Appendix

The calculations described herein were carried out with a force field used previously[1] which differs slightly from that described earlier,[19] specifically by the replacement of the absolute value in the stretch–bend interaction by a signed quantity, and the addition of a cubic stretching term, followed by a general reoptimization of parameters. These changes lead to only trivial changes in the geometries and energies of molecules such as those discussed here, so the numerous numerical details will not be elaborated. In addition, a refinement in our energy minimization scheme has been made which utilizes second derivatives including cross products of the type $(\partial^2/\partial x \partial y)$ in locating the energy minimum. There are enough second derivatives that, proceeding as described earlier, it is not necessary to move the atom and recalculate derivatives to get enough equations to solve for the unknowns. The overall scheme is approximately twice as fast as that described earlier, and to minimize the energy of a typical steroid like those studied here takes about 5 min of CPU time on the IBM 360/65, and somewhat less on the 360/67. Because of the experimental difficulties involved in studies of transient species of all kinds, including transition states, we suggest that this is a method of potentially great power for such studies.
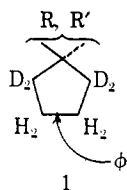
Nmr Spectroscopy of Cyclopentane Derivatives. III. Methylcyclopentane[1]

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Abstract: A complete iterative nmr spectra analysis has been accomplished for two specifically deuterated methylcyclopentane derivatives, 7 and 11, at three temperatures over a range of 117°. The magnitudes of the resulting vicinal interproton coupling constants have subsequently been related to a restricted pseudorotation model involving ten half-chair and ten envelope conformations and were found to be consistent with a conformational preference for those states (a, b, b̄, c, c̄, d, and d̄) in which the methyl substituent is equatorially bonded.

In the previous paper in this series, nmr parameters were reported for a series of specifically deuterated mono- and 1,1-disubstituted cyclopentanes (1).[2] The derived values obtained for the average ring torsional angle, ϕ, about the 3,4-carbon–carbon bond are consistent with a pseudorotation model having potential maxima and minima at $\phi \approx 50$ and 0°, respectively.

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While this previous work sheds light on the conformational mobility of the substituted cyclopentane ring, it affords no information regarding possible axial–equatorial bonding preference for the substituents.

A methyl group axially substituted on a *cyclohexane* ring experiences substantial 1,3-diaxial steric interactions when viewed in a space-filling model. For a *cyclopentane* ring, however, an axial methyl appears to experience no comparable steric hindrance. A comparison of these 1,3-diaxial interactions in the two ring systems is illustrated in Figure 1. On this steric basis alone, the energy difference between axial and equatorial methylcyclopentane (3a ⇌ 3b) is likely to be substantially lower than in the corresponding methylcyclo-

hexane equilibrium (2a ⇌ 2b). Pitzer and Donath estimate the energy difference for 3a ⇌ 3b to be about 0.54 kcal/mol,[3] a value substantially lower than that of 1.7 kcal/mol for 2a ⇌ 2b.[4]

The actual methylcyclopentane conformational equilibrium is not limited solely to the two envelope forms 3a and 3b but includes to some extent all ring conformations encountered in the course of pseudorotation. The absence of any steep potential wells is reflected in the gradual change in conformational energy for the six possible half-chair conformers of methylcyclopentane recently calculated by Allinger and coworkers.[5]

Results

In order to assess the extent of axial–equatorial bonding preference, two specifically deuterated methylcyclopentane derivatives, 7 and 11, were synthesized (Scheme I) for nmr analysis. The deuterium-decoupled 100-MHz pmr spectra were obtained for 7 and 11 at three temperatures over a range of 117° (Figures 2–5) and their corresponding solution parameters obtained iteratively using LAOCOON 3.[6] The results are tabulated in Tables I and II, and the stereochemical assignments are shown in Figure 6. The details of the analysis and the

(1) Address correspondence to R. L. L., 53 Winthrop Road, Brookline, Mass. 02146.

(2) R. L. Lipnick, *J. Mol. Struct.*, in press.

(3) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 81, 3213 (1959).

(4) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 44.

(5) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminksi, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, 90, 1199 (1968).

(6) S. M. Castellano and A. A. Bothner-By, "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y. 1968, pp 10–39.
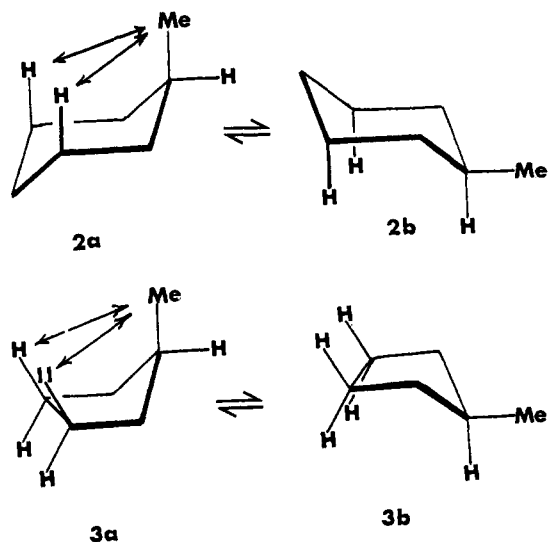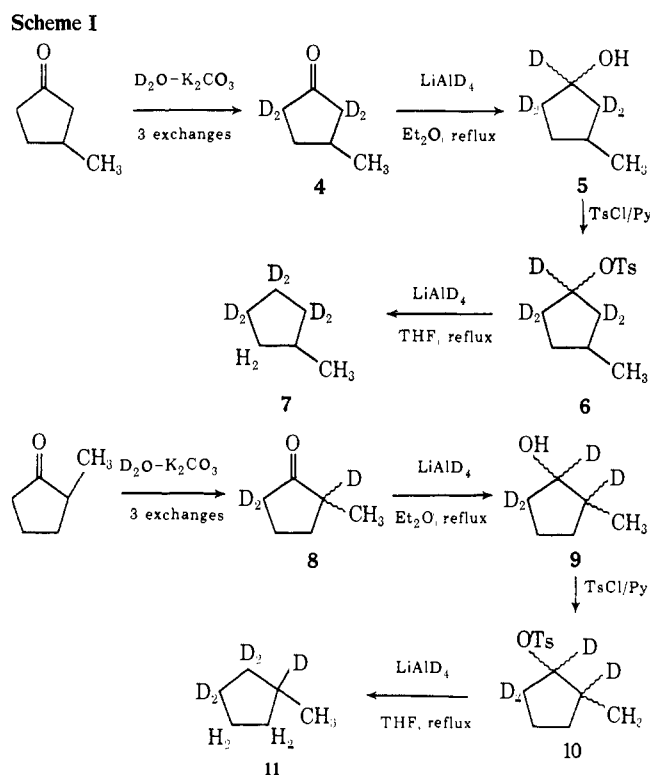
Figure 1. The 1,3-diaxial H–H interactions are compared for axial (**2a**) and equatorial (**2b**) methylcyclohexane and for axial (**3a**) and equatorial (**3b**) methylcyclopentane.

Scheme I

stereochemical assignment are provided in the Experimental Section.

