and the calculated best-fit parameters are given in Table II and Figure 6. They correspond to a puckering amplitude $q = 0.463$ Å. The agreement between the experimental and calculated $\bar{D}_{ij}$'s for this model is perfect, in particular considering the fact that only a single adjustable parameter is involved.

## Conclusions

In the present work we have measured the average intramolecular dipolar interactions of the protons in cyclopentane dissolved in nematic solvents. The results are in excellent agreement with the pseudorotation model of Pitzer and their interpretation provides

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(25) D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).

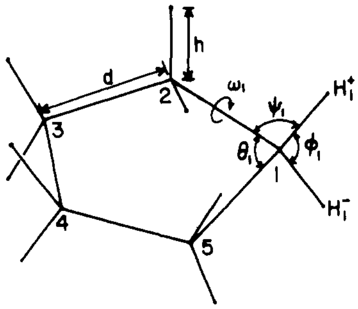

**Figure 7.** Atomic numbering and definitions of the geometrical parameters: $d$ and $h$ are respectively the C–C and C–H bond distances; $\theta_i$, $\phi_i$, and $\psi_i$, are respectively the bond angles $C_{i-1}C_iC_{i+1}$, $H_i^+C_iH_i^-$, and $C_{i\pm1}C_iH_i^\pm$; and $\omega_i$ is the dihedral angle of the bond $C_i$–$C_{i+1}$.

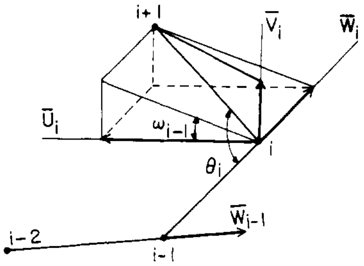

**Figure 8.** The auxiliary coordinate system on carbon $i$: $\bar{\mathbf{W}}_i$ is along the $C_{i-1}$–$C_i$ bond; $\bar{\mathbf{V}}_i$ is perpendicular to both $\bar{\mathbf{W}}_{i-1}$ and $\bar{\mathbf{W}}_i$; $\bar{\mathbf{U}}_i$ is perpendicular to $\bar{\mathbf{W}}_i$ and $\bar{\mathbf{V}}_i$; $\theta_i$ is the bond angle $C_{i-1}C_iC_{i+1}$; and $\omega_{i-1}$ is the dihedral angle of the $C_{i-1}$–$C_i$ bond.

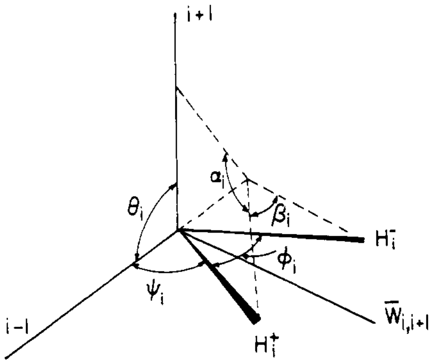

**Figure 9.** Definitions of angles and auxiliary coordinates for the calculation of the position vectors for the hydrogens.

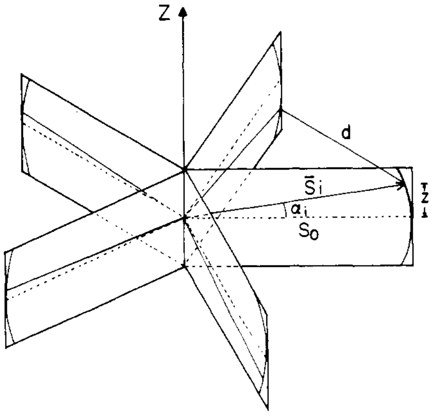

**Figure 10.** The coordinate system of Adams, Geise, and Bartell. See Appendix B for definitions.

an accurate value for the amplitude of the puckering motion. It should however be pointed out that our results do not provide information on the potential of the pseudorotation pathway, i.e., whether it contains barriers or whether it is flat. This is so because the $D_{ij}$'s for a given conformation (i.e., a particular phase $P$) when averaged over similarly related protons are essentially independent of $P$. Thus if, e.g., the pseudorotation of cyclopentane would consist of fast hopping between the ten envelope conformations, or between the ten half-chair states or any other set of equivalent conformations, the average dipolar splittings would still be the same as long as the amplitude, $q$, is unchanged. As indicated in the introduction, theoretical and other experimental evidence[1] indicate that apparently the potential is flat.

