Finally, we note that the reactions of pyrene radical anion with protonating agents do not seem to have been previously investigated. The simplest interpretation of our results is that they proceed by Scheme I, although they could proceed only partially by Scheme I or its variants.

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Determination of Anisotropy of Molecular Motion with ^{13}C Spin-Lattice Relaxation Times[1a]

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Abstract: A computer program has been written to calculate the rotation diffusion tensor for anisotropic motion from ^{13}C spin-lattice relaxation-time data. Application of this program to ^{13}C spin-lattice relaxation-time measurements of methyl-substituted cycloalkanes is shown. The degree of anisotropic motion within this series of compounds becomes smaller with increasing ring size. The lower limits of the barriers of rotation for the methyl groups are estimated.

Introduction

Although the basic theory for the evaluation of anisotropy of molecular motion by measuring spin-lattice relaxation times has been given by Woessner[2] more than 10 years ago, there is, to our knowledge, up to now, no extensive application of Woessner's formalism for ^{13}C relaxation times in the literature. Most of the current, steadily increasing literature on ^{13}C relaxation times[3,4] deals, at most, with an interpretation of these data in terms of isotropic overall motion of a given molecule. This approximation can result in misinterpretation of data and, more seriously, in a considerable loss of information given by ^{13}C spin-lattice relaxation times. The first application of the theory of anisotropic motion toward ^{13}C relaxation times was given by Grant and coworkers,[5] wherein they studied molecules containing only three T_1's with three rotational diffusion constants. A similar approach, using quadrupole relaxation of the ^{14}N and ^{2}H nuclei, was recently given by Lehn.[6]

In this work, we add a least-squares treatment which allows us to secure the best three rotational diffusion constants when an overdetermined (more than three) set of T_1 values is available. As an extension of our work on unsubstituted cycloalkanes,[7] we have measured the ^{13}C relaxation times of the asymmetric tops, methylcyclopropane through methylcyclooctane, and present here an interpretation of these data within the concept of anisotropic motion in the liquid phase.

Computational Method. The original equation of Woessner[3] for dipolar relaxation in a molecule undergoing anisotropic motion has the following general form

$$\frac{1}{T_{1(j)}} = \mathrm{f}(R_1, R_2, R_3, \lambda_{ij}, \mu_{ij}, \nu_{ij}) \qquad (1)$$

where R_1, R_2, and R_3 are the diagonal components of the rotational diffusion tensor in the principal axis system, and λ_{ij}, μ_{ij}, and ν_{ij} are directional cosines relative to this coordinate system for the appropriate ij proton-carbon-13 interactions. To obtain all three Rs, the T_1's and directional cosines of at least three (j = 1, 3) different carbons must be determined. When $j > 3$ for a rigid molecule, the T_1 data set is overdetermined, and a nonlinear least-squares approach is used by minimization of the sum of squared deviations, S, in experimental and calculated relaxation rates, $1/T_1$.

$$S = \sum_{j=1}^{m} \left\{ \frac{1}{T_{ij(\mathrm{exp})}} - \sum_{i=1}^{n} \mathrm{f}(R_1, R_2, R_3, \lambda_{ij}, \mu_{ij}, \nu_{ij}) \right\}^2 \qquad (2)$$

Here, m is the number of carbon atoms for which experimental data are used in the analysis and n is the total number of hydrogens in the molecule. This search for the best R_1, R_2, and R_3 parameters is achieved using the "simplex method" for function minimization of Nelder and Mead.[8] The procedure only requires that m be at least equal to the number of different R values to be determined. Use of $m > 3$, of course, improves the statistical estimate of these rotational diffusion constants. The explicit form of the Woessner equation,[3] including resonance frequency, is

$$\mathrm{f}(R_1, R_2, R_3, \lambda, \mu, \nu) = \frac{C_+ b_+}{b_+^2 + \omega^2} + \frac{C_- b_-}{b_-^2 + \omega^2} + \frac{C_1 b_1}{b_1^2 + \omega^2} + \frac{C_2 b_2}{b_2^2 + \omega^2} + \frac{C_3 b_3}{b_3^2 + \omega^2} \qquad (3)$$

where the five b variables are linear combinations of the rotational diffusion constants

$$\begin{aligned} b_1 &= 4R_1 + R_2 + R_3 \\ b_2 &= R_1 + 4R_2 + R_3 \\ b_3 &= R_1 + R_2 + 4R_3 \\ b_\pm &= 6R \pm 6\sqrt{R^2 - L^2} \end{aligned} \tag{4}$$