Experimental Section

General. Boiling points are uncorrected. Infrared spectra were recorded routinely on a Perkin-Elmer 257 infrared spectrometer. Preparative vapor phase chromatography was performed on a Varian Aerograph Model 90P3 thermal conductivity instrument.

Nmr Spectral Determinations. All nmr spectra were recorded as described previously[2] on a Varian XL-100-15 spectrometer equipped with a Gyrocode frequency synthesizer and a variable-temperature controller. All experimental line frequencies were obtained from the average of two upfield and two downfield sweeps (50 Hz sweep width, 1000 sec sweep time).

Nmr Spectral Analysis. Methylcyclopentane-$1,2,2,3,3$-d_5 (**11**). The deuterium-decoupled pmr spectrum of methylcyclopentane-$1,2,2,3,3$-d_5 (**11**) is the product of seven interacting H nuclei, three of which (methyl protons) are only distantly coupled to the remain-
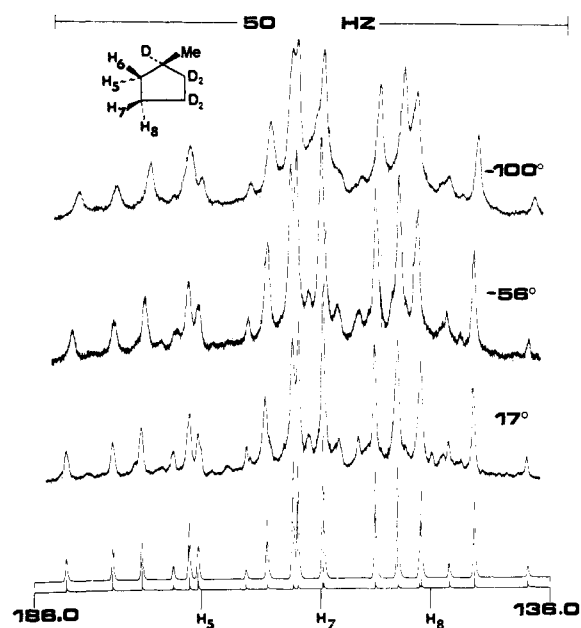

Figure 2. The downfield portions of the 100-MHz deuterium-decoupled pmr spectra of methylcyclopentane-$1,2,2,3,3$-d_5 (**11**) in 10% v/v CS_2 at −100, −56, and 17° are shown in the upper traces. The bottom spectrum was simulated using the iterative solution values obtained at 17°. The lowermost tic marks indicate the chemical shifts of H_5, H_7, and H_8 from left to right. The lower frequency scale refers only to the spectrum at 17°.
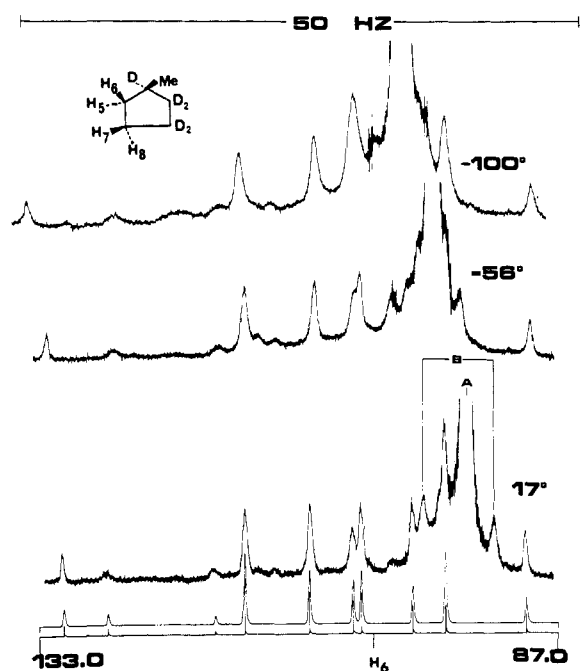

Figure 3. The upfield portions of the 100-MHz deuterium-decoupled pmr spectrum of methylcyclopentane-$1,2,2,3,3$-d_5 (**11**) in 10% v/v CS_2 at −100, −56, and 17° are shown in the upper traces. The bottom spectrum was simulated using the iterative solution values obtained at 17°. The single lowermost tic mark indicates the chemical shift for H_6. The lower frequency scale refers only to the spectrum at 17°.

ing four.[7] Those spectral transitions arising from the latter four ring protons may be analyzed independently as a four-spin system.

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(7) The protons have been numbered consecutively for both derivatives so that the derived chemical shifts and coupling constants are assigned consistently.
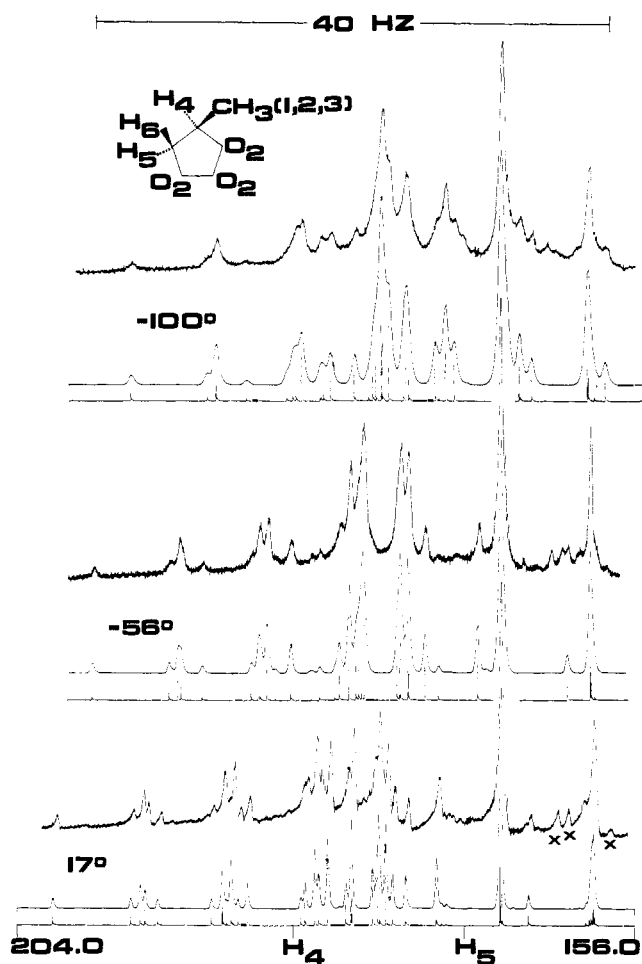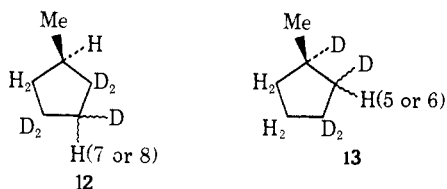
├────────── 40 HZ ──────────┤

H4 CH3(1,2,3)
H6
H5
D2
D2 D2

-100°

-56°

17°

x x x

204.0   H4   H5   156.0

Figure 4. The downfield portion (H₄ and H₅) of the 100-MHz deuterium-decoupled pmr spectra of methylcyclopentane-2,2,-3,3,4,4-d₆ (7) in 10% v/v CS₂ at −100, −56, and 17° is shown along with the corresponding theoretical spectra which were simulated using the final iterative solution values. The lowermost tic marks indicate the chemical shifts for H₄ and H₅. The lower frequency scale refers only to the spectrum at 17°. Experimental lines marked X arise from traces of an isotopic impurity.