**Acknowledgment.** This work was partly supported by a grant from the United States–Israel Binational Science Foundation, Jerusalem. We wish to thank Ishai Manassen for help in the interpretation of the CP-$d_5$ spectra.

## Appendix A

**Position Coordinates and Dipolar Interactions in Puckered Cycloalkanes.** In this appendix we describe the stages for the calculation of the dipolar interactions described in the main text. For five-membered rings there are several specific geometrical properties that could be used,[26] but we prefered to employ a general procedure suitable for any cycloalkane. We first calculate the position coordinates $x$, $y$, $z$ of all atoms (carbons and hydrogens) in an arbitrary coordinate system from the raw data, i.e., bond lengths as well as bond and dihedral angles (for definitions of angles and bonds see Figure 7, which applies to cyclopentane). Next we transform these position coordinates by translation to a coordinate system whose origin is at the center of gravity of the molecule. Finally the coordinate system is rotated so that the new $XY$ plane corresponds to the molecular "mean plane" as defined by Cremer and Pople.[25] The dipolar interactions between the magnetic nuclei are then calculated by using the latter coordinates with $Z$ corresponding to the mean symmetry axis of the molecule.

**Position Coordinates from Raw Data.** The first three carbon atoms are arbitrarily located in the $xy$ plane, so that carbon number 1 is at the origin and carbon 2 is along the positive $x$ coordinate. The position vectors for $C_1$, $C_2$, and $C_3$ then are:

$$\bar{C}_1 = (0,0,0) \qquad \bar{C}_2 = d(1,0,0)$$

$$\bar{C}_3 = \bar{C}_2 + d(\cos(\pi - \theta_2), \sin\theta_2, 0) = d(1 - \cos\theta_2, \sin\theta_2, 0) \tag{A1}$$

To proceed we define an auxiliary set of orthogonal coordinates $\bar{\mathbf{W}}_i$, $\bar{\mathbf{V}}_i$, $\bar{\mathbf{U}}_i$ (Figure 8) on carbon $i$ starting with carbon number 3: $\bar{\mathbf{W}}_i$ is along the bond from carbon $i-1$ to carbon $i$. The unit vector along this direction is

$$\bar{\mathbf{w}}_i = (\bar{\mathbf{C}}_i - \bar{\mathbf{C}}_{i-1})/d \tag{A2}$$

$\bar{V}_i$ is perpendicular to $\bar{\mathbf{W}}_i$ and $\bar{\mathbf{W}}_{i-1}$. Its unit vector is

$$\bar{\mathbf{v}}_i = \bar{\mathbf{w}}_{i-1} \times \bar{\mathbf{w}}_i/(\sin\theta_{i-1}) \tag{A3}$$

$\bar{\mathbf{U}}_i$ lies in the plane defined by $\bar{\mathbf{W}}_i$ and $\bar{\mathbf{W}}_{i-1}$ and is perpendicular to $\bar{\mathbf{W}}_i$ and $\bar{\mathbf{V}}_i$. Its unit vector is

$$\bar{\mathbf{u}}_i = \bar{\mathbf{v}}_i \times \bar{\mathbf{w}}_i \tag{A4}$$

The position vector of carbon $i + 1$ is then given by

$$\bar{\mathbf{C}}_{i+1} = \bar{\mathbf{C}}_i + d\{-\bar{\mathbf{w}}_i \cos\theta_i + \bar{\mathbf{v}}_i \sin\theta_i \sin\omega_{i-1} + \bar{\mathbf{u}}_i \sin\theta_i \cos\omega_{i-1}\} \tag{A5}$$