with

$$R = \tfrac{1}{3}(R_1 + R_2 + R_3) \tag{5}$$

$$L^2 = \tfrac{1}{3}(R_1R_2 + R_2R_3 + R_3R_1) \tag{6}$$

As given by Woessner, the C_1, C_2, and C_3 coefficients are a function only of the directional cosines, while the C_+ and C_- terms depend on both directional cosines and the R_1, R_2, and R_3 variables. It should be noted that both C_+ and C_- contain a singularity at $R^2 = L^2$ or $R_1 = R_2 = R_3$, and these terms in eq 3 were transformed to remove this difficulty so that the program also would be operative for the isotropic case. The program accepts as an input the coordinates together with the atomic numbers of the atoms of a molecule, experimental T_1 values, and the nmr frequency. Three vectors which define the motional principal-axis system, and three initial guesses for R_1, R_2, and R_3 have to be supplied. After finding the best solution for eq 2, the program then calculates from the rotation diffusion tensor, the T_1 data for all carbon atoms in the molecule even though no experimental T_1's are given. The program calculates the relaxation contribution of every C-H vector in the molecule, and this is printed to provide the user with information about the relative efficiency of the various proton-carbon interactions. Standard deviation of experimental *vs.* calculated T_1 is given, as well as a standard error analysis[9] of the diagonal rotation diffusion tensor elements. This error analysis is accomplished using the standard deviation in the fit, and by assuming a constant weight matrix for the errors in each T_1 value. Use of a population matrix based on 10% relative errors does not greatly alter the error limits in this study, and, therefore, the former and simpler assumption was used to determine error ranges in the rotation diffusion constants. The agreement between experimental and calculated T_1 data can be used for (i) assignment proof, (ii), check for consistency of the data set, and (iii), failure to achieve agreement may be used to determine segmental motion, lack of molecular rigidity, etc. A major problem in the treatment of rotational diffusion of asymmetric tops lies in the choice of the principal axis system. We have selected these axes to be the principal axes of its moment of inertia tensor. This approximation relies on the assumption that the moment of inertia tensor reflects the overall shape of the molecule and that other factors do not affect the rotational diffusion tensor. For molecules with no very heavy atoms and insignificantly few polar groups, this procedure is felt to be justified. In the simple hydrocarbons studied here, only shape and mass are probably important and, for this reason, the moments of inertia undoubtedly provide the optimum choices for a principal-axis system. It should be emphasized that only pairwise C-13, H-1 interactions are assumed to be important. The contributions of 3- and 4-spin cross correlation effects are neglected. The present program, MOTION, can handle up to 50 atoms and has been successfully applied to compounds as large as retinal.[10]

Experimental Section

The relaxation times were determined using the progressive saturation method[11] with our Brukarian DFS-60[12] spectrometer at a resonance frequency of 15.09 MHz. The solutions (5 *M* in $CDCl_3$) were degassed by three freeze and thaw cycles and sealed in special bulbs which matched the geometry of the rf coil in order to avoid diffusion effects within the liquid sample and the effect of gas-liquid exchange. The probe temperature was held at 30°. A spectral width of 300 Hz was used giving 3070 data points (acquisition time, 5 sec) to monitor the free-induction decay. An 8 K Fourier transform provided a resolution of 0.13 Hz/pt. The 90° pulse width was 12 μsec. To evaluate the peak integrals, a very small weighting function was applied to the free-induction decay, which provided broad symmetrical peaks with peak intensities directly proportional to their integrals.[13] This method could, however, not be used for the carbon atoms 3 and 4 in methylcyclohexane, and for the carbon atoms 1 and 2 in methylcyclopentane, because these signals are too close together to allow the peak broadening method. The T_1 data of these carbon atoms have, therefore, perhaps a higher than usual 10% error limit, although they have been measured many times more than the other compounds.

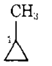
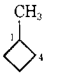
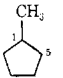
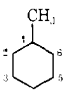
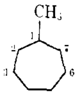
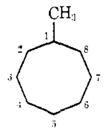
NOE measurements have been performed using a gated decoupling technique described earlier by Kuhlmann and Grant.[14] The factorization in spin-rotation and dipole-dipole relaxation was done with the usual equations,[4] assuming the absence of any other relaxation mechanisms.

The coordinates of the molecules which were needed as an input for the program MOTION have been calculated using the program COORD by Dewar.[15] We modified this program to include two subroutines which calculate the moment of inertia tensor and transform the coordinates in respect to the principal axis of the molecules. As input data for COORD we have chosen bond distances, bond angles, and dihedral angles as given in recent electron diffraction work and reviews on the conformation of these compounds.[16] The proton positions, however, which are mostly not given in the cited literature, were assumed with standard values.