├────────── 30 HZ ──────────┤

H4
H6
H5
CH3(1,2,3)
D2
D2 D2

-100°

-56°

17°

118.0   H6   H1,2,3   84.0

Figure 5. The upfield portion (H₁, H₂, H₃, and H₆) of the 100-MHz deuterium-decoupled pmr spectrum of methylcyclopentane-2,2,-3,3,4,4-d₆ (7) in 10% v/v CS₂ at −100, −56, and 17° is shown along with the corresponding theoretical spectra which were simulated using the final iterative solution values. The lowermost tic marks indicate the chemical shifts for H₁, H₂, H₃, and H₆. The lower frequency scale refers only to the spectrum at 17°.

These ring protons constitute an ABCD spin system, wherein all four protons (H₅, H₆, H₇ and H₈) are chemically nonequivalent, and their chemical shift separation from one another is essentially the same order of magnitude as the coupling constants between them.[8] Estimates of the values for these four chemical shifts in 11 were obtained from the nmr spectra of two additional derivatives, methylcyclopentane-2,2,3,4,4-d₅ (12) and methylcyclopentane-1,2,3,3-d₄ (13). Each of these derivatives consists of an isomeric

Me
H
H₂
D₂
D₂
D
H(7 or 8)
12

Me
D
D
H₂
H(5 or 6)
H₂
D₂
13

pair, wherein the single magnetically isolated proton is either cis or trans to the methyl substituent and gives rise to a complex nmr spectrum containing two well-defined singlets whose chemical shifts can be measured directly.

Six nondegenerate interproton coupling constants are required for the analysis of the ABCD spin system in 11. As an initial approximation, the two geminal couplings $J_{5,6}$ and $J_{7,8}$ were each

D
Me(1,2,3)
H6
H5
H7
H8
D2
D2

H4
Me(1,2,3)
H6
H5
D2
D2
D2

11   7

Figure 6. The relationship of the derived nmr parameters for 11 and 7 to ring stereochemistry.

set equal to −12.9 Hz, an average geminal coupling measured in five monosubstituted cyclopentanes.[2] For the sake of analysis, the cis and trans couplings were regarded as degenerate pairs ($J_{5,8} = J_{6,7}$ and $J_{5,7} = J_{6,8}$) and the resulting two parameter sets varied systematically with the remaining nmr parameters held fixed at their estimated values. A series of theoretical nmr spectra was calculated from the above parameters using LAOCOON 3,[6] and the corresponding computer-drawn spectral plots compared visually with

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, p 425.
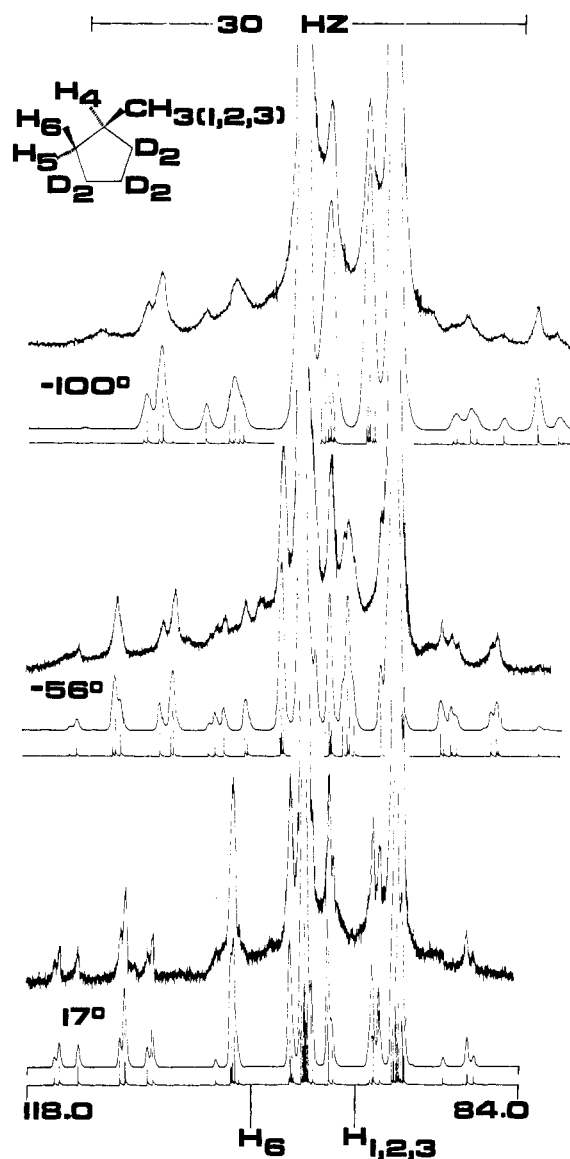
Table I. Temperature Dependences of the Nmr Parameters for Methylcyclopentane-*1,2,2,3,3-d5* (**11**)[a]

T, °C	ν_6[b,c]	ν_5[b,c]	ν_7[b,c]	ν_8[b,c]	$J_{5,6}$[c,d]
−100	99.051 ± 0.017	168.895 ± 0.016	157.782 ± 0.022	146.611 ± 0.022	−12.305 ± 0.026
−56	100.974 ± 0.014	169.278 ± 0.014	157.857 ± 0.021	147.009 ± 0.021	−12.357 ± 0.025
17	103.500 ± 0.006	169.946 ± 0.009	158.262 ± 0.010	147.632 ± 0.011	−12.485 ± 0.014

T, °C	$J_{6,7}$[c,d]	$J_{6,8}$[c,d]	$J_{5,7}$[c,d]	$J_{5,8}$[c,d]	$J_{7,8}$[c,d]	Rms
−100	8.970 ± 0.036	9.100 ± 0.035	3.451 ± 0.031	7.973 ± 0.027	−12.818 ± 0.021	0.031
−56	8.888 ± 0.031	8.618 ± 0.035	3.930 ± 0.030	8.057 ± 0.024	−12.803 ± 0.021	0.036
17	8.652 ± 0.012	8.129 ± 0.016	4.494 ± 0.014	8.073 ± 0.013	−12.752 ± 0.010	0.020

[a] All data were obtained in 10% v/v CS_2 solution at 100.1 MHz. The stereochemical assignment is shown in Figure 6. [b] In Hz, downfield from internal TMS. [c] Error limits are probable errors obtained from the LAOCOON 3 solutions. [d] In Hz.