For the hydrogen atoms on carbon $i$ we assume a local $C_{2v}$ symmetry, i.e., we assume that they lie in a plane which is perpendicular to the plane formed by $\bar{\mathbf{W}}_i$ and $\bar{\mathbf{W}}_{i+1}$ and which contains the bisector of these vectors at $C_i$. The two hydrogens lie symmetrically above ($H_i^+$) and below ($H_i^-$) the sector $\bar{\mathbf{W}}_{i,i+1}$, which bisects both the angle $\phi_i$ and $\theta_i$. Defining the projection angles as in Figure 9, the position vectors of the two $H_i^\pm$ hydrogens are

$$\bar{\mathbf{H}}_i^\pm = \bar{C}_i + h\{-\bar{\mathbf{w}}_i \cos\psi_i + \bar{\mathbf{v}}_i \sin\psi_i \sin(\omega_{i-1} + \pi \mp \tfrac{1}{2}\beta_i) + \bar{\mathbf{u}}_i \sin\psi_i \cos(\omega_{i-1} + \pi \mp \tfrac{1}{2}\beta_i)\} \tag{A6}$$

where the angles $\psi_i$ and $\beta_i$ are related to $\theta_i$ and $\phi_i$ by

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(26) J. D. Dunitz, *Tetrahedron*, **28**, 5459 (1972); J. D. Dunitz and J. Waser, *Elem. Math.*, **27**, 25 (1972). See also: J. D. Dunitz and J. Waser, *J. Am. Chem. Soc.*, **94**, 6645 (1972).

$$\cos \psi_i = -\cos (\tfrac{1}{2}\theta_i) \cos (\tfrac{1}{2}\phi_i) \qquad \text{(A7)}$$

$$\cos \beta_i = (\cos \phi_i - \cos^2 \psi_i)/\sin^2 \psi_i \qquad \text{(A8)}$$

According to the raw data available it may in certain instances be more convenient to determine the hydrogen positions with the auxiliary vectors $\bar{\mathbf{V}}_i$ and $\bar{\mathbf{W}}_{i,i+1}$ defined above. The hydrogen positions are then given by

$$\bar{\mathbf{H}}_i^{\pm} = \bar{\mathbf{C}}_i + h\{\pm\bar{\mathbf{v}}_i \sin (\tfrac{1}{2}\phi_i) + \bar{\mathbf{w}}_{i,i+1} \cos (\tfrac{1}{2}\phi_i)\} \qquad \text{(A9)}$$

where $\bar{\mathbf{w}}_{i,i+1}$ is the unit vector along $\bar{\mathbf{W}}_{i,i+1}$

$$\bar{\mathbf{w}}_{i,i+1} = (\bar{\mathbf{W}}_i - \bar{\mathbf{W}}_{i+1}) \Big/ \left|\sqrt{2(1 + \cos \theta_i)}\right| \qquad \text{(A10)}$$

**Transformation to the Cremer–Pople Coordinate System.**[25] The first step in this transformation is a translation of the origin of the coordinate system from $C_1$ to the center of gravity. The position vector of this point is

$$\bar{\mathbf{G}} = \frac{1}{M}\sum_i^N(12\bar{\mathbf{C}}_i + \bar{\mathbf{H}}_i^+ + \bar{\mathbf{H}}_i^-) \qquad \text{(A11)}$$

where $M$ is the molecular weight and $N$ the number of carbon atoms in the cycloalkane molecule. If we consider only the carbon atoms as was in fact done in practice, eq A11 becomes

$$\bar{\mathbf{G}} = \frac{1}{N}\sum_i \bar{\mathbf{C}}_i \qquad \text{(A12)}$$

The position coordinates of the carbon and hydrogen atoms in the center of gravity coordinate systems are respectively

$$\overline{\mathbf{CG}}_i = \bar{\mathbf{C}}_i - \bar{\mathbf{G}} \qquad \text{(A13)}$$

$$\overline{\mathbf{HG}}_i^{\pm} = \bar{\mathbf{H}}_i^{\pm} - \bar{\mathbf{G}} \qquad \text{(A14)}$$