Table II. Temperature Dependences of the Nmr Parameters for Methylcyclopentane-*2,2,3,3,4,4-d6* (**7**)[a]

T, °C	ν_1, ν_2, ν_3[b,c]	ν_4[b,c]	ν_5[b,c]	ν_6[b,c]	$J_{1,4}$, $J_{2,4}$, $J_{3,4}$[c,d]
−100	97.216 ± 0.016	174.821 ± 0.013	168.166 ± 0.014	97.805 ± 0.013	6.534 ± 0.013
−56	96.375 ± 0.009	178.505 ± 0.008	168.537 ± 0.008	100.012 ± 0.007	6.608 ± 0.008
17	95.691 ± 0.010	182.619 ± 0.006	169.254 ± 0.008	102.519 ± 0.007	6.653 ± 0.006

T, °C	$J_{1,5}$, $J_{2,5}$, $J_{3,5}$[c,d]	$J_{1,6}$, $J_{2,6}$, $J_{3,6}$[c,d]	$J_{4,5}$[c,d]	$J_{4,6}$[c,d]	$J_{5,6}$[c,d]	Rms
−100	−0.228 ± 0.016	−0.175 ± 0.014	6.826 ± 0.016	9.695 ± 0.022	−12.344 ± 0.024	0.078
−56	−0.212 ± 0.009	−0.090 ± 0.008	7.071 ± 0.008	9.022 ± 0.013	−12.395 ± 0.013	0.045
17	−0.172 ± 0.009	−0.121 ± 0.008	7.254 ± 0.008	8.285 ± 0.010	−12.454 ± 0.014	0.038

[a] All data were obtained at 100.1 MHz from solutions 10% v/v in CS_2. The stereochemical assignment is shown in Figure 6. [b] In Hz, downfield from internal TMS. [c] Error limits are probable errors obtained from the iterative LAOCOON 3 solution. [d] In Hz.

the experimental spectrum obtained at 17°. A tentative line assignment was made to the most closely matched simulated spectrum and was used as the basis for an initial LAOCOON 3 iteration. A subsequent spectral simulation based upon the initial iterative solution parameters revealed several false line assignments. This iterative process was repeated until all 28 experimentally observed lines were properly assigned. In the final iterative calculations all ten nmr parameters were allowed to vary independently of one another. The low-temperature spectra were analyzed similarly, in each case basing the initial line assignments on the final iterative solution parameters obtained at the next higher temperature. The final iterative solution parameters for **11** at 17, −56, and −100° are tabulated in Table I. The corresponding theoretical and experimental spectra are presented in Figures 2 and 3.

It is not possible to make a direct stereochemical assignment of the four ring protons and their respective coupling constants from the nmr analysis alone. The two coupling constants ($J_{5,6}$ and $J_{7,8}$) of opposite algebraic sign to the remaining four are evidently the two geminal couplings and are assigned negative values by convention. This assignment establishes that H_5 and H_6 are attached to one carbon atom and that H_7 and H_8 are attached to the other, in agreement with the original assignment obtained from **12** and **13**. At 17°, these four protons were found to resonate at 103.5 (H_6), 169.9 (H_5), 158.3 (H_7), and 147.6 (H_8) Hz downfield from TMS. The chemical shift for H_6 falls well upfield of the other three and was assigned to the proton cis and vicinal to the methyl substituent in accordance with the known deshielding at this location in a methyl-substituted five- or six-membered ring.[9]

The remaining four vicinal coupling constants are positive in sign and belong to two sets: (1) $J_{5,8}$, $J_{6,7}$ and (2) $J_{5,7}$, $J_{6,8}$. One set corresponds to the two cis coupling constants and the other to the two trans coupling constants. An approximate theory, presented later in this paper, predicts that the two cis coupling constants should be equal. In fact, the J values of set 1 are approximately equal while those of set 2 are quite different. The J values of set 1 are therefore assigned to the cis proton interactions, and the complete stereochemical assignment (Figure 6) follows.

Methylcyclopentane-*2,2,3,3,4,4-d6* (**7**). The deuterium-decoupled pmr spectrum of methylcyclopentane-*2,2,3,3,4,4-d6* (**7**) is comprised of six interacting protons which must be treated as a single system for an exact analysis. The resulting six-spin system is of the $ABCD_3$ type and requires for its solution 11 independent parameters (four chemical shifts and seven coupling constants).

In order to begin an analysis of the six-spin system, it was necessary to generate a theoretical simulated spectrum whose overall appearance was sufficiently close to that obtained experimentally to permit a line assignment. The analysis is somewhat simplified by the insensitivity of such a spectrum to the value of the geminal coupling across the methyl substituent. Four of the six required coupling constants, and three of the four required chemical shifts, can be estimated prior to the actual analysis. The two sets of long range coupling constants are expected to be less than 1 Hz and are set equal to zero. The geminal interproton coupling ($J_{5,6}$) is expected to be very close to the value (−12.5 Hz) obtained for this parameter in **11**. First-order estimates of $J_{1,4}$ and ν_1 were obtained from the methyl doublet. The chemical shifts obtained for the corresponding protons in **11** were used as estimates for ν_5 and ν_6. The value of the remaining chemical shift, ν_4, was estimated from the location of its corresponding spectral envelope in the downfield region of the nmr spectrum.

The spectral transitions arising from H_6 are superimposed upon the methyl doublet in the upfield spectral region (84–118 Hz) and are conveniently isolated from those transitions due to the other two ring protons.

Since the H_6 transitions depend directly upon only one of the unknown vicinal couplings, $J_{4,6}$, the theoretical simulation of this portion of the spectrum provides a convenient starting point for LAOCOON 3 analysis of the entire $ABCD_3$ system. For the sake of these initial calculations, $J_{4,5}$ was assigned a nominal value of 8.4 Hz, the average of the two cis vicinal couplings in **11**, and $J_{4,6}$ was allowed to vary systematically from 1–12 Hz. The remaining parameters were held constant at their previously estimated values, and the resulting set of theoretical spectra was computer simulated. That simulation which provided the closest experimental match for the H_6 transitions at 17° was used as the basis for the line assignment of these transitions. In a subsequent iterative LAOCOON 3 analysis, $J_{4,6}$ and ν_6 were allowed to vary independently to provide a best theoretical fit to the experimental H_6 transitions. The subsequent improvement in these two adjusted parameters was sufficient to permit additional line assignments in the downfield portion of the spectrum. A second iterative refinement employing these additional assignments and the two lines of the methyl doublet provided both additional and corrected line assignments for the downfield transitions. This refinement process was repeated successively until all 49 experimentally observed lines had been correctly assigned. In the final iterations, only the indeterminate geminal coupling across the methyl substituent was held fixed, and the remaining parameter sets were allowed to vary independently. The final simulated spectrum at 17° is shown in Figures 4 and 5.

The data at the two lower temperatures were analyzed similarly,

(9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, pp 236–237.

in each case using the best simulated spectrum obtained at the next higher temperature as a basis for initial line assignments. The final iterative nmr parameters obtained for 7 are shown in Table II.

3-Methylcyclopentanone-2,2,5,5-d₄ (4). A 15.0-g (0.153 mol) sample of 3-methylcyclopentanone (Chemical Samples Co., 99%) was refluxed overnight with 26.0 g (0.188 mol) of anhydrous potassium carbonate and 40 g (2.0 mol) of deuterium oxide (Aldrich, 99.7% *d*). The aqueous phase was removed in a separatory funnel and discarded and the exchange process repeated twice using fresh potassium carbonate and deuterium oxide. Following the final exchange, the ketone phase was dried over anhydrous magnesium sulfate, filtered, and distilled through a vacuum-jacketed Vigreaux column. The initial distillate was discarded, and 9.37 g (60% theory) of pure product was collected at 56° (29 mm) (lit.[10] bp 57–59° (29 mm)). The product was found to be >96% *d* from nmr, in the presence of sufficient europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (Eu(fod)₃)[11] (Pierce Chemical Co.) to resolve the exchangeable protons. The infrared spectrum exhibits bands at 2960 (s), 2940 (s), 2870 (s), 2210 (w), 2120 (w), and 1740 (s) cm⁻¹.

3-Methyl-1-cyclopentanol-1,2,2,5,5-d₅ (5). A 2.0-g (0.047 mol) sample of LiAlD₄ (Stohler, 99% *d*) was finely pulverized and added to 100 ml of freshly opened anhydrous ether contained in a 500-ml three-necked reaction flask, fitted with a large magnetic stirrer, efficient condenser, drying tube, and dropping funnel. The suspension was stirred for 1 hr at room temperature.

An 8.0-g (0.0783 mol) sample of 3-methylcyclopentanone-2,2,5,5-d₄ (4), dissolved in 100 ml of anhydrous ether was added dropwise with stirring to the LiAlD₄ suspension. The resulting mixture was stirred overnight at room temperature and heated to reflux for 7 hr. The cooled reaction mixture was worked up with slow, dropwise addition of a saturated aqueous ammonium chloride solution and filtration of the resulting precipitate. The solvent was subsequently removed at atmospheric pressure and the residue distilled through a vacuum-jacketed Vigreaux column under reduced pressure. The final product, 5.29 g (64.4% theory), a mixture of cis and trans isomers, was collected at 76.5–77.0° (33 mm) (lit.:[12] trans bp 62–62.5° (15 mm); cis bp 60° (15 mm)). The pmr spectrum (CDCl₃) of 5 shows peaks at δ 1.0 (two doublets, *J* = 7.0 Hz, 3 H, two methyl doublets corresponding to the cis and trans isomers) and 1.2–2.2 (envelope, 4 H). In the presence of ~10% Eu(fod)₃, the –OH envelope is shifted downfield and resolved into two broad singlets of equal area, indicating that the cis and trans isomers have formed in approximately equal quantity.

3-Methyl-1-cyclopentanol-1,2,2,5,5-d₅ Tosylate (6). To a cold solution of 3.0 g (0.0286 mol) of anhydrous reagent grade pyridine was added a chilled solution of 7.10 g (0.0372 mol, 30% excess) of *p*-toluenesulfonyl chloride (Matheson Coleman and Bell) in 30 ml of pyridine. The mixture was reacted at 0° for 48 hr and poured into a large beaker containing excess HCl, ice, and ether. The mixture was transferred to a separatory funnel and the product extracted into the ether phase. The ether extract was subsequently washed with cold dilute HCl, water, and saturated bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed at room temperature on a rotary evaporator to yield 7.32 g (98% theory) of colorless oil. Attempts to crystallize this oil were unsuccessful, probably because it is a mixture of cis and trans isomers. The pmr spectrum shows peaks at δ 0.98 (two doublets, *J* = 7.0 Hz, 3 H, two alicyclic methyl doublets corresponding to the cis and trans isomers), 1.2–2.2 (broad envelope, 3 H, alicyclic ring protons), 2.47 (singlet, 3 H, aromatic methyl), and 7.58 (AB quartet, *J* = 8.0 Hz, 4 H, aromatic ring protons). The infrared spectrum exhibits peaks at 2950 (m), 2870 (m), 2220 (w), and 2100 (w) cm⁻¹.

Methylcyclopentane-2,2,3,3,4,4-d₆ (7). To 50 ml of reagent grade THF in a three-necked 250-ml reaction flask equipped with a magnetic stirrer, reflux condenser, drying tube, and dropping funnel was added 2.0 g (0.0476 mol) of finely crushed LiAlD₄ (Stohler, 99% *d*). The mixture was heated to 70° for 0.5 hr, and 7.3 g (0.0282 mol) of 3-methyl-1-cyclopentanol-1,2,2,5,5-d₅ tosylate (6), dissolved in 20 ml of THF, was added dropwise with stirring to the slowly refluxing suspension. After addition, the mixture was allowed to stir at reflux for 0.5 hr and cooled. Any unreacted

LiAlD₄ was subsequently destroyed by careful dropwise addition of 3:1 THF–water, and 5 ml of reagent grade *n*-octane was added. The reaction mixture was decanted into a separatory funnel containing ice and sufficient 20% sulfuric acid to dissolve the inorganic aluminum salts and shaken to extract the deuterated product into the organic phase. The octane extract was separated, washed four times with small portions of concentrated sulfuric acid and once each with water and saturated bicarbonate solution, and dried over anhydrous sodium sulfate. A pure sample for nmr spectral determination of the product (7) was obtained from the octane extract by preparative glpc at 50° on an 8-ft column (20% Carbowax, 20 M on 60–80 Chromosorb P). This product gave the same retention time, under these conditions, as an authentic sample of the nondeuterated compound.

2-Methylcyclopentanone-2,5,5-d₃ (8). A 14.6-g (0.149 mol) sample of 2-methylcyclopentanone (Chemical Samples Co., 99.5%) was exchanged overnight at reflux with 26.0 g (0.188 mol) of anhydrous potassium carbonate and 40 g of deuterium oxide (Aldrich, 99.7% *d*) according to the procedure used for producing **4**. This exchange was repeated twice. The final exchange product yielded 9.66 g (64% theory) of distillate, bp 53.5–54.5° (33 mm) (lit.[13] bp 44° (18 mm)). The nmr spectrum shows from integration that deuterium exchange is >95%. The infrared spectrum exhibits bands at 2970 (s), 2940 (s, sh), 2880 (s), 2220 (w), 2130 (w), and 1740 (s) cm⁻¹.

2-Methyl-1-cyclopentanol-1,2,5,5-d₄ (9). 2-Methylcyclopentanone-2,5,5-d₃ (8), 8.0 g (0.0792 mol) dissolved in 75 ml of anhydrous ether, was added dropwise to a suspension of 2.0 g (0.0476 mol) of lithium aluminum deuteride (Stohler, 99% *d*) in 150 ml of anhydrous ether and reacted according to the procedure used for preparing **5**. The final product, a mixture of cis and trans isomers, was purified by fractional distillation, and 6.73 g (82% theory) of colorless distillate was collected at 74.0–76.0° (33 mm) (lit.:[14] trans, bp 83° (47 mm); cis bp 76° (54 mm)). The pmr spectrum exhibits peaks at δ 1.0 (broad singlet, 3 H, methyl), 1.3–2.1 (envelope, 4 H, ring protons), and 2.2 (broad singlet, 1 H, –OH). Addition of ~10% Eu(fod)₃ causes the resolution of the –OH and methyl resonances into "doublets" corresponding to the cis and trans isomers. The more downfield –OH resonance corresponds to 46% of one isomer, with the more upfield resonance comprising 54% of the other. The infrared spectrum exhibits peaks at 3360 (m, br), 2960 (s), 2880 (m), 2210 (w), and 2130 (w, br) cm⁻¹.