To obtain the position coordinates in the Cremer–Pople system we now have to reorient the coordinate system about its origin so that the new $XY$ plane becomes the "mean plane" of the cycloalkane molecule and the new $Z$ its "mean symmetry axis". The axis is defined by the requirements

$$\sum_i^N C(Z_i) = 0 \qquad \text{(A15)}$$

$$\sum_i^N C(Z_i) \cos [2\pi(i - 1)/N] = 0 \qquad \text{(A16)}$$

$$\sum_i^N C(Z_i) \sin [2\pi(i - 1)/N] = 0 \qquad \text{(A17)}$$

where $C(Z_i)$ is the $i$'s carbon coordinate along the $Z$ direction. The first requirement, eq A15, is already fulfilled by the fact that the origin corresponds to the center of gravity (with respect to the carbons). To satisfy (A16) and (A17) we define the two vectors

$$\bar{\mathbf{R}}' = \sum_i \overline{\mathbf{CG}}_i \sin [2\pi(i - 1)/N] \qquad \text{(A18)}$$

$$\bar{\mathbf{R}}'' = \sum_i \overline{\mathbf{CG}}_i \cos [2\pi(i - 1)/N] \qquad \text{(A19)}$$

and construct the unit vector

$$\bar{\mathbf{n}} = \bar{\mathbf{R}}' \times \bar{\mathbf{R}}''/|\bar{\mathbf{R}}' \times \bar{\mathbf{R}}''| \qquad \text{(A20)}$$

perpendicular to $\bar{\mathbf{R}}'$ and $\bar{\mathbf{R}}''$. This $\bar{\mathbf{n}}$ vector is now identified with the mean symmetry axis, $Z$, of the molecule. Clearly it is perpendicular to $\bar{\mathbf{R}}'$ and $\bar{\mathbf{R}}''$ and thus conditions in (A16) and A(17) are satisfied. The vectors $\bar{\mathbf{R}}'$ and $\bar{\mathbf{R}}''$ lie in the "mean molecular plane" and the perpendicular displacement of the carbon and hydrogen atoms from this plane, $C(Z_i)$ and $H(Z_i^{\pm})$, can readily be computed from the relations

$$C(Z_i) = \overline{\mathbf{CG}}_i \cdot \bar{n} \qquad \text{(A21)}$$

$$H(Z_i^{\pm}) = \overline{\mathbf{HG}}_i \cdot \bar{n} \qquad \text{(A22)}$$

Finally we can determine the amplitude and phase of the pseudorotation by transposing Pitzer's equation (eq 1 where $Z_i \equiv C(Z_i)$):

$$q = \sqrt{\sum_i (C(Z_i))^2} \qquad \text{(A23)}$$

$$P = \frac{4\pi}{5}(i - 1) - \cos^{-1}\left[\sqrt{\frac{5}{2}}(C(Z_i))/q\right] \text{ for any } i \qquad \text{(A24)}$$

**Determination of the Proton–Proton Dipolar Interaction.** With the assumption of a mean axial symmetry the proton dipolar interactions depend on only one motional constant (eq 3) and they are given by

$$D_{ij} = -\frac{2}{\sqrt{5}}KC_{3z^2-r^2}[3(H(Z_i) - H(Z_j))^2 - r_{ij}^2]/r_{ij}^5 \qquad \text{(A25)}$$

where the distance $r_{ij}$ can be obtained from the hydrogen position vectors in any coordinate system, e.g., from the original one given by eq A6:

$$r_{ij} = \bar{\mathbf{H}}_i - \bar{\mathbf{H}}_j = [(H(x_i) - H(x_j))^2 + (H(y_i) - H(y_j))^2 + (H(z_i) - H(z_j))^2]^{1/2} \qquad \text{(A26)}$$

(For simplicity of presentation we have suppressed the ± superscrips in the last equation.)

## Appendix B

**The Adams, Geise, and Bartell[5] Pseudorotation Model.** In this approach the Pitzer pseudorotation model is slightly modified so as to ensure that during the puckering the C–C bond distances remain constant. Thus instead of describing the puckering in terms of the displacements $Z_i(q,P)$ of the carbon atoms relative to the unpuckered configuration of $D_{5h}$ symmetry (eq 1), the pseudorotation is characterized by the tilt angles $\alpha_i(q,P)$ given by

$$\alpha_i = \alpha_i(q,P) = \tan^{-1} (Z_i(q,P)/S_0) \qquad \text{(B1)}$$

where (see Figure 10) $S_0$ is the length of the vectors connecting the center of the unpuckered pentagon and the carbon atoms

$$S_0 = (d/2)/\sin (2\pi/10) \qquad \text{(B2)}$$

and the $Z_i(q,P)$'s are the "Pitzer displacements" as calculated from eq 1. The carbon atoms are assumed to lie along the directions connecting the center of the pentagon and the tip of the displacement vectors $Z_i$, but at a distance $|\bar{\mathbf{S}}_i|$ from the center so that the distance between neighboring carbons is constant and equal to the assumed C–C bond length, i.e.,

$$|\bar{\mathbf{S}}_i - \bar{\mathbf{S}}_{i+1}|^2 = |\bar{\mathbf{S}}_i|^2 + |\bar{\mathbf{S}}_{i+1}|^2 - 2|\bar{\mathbf{S}}_i||\bar{\mathbf{S}}_{i+1}| \cos (\bar{\mathbf{S}}_i,\bar{\mathbf{S}}_{i+1}) = d^2 \qquad \text{(B3)}$$

where $(\bar{\mathbf{S}}_i,\bar{\mathbf{S}}_{i+1})$ is the angle between the adjacent $\bar{\mathbf{S}}_i$ and $\bar{\mathbf{S}}_{i+1}$ vectors. The cosine of this angle is given by

$$\begin{aligned}\mathrm{COS}_{i,i+1} = \cos (\bar{\mathbf{S}}_i,\bar{\mathbf{S}}_{i+1}) &= \sin \alpha_i \sin \alpha_{i+1} + \cos\left(\frac{2\pi}{5}i\right) \times \\ &\cos\left(\frac{2\pi}{5}(i + 1)\right) \cos \alpha_i \cos \alpha_{i+1} + \sin\left(\frac{2\pi}{5}i\right) \times \\ &\sin\left(\frac{2\pi}{5}(i + 1)\right) \sin \alpha_i \sin \alpha_{i+1} = \sin \alpha_i \sin \alpha_{i+1} + \\ &\cos\left(\frac{2\pi}{5}\right) \cos \alpha_i \cos \alpha_{i+1} \qquad \text{(B4)}\end{aligned}$$

To solve for the five $\bar{\mathbf{S}}_i$ position vectors for each $q$,$P$ puckering state we need to solve a set of five nonlinear and inhomogeneous equations of the form

$$S_i^2 + S_{i+1}^2 - 2S_iS_{i+1}(\mathrm{COS}_{i,i+1}) = d^2 \qquad \text{(B5)}$$

After solving for the $S_i$'s (by iteration) the position vectors

$$\bar{\mathbf{C}}_i = S_i\left[\bar{\mathbf{i}} \cos \alpha_i \cos\left(\frac{2\pi}{5}i\right) + \bar{\mathbf{j}} \cos \alpha_i \sin\left(\frac{2\pi}{5}i\right) + \bar{k} \sin \alpha_i\right] \qquad \text{(B6)}$$

for each of the carbons are determined. Because of the puckering displacements, the origin of the coordinate system of the $\bar{C}_i$ vectors will not in general coincide with the Cremer–Pople coordinate system or even that of the molecular center of gravity. Therefore to proceed in the calculations of the $D_{ij}$'s we resort to the procedure described in Appendix A, i.e., first transform the origin to the new center of gravity and then to the Cremer–Pople coordinate system.

**Registry No.** Bis(4-hexyloxy)azoxybenzene, 2857-42-0; phase V, 37268-47-6; cyclopentane, 287-92-3; 1,2,2,5,5-pentadeuteriocyclopentane, 82544-88-5; cyclopentanone, 120-92-3; 2,2,5,5-cyclopentanone-$d_4$, 3997-89-5; 2,2,5,5-cyclopentanol-$d_4$, 35447-71-3; 2,2,5,5-cyclopentyl-$d_4$ bromide, 75621-29-3.