2-Methyl-1-cyclopentanol-1,2,5,5-d₄ Tosylate (10). 2-Methyl-1-cyclopentanol-1,2,5,5-d₄ (9), 3.0 g (0.0286 mol), was reacted in the cold in pyridine with 7.10 g (0.0372 mol) of *p*-toluenesulfonyl chloride according to the procedure described in the synthesis of **6**. The final product was freed of solvent on a rotary evaporator to yield 7.43 g (100% theory) of colorless oil. The pmr spectrum exhibits peaks at δ 0.85 (singlet, 3 H, alicyclic methyl), 1.2–2.0 (envelope, 4 H, alicyclic ring protons), 2.47 (singlet, 3 H, aromatic methyl), and 7.53 (AB quartet, *J* = 8.0 Hz, 4 H, aromatic ring protons). The infrared spectrum exhibits bands at 2960 (m), 2870 (m), 2210 (w), and 2120 (w, br) cm⁻¹.

Methylcyclopentane-1,2,2,3,3-d₅ (11). A 7.0-g (0.0271 mol) sample of 2-methyl-1-cyclopentanol-1,2,5,5-d₄ tosylate (10), dissolved in 20 ml of reagent grade THF, was added dropwise to a gently refluxing suspension of 2.0 g (0.0476 mol) of lithium aluminum deuteride (Stohler, 99% *d*) in 50 ml of THF. This addition and subsequent work-up follow the procedure previously described for the synthesis of **7**. A pure sample of **11** suitable for subsequent nmr study was obtained from the final purified octane extract by preparative glpc at 50° on an 8-ft column (20% Carbowax, 20 M on 60–80 Chromosorb P). This product provides the same retention time, under these conditions, as an authentic sample of the nondeuterated hydrocarbon.

Methylcyclopentane-2,2,3,4,4-d₅ (12). 3-Methyl-1-cyclopentanol-1,2,2,5,5-d₅ tosylate (6), 2.80 g (0.0108 mol), dissolved in 15 ml of reagent grade THF, was added dropwise with stirring to a slowly refluxing suspension of 1.5 g (0.0395 mol) of finely crushed lithium aluminum hydride in 40 ml of THF. This addition, subsequent work-up, and purification follow the procedure used for the production of **7**. The glpc-purified product gives the same retention time as an authentic sample of the nondeuterated hydrocarbon.

Methylcyclopentane-1,2,3,3-d₄ (13). Methylcyclopentane-1,2,3,-3-d₄ was prepared from 3.23 g (0.0125 mol) of 2-methyl-1-cyclo-

(10) Bayer and Co., D.R.P., 256622; *Chem. Zentralbl.*, 1, 865 (1913).

(11) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

(12) M. Godchot, G. Cauquil, and R. Calas, *Bull. Soc. Chim. Fr.*, 6, 1358 (1939).

(13) M. Tiffeneau and G. Vaissière, *C. R. Acad. Sci.*, 209, 449 (1939).

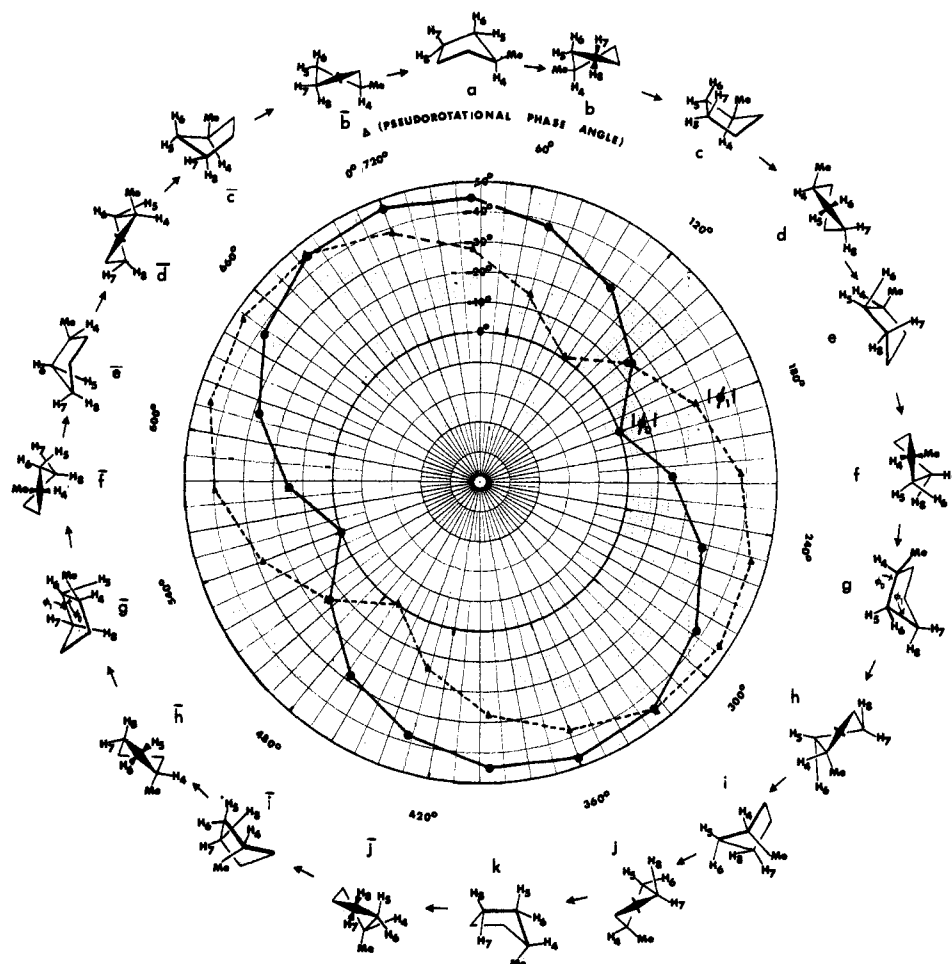(14) W. Hückel and E. Mogle, *Justus Liebigs Ann. Chem.*, 649, 13 (1961).

Figure 7. One complete pseudorotational circuit for methylcyclopentane is represented by the perspective drawings of the ten envelope and ten half-chair conformations that are encountered in this process. The hydrogen atoms are numbered in accordance with the notation used for **7** and **11** in order to show the relationship between conformation and vicinal interproton coupling for these deuterated derivatives. The inner polar graph depicts the quantitative relationship (eq 1) of conformation (Δ) to the absolute values of the two projected ring torsional angles (indicated in g and $\bar{g}$), ϕ_0 ($\bullet$, solid line) and ϕ_1 ($\blacktriangle$, dotted line). For illustrative purposes, only one enantiomer of the deuterated derivatives is shown, since the treatment of the other is equivalent.

pentanol-$1,2,5,5$-d_4 tosylate (**10**) and 1.5 g (0.0395 mol) of lithium aluminum hydride following the procedure used for the synthesis of **7**. The glpc-purified product gave the same retention time as an authentic sample of the nondeuterated hydrocarbon.

Discussion

Geminal Coupling. Two of the three geminal couplings ($J_{5,6}$ = -12.5 Hz and $J_{7,8}$ = -12.8 Hz at 17°) on the methylcyclopentane ring have been determined in this study and were found to be in agreement with the normal value expected for an unstrained alicyclic ring.[15]

Long Range Coupling. It has been predicted from theoretical considerations that ^nJ for interproton coupling is negative in sign for even values of n and positive for odd values of n.[16] The two sets of long range couplings determined in **7** extend across four bonds (^4J) and are predicted to be negative in sign, which is in agreement with the experimental results (Table II).

Chemical Shift. The chemical shifts for H_5 and H_6 have been precisely determined in two different deuterated derivatives and were found to exhibit a sub-

(15) See ref 9, p 275.
(16) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 145.

stantial deuterium isotopic shift (at 17°, $\Delta\nu_6$ = 0.981 Hz and $\Delta\nu_5$ = 0.692 Hz).

Vicinal Coupling and Stereochemistry. The methylcyclopentane ring does not appear to exist as a single discrete conformer and may be regarded as undergoing pseudorotation through an undetermined number of potential minima which are separated by low energy barriers. One complete pseudorotational circuit may conveniently be represented by the ten envelope and ten half-chair conformations shown in Figure 7 that are encountered consecutively in this process. The relative location of each such point in the cycle can be described by a phase angle, Δ, which assumes values from 0 to 720° during one complete circuit. The jth ring torsional angle, ϕ_{ij}, at the ith phase angle, Δ_i, may be obtained from eq 1, where j = 0, 1, 2, 3, and 4 and ϕ_m is the amplitude of puckering.[17,18] In the course

(17) (a) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron Lett.*, 1383 (1967); (b) C. Altona and A. P. M. Van Der Veek, *Tetrahedron*, 24, 4377 (1968); (c) C. Altona, "Conformational Analysis: Scope and Present Limitations," E. Chiurdogu, Ed., Academic Press, New York, N. Y., 1971, pp 1–13.
(18) The value ϕ_m = 47°, derived from an examination of ring geometry in a number of steroid derivatives,[19] was used in all calculations involving eq 1.
(19) C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 24, 13 (1968).

$$\phi_{ij} = \phi_m[\cos (\tfrac{1}{2}\Delta_i - \tfrac{4}{5}\pi j)] \tag{1}$$

of pseudorotation, the methyl substituent periodically occupies an axial, equatorial, or bisectional bonding position on the ring such that seven equatorial (0, 36, 72, 108, 144, 646, and 684°), seven axial (288, 324, 360, 396, 432, 468, and 504°), and six bisectional (180, 216, 252, 540, 576, and 612°) conformations are encountered in one cycle. The extent to which one or more of these pseudorotameric states predominates in the equilibrium is a measure of equatorial or axial bonding preference and the degree of ring puckering adjacent to the methyl substituent.

Each of the experimental vicinal interproton coupling constants derived from **7** and **11** are weighted averages of the corresponding theoretical coupling constants over all of the conformations encountered in one circuit. A qualitative estimate of the relative populations of the 20 model conformations may be obtained from a comparison of the magnitudes of their individual theoretical coupling constants with the corresponding experimental values. The required theoretical coupling constants were obtained from eq 3–7; these equations

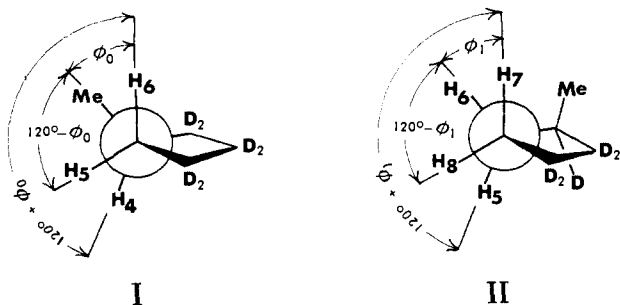$$J = A \cos^2 \phi \tag{2}$$

$$J_{4,5} = A \cos^2 \phi_0 \tag{3}$$

$$J_{4,6} = A \cos^2 (120° + \phi_0) \tag{4}$$

$$J_{6,7} = J_{5,8} = A \cos^2 \phi_1 \tag{5}$$

$$J_{5,7} = A \cos^2 (120° + \phi_1) \tag{6}$$

$$J_{6,8} = A \cos^2 (120° - \phi_1) \tag{7}$$

were derived from eq 1 and 2[20] and from the dihedral angular relationships apparent in projections I and II.[21] A value of $A = 13.9$ Hz, an average derived from

I   II

the nmr parameters of nine mono- and disubstituted cyclopentanes, was used for all calculations.[2,22]

The relationship of theoretical vicinal coupling to conformational preference is further simplified by the fact that there are nine enantiomeric pairs[23] (b–b̄, c–c̄, d–d̄, ..., j–j̄) resulting in only eleven different pseudo-

(20) (a) J. B. Lambert, J. Amer. Chem. Soc., **89**, 1836 (1967); (b) H. R. Buys, Recl. Trav. Chim. Pays-Bas, **88**, 1003 (1969).

(21) The projections shown correspond to conformations in which the values calculated for ϕ_0 and ϕ_1 from eq 1 are positive in each case. For negative-valued ring torsional angles, the correct relationships for the corresponding conformers are obtained automatically from the algebraic sign. The ring torsional angles, ϕ_j, are numbered counterclockwise as viewed in the projections in Figure 7. All projected geminal angles are considered to be 120°.

(22) Individual values of A were obtained from the relationship $A = J_{cis}/\cos^2 \phi_{av}$, using the values in Tables I and IV in ref 2.

(23) These pairs are not strictly enantiomeric due to the asymmetric deuterium labeling present. However, any deuterium effect is unlikely to influence the energetics to a measurable extent and may be neglected.[24]

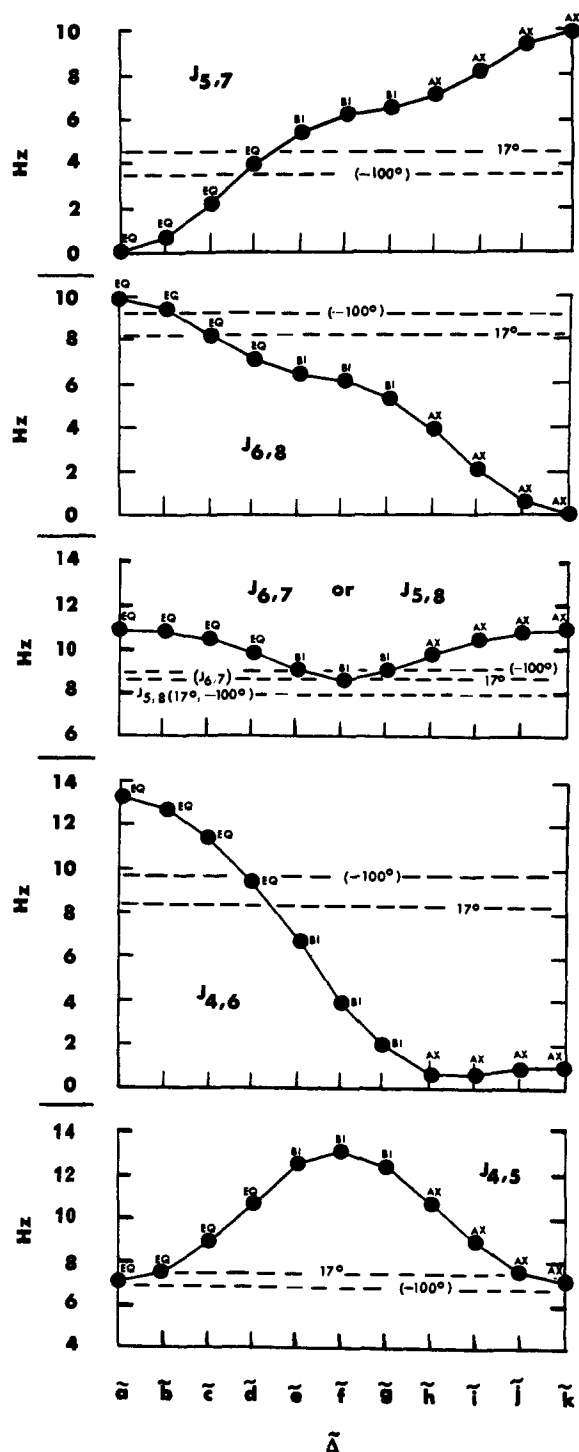(24) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., J. Amer. Chem. Soc., **86**, 1733 (1964).