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# Preferential Solvation of Hydrogen Ions in Mixed Clusters of Water, Methanol, and Ethanol

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*Received January 11, 1982*

**Abstract:** The electron-impact ionization of neutral mixed clusters composed of water and alcohol molecules results in the formation of $\{(ROH)_n\cdot(H_2O)_m\}H^+$ ion clusters. With use of a combined molecular beam–mass spectrometer apparatus, clusters of the above type have been formed for $n + m < 25$ and for ROH = $CH_3OH$ and $C_2H_5OH$. By monitoring the competitive decomposition processes via the metastable peak intensities, it has been possible to determine which of the species present in the ion cluster is preferentially bound to the proton. The results show that in $\{(ROH)_n\cdot H_2O\}H^+$ clusters the alcohol molecules are preferentially attached to the proton up to $n = 9$ for methanol and $n = 10$ for ethanol; thereafter the water molecule is the most strongly bound species. These results can be rationalized in terms of the ion–dipole and ion–induced dipole interactions present in the cluster.

A study of the reactions of ionic clusters can provide information at a microscopic level on the interations that exist between an ion and one or more solvent molecules.[1-4] In particular, the use of techniques to study cluster complexes in the gas phase has the advantage that ions at varying stages in the solvation process can be examined without interference from either the bulk solvent or ions of the opposite sign.

Two main techniques have been used to produce and study ion clusters. Kebarle and co-workers have used high-pressure mass spectrometry with considerable success to determine equilibrium data for both metallic and nonmetallic ions in a variety of solvents.[1,2] The alternative technique of using free-jet expansion[5] to produce clusters can take two forms. Either neutral clusters can be ionized by electron or photon impact following the expansion process[6-8] or ions can be expanded along with the solvent of interest.[9] For those examples where there is an overlap, results show that all three techniques can yield similar information even if the comparison can only be made at a qualitative level.[8-11] However, producing ion clusters by electron or photon impact following the adiabatic expansion of neutral molecules results in a nonequilibrium distribution of cluster sizes, and this places a severe limitation on the amount of qualitative thermodynamic information such studies can yield. Also the lack of data on ionization efficiencies means that there is no direct relationship between the distributions of neutral and ionic clusters.

In this paper the results of a series of experiments in which we have used ion clusters to study the competitive solvation of hydrogen ions in solvent mixtures are presented. Although the clusters are initially formed as the neutral species by adiabatic expansion, information on the competitive aspect of the solvation process has been obtained by considering the relative intensities of reaction products from the unimolecular decomposition of ion clusters at varying stages of solvation.

Table I

| molecule | $\mu$,[a] D | $\alpha_p$,[b] $Å^3$ | PA,[c] kJ $mol^{-1}$ |
|---|---|---|---|
| $H_2O$ | 1.85 | 1.48 | 727 |
| $CH_3OH$ | 1.70 | 3.23 | 777 |
| $C_2H_5OH$ | 1.69 | 5.62 | 799 |

[a] Dipole moment, taken from ref 13. [b] Polarizability, taken from ref 13. [c] Proton affinity, taken from ref 14.

In a previous study of the water–methanol system using a high-pressure mass spectrometer, Kebarle et al. formed ion clusters of the type $\{(CH_3OH)_n\cdot(H_2O)_m\}H^+$ for $m + n \leq 6$.[12] Their results showed that in small ion clusters the proton is preferentially solvated by the methanol molecules. By extrapolation they concluded that there is no preference when $m + n = 9$ and that when $m + n > 9$ the interaction with water will be stronger than that with methanol. In the present study we have been able to form mixed ion clusters of the type $\{(CH_3OH)_n\cdot(H_2O)_m\}H^+$, $\{(C_2H_5OH)_n\cdot(H_2O)_m\}H^+$, and $\{(C_2H_5OH)_n\cdot(CH_3OH)_m\}H^+$ for $m + n \leq 25$, and we have been able to monitor the reactions of those

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