Figure 8. The estimated theoretical (●, solid lines) vicinal interproton couplings, $(J_{m,n})_{\tilde{\Delta}}$, are plotted as a function of the pseudorotational energy state, $E_{\tilde{\Delta}}(\tilde{\Delta} = \tilde{a}$ to $\tilde{k})$, in five separate graphs along with the corresponding experimentally determined values (dotted lines) at 17 and $-100°$. The bonding position (EQ = equatorial, BI = bisectional, AX = axial) of the methyl substituent for each conformational state is indicated adjacent to the point corresponding to that state. All of the parameters have been presented at the same vertical scale so that their relative sensitivities to conformational change may be readily compared.

rotameric states which must be considered. These enantiomeric pairs are related by a C_s symmetry axis that extends along a line joining $\Delta = 36°$ and $\Delta = 396°$ in Figure 7, such that $\Delta + \bar{\Delta} = 792°$. Each theoretical coupling constant, $(J_{m,n})_{\tilde{\Delta}}$, for a given pseudorotational

energy state, $E_{\bar{\Delta}}^-(\bar{\Delta} = \bar{a}$ to $\bar{k})$, is the arithmetic average of those parameters for the corresponding enantiomers. The relationship of the five averaged theoretical vicinal coupling parameters to those values determined experimentally is depicted graphically in Figure 8.

The magnitudes of the cis vicinal couplings are independent of the algebraic sign of the corresponding ring torsional angle and provide information regarding only the *degree* of ring puckering adjacent to the substituent. The magnitude of $(J_{4,5})_{\bar{\Delta}}$ is highly sensitive to such puckering, and the small magnitude of the experimental value suggests that conformers e, $\bar{e}$, f, $\bar{f}$ g, and $\bar{g}$ (bisectional bonding) are sparsely populated. The behavior of $(J_{5,8})_{\bar{\Delta}}$ and $(J_{6,7})_{\bar{\Delta}}$ is less informative because of the relative insensitivity of these parameters to conformational change, and the apparent better fit of these parameters to a less puckered model is accorded little significance.[25]

The behavior of the trans coupling constants, $(J_{4,6})_{\bar{\Delta}}$, $(J_{5,7})_{\bar{\Delta}}$, and $(J_{6,8})_{\bar{\Delta}}$, reflects both the magnitude and sign of the corresponding ring torsional angles and is therefore sensitive to any axial or equatorial bonding preference for the methyl substituent. The magnitudes of each of these parameters is consistent with a pseudorotation model involving substantial preference for those conformers (a, $\bar{a}$, b, $\bar{b}$, c, $\bar{c}$, d, and $\bar{d}$) in which the methyl group is equatorial and appears to rule out any substantial population of those states in which the methyl substituent is either axial or bisectional.

(25) In fact, the small but systematic increase of $J_{6,7}$ with decreasing temperature is in the direction expected for a highly puckered minimum energy conformation.

At a given temperature, the value of each nmr parameter is an average which reflects the conformer distribution at that temperature. As the temperature is decreased, the Boltzmann distribution law favors increased population of the lowest energy pseudorotameric states, *i.e.*, those conformations in which the methyl substituent is equatorially bonded. Each of these vicinal couplings studied here was found to exhibit a systematic temperature dependence in the direction expected from the above model. This dependence is most dramatic in the case of $J_{5,7}$ and $J_{6,8}$, which involve trans coupling between diastereotopic protons and which undergo large temperature changes in opposite directions.

Conclusion

From the above systematic analysis, it has been clearly demonstrated that with the addition of a methyl substituent, the cyclopentane ring can no longer undergo free pseudorotation but is somewhat restricted to those conformations (a, $\bar{a}$, b, $\bar{b}$, c, $\bar{c}$, d, and $\bar{d}$) in which the substituent is equatorially bonded. This result is in qualitative agreement with the simple prediction based on 1,3-H–H diaxial interactions (Figure 1) and the semiquantitative estimates of Pitzer and Donath[3] and Allinger.[4]

Effects of Polar Substituents on Photoreduction and Quenching of Aromatic Ketones by Amines. Fluorenone and Substituted Dimethylanilines

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Abstract: Photoreduction of fluorenone by dimethylaniline in benzene leads to the 9-hydroxy-9-fluorenyl radical I and the N-methylanilinomethyl radical II, addition of II to the oxygen of ground state fluorenone forming radical III, and combination and cross combination of radicals I and III. Hydrolysis of these products leads to fluorenone pinacol, 97% yield, and to high yields of N-methylaniline and formaldehyde. Quantum yields for the photoreduction are at a maximum, ~ 0.8, with the unsubstituted dimethylaniline and with weak electron donating or withdrawing substituents. Quantum yields decrease with strong electron donating or withdrawing substituents. Very strong electron donation may lead to no photoreduction but to efficient quenching, presumably due to excessive stability of the initially formed charge-transfer complex. Values of k_{ir}, rate constant for charge-transfer interaction of excited fluorenone triplet with the substituted dimethylanilines, have been measured in quenching studies. They vary from $3.2 \times 10^6 \ M^{-1} \ sec^{-1}$ for the p-CN compound to $\sim 10^{10} \ M^{-1} \ sec^{-1}$ for the p-OEt and p-N(CH$_3$)$_2$ compounds and lead to a linear plot of log k_{ir} *vs.* σ values, σ^+ for the strong electron donating substituents, σ^- for p-CN, with $\rho = -1.96$. Photoreductions of Methylene Blue by substituted phenylglycines, of benzophenone by substituted dimethylanilines and benzylamines, and of p-aminobenzophenone by dimethylanilines are discussed.

I t has been proposed[1–3] that photoreduction by amines proceeds *via* rapid charge-transfer type interaction of

(1) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968).
(2) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).
(3) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).

excited acceptor with the n electrons of nitrogen, k_{ir}, followed either by spin inversion, charge destruction and quenching, k_e, or hydrogen transfer and electron reorganization, k_h, as indicated for reduction of excited triplet carbonyl compounds in eq 1. Such a mechanism is consistent with low sensitivity of quantum yield