Results and Discussion

The experimental T_1 and NOE data, together with a factorization into dipole-dipole relaxation and spin-relaxation, are given in Table I. As for the unsubstituted cycloalkanes,[7] spin-rotation is negligible for the compounds with a ring size $n \geq 6$ and becomes more important for the smaller molecules and finally dominates the relaxation times in methylcyclopropane. Table II contains the rotational diffusion tensors, the standard deviations of the fits, and the cal-

Table I. Relaxation Times and Nuclear Overhauser Enhancements for ^{13}C in Methyl-Substituted Cycloalkanes at 30°

Compound	Carbon atom	T_1 (exptl), sec	NOE ($\eta + 1$)	T_{1DD}, sec[a]	T_{1SR}, sec[b,c]
	1	15.2	1.49	61.6	20.2
	2,3	13.5	1.60	44.7	19.3
	Me	12.2	1.82	29.7	20.8
	1	42.8	2.63	52.2	238
	2,4	31.0	2.83	33.7	394
	3	22.6	2.90	23.6	514
	Me	30.5	2.68	36.1	198
	1	34.2	2.81	37.5	384
	2,5	26.3	2.66	31.5	160
	3,4	27.9	2.74	31.7	225
	Me	17.1	2.93	17.6	602
	1	21.7	3.0	21.7	>150[d]
	2,6	13.7	3.0	13.7	
	3,5	14.0	3.0	14.0	
	4	12.7	3.0	12.7	
	Me	11.6	3.0	11.6	
	1	17.7	3.0	17.7	>150[d]
	2,7	12.2	3.0	12.2	
	3,6	13.3	3.0	13.3	
	4,5	12.6	3.0	12.6	
	Me	8.7	3.0	8.7	
	1	11.5	3.0	11.5	>150[d]
	2,8	7.6	3.0	7.6	
	3,7	7.8	3.0	7.8	
	4,5	8.0	3.0	8.0	
	5	7.2	3.0	7.2	
	Me	6.2	3.0	6.2	

[a] Contribution to the overall T_1 of dipolar relaxation. [b] Contribution to the overall T_1 of spin rotation relaxation. [c] Numbers are not significant for values exceeding 200 sec. [d] Lower limit estimated with the assumption of a 10% error in the NOE measurements.

Table II. Calculated and Experimental Dipolar Relaxation Times and Rotational Diffusion Constants for Methyl-Substituted Cycloalkanes $(CH_2)_{n-1}CH{-}CH_3$

n	Carbon atoms	T_{1DD}, sec[a] (calcd)	T_{1DD}, sec[b] (calcd)	T_{1DD}, sec (exptl)	$R_1 \pm dR$[c]	$R_2 \pm dR$[c]	$R_3 \pm dR$[c]	σ[d]
4	1	51.7	56.8	52.2	61 ± 15	<4	25 ± 3	0.0006
	2,4	33.5	38.1	33.7				
	3	23.8	26.8	23.6				
	Me	23.0	25.9	36.1				
5	1	39.1	36.7	37.5	<16	24 ± 19	95 ± 28	0.0026
	2,5	31.3	30.9	31.5				
	3,4	31.6	30.6	31.7				
	Me	19.2	18.4	17.6				
6	1	21.7	22.0	21.7	6	13 ± 0.6	19 ± 2	0.001
	2,6	13.8	13.8	13.7				
	3,5	13.8	13.8	14.0				
	4	12.7	12.7	12.7				
	Me	11.8	11.7	11.6				
7	1	22.1	23.0	17.7	13 ± 5	9 ± 3	8.0 ± 5	0.009
	2,7	12.7	12.1	12.1				
	3,6	12.9	12.4	13.3				
	4,5	12.0	12.0	12.6				
	Me	10.4	9.5	8.7				
8	1	13.1	13.1	11.5	5 ± 0.6	5 ± 1	9.0 ± 2	0.005
	2,8	7.4	7.4	7.6				
	3,7	7.9	7.9	7.8				
	4,6	7.9	7.9	8.0				
	5	7.3	7.3	7.2				
	Me	6.2	6.2	6.2				

[a] Calculated without including the methyl group T_1 in the minimzation. [b] Calculated by including the methyl group T_1 in the minimization. [c] Given in units of 10^{10} rad/sec. For all compounds except methylcyclobutane. Taken from the fit where the methyl group was included. [d] Calculated with $\sigma = \Sigma_{j=1}^{m}(1/T_{1j}\,(\text{exptl})) - (1/T_{1j}\,(\text{calcd}))^2/(m - 3)$.

Table III. Lower Limit of the Rotational Barrier of Methyl Groups in Methyl-Substituted Cycloalkanes, $(CH_2)_{n-1}CH{-}CH_3$

$n = 5$	>2.3 kcal/mol
$n = 6$	>3.0 kcal/mol
$n = 7$	>3.1 kcal/mol
$n = 8$	>3.3 kcal/mol

culated *vs.* experimental T_{1DD}. The calculation of these diffusion constants has been made twice for each molecule:[17] first, without including the T_1 data for the methyl groups in the minimization progress, and then with consideration of the methyl groups. It could be shown that, in the compounds methylcyclooctane through methylcyclopentane, the T_1's of the methyl groups were very well predicted (*cf.* first column in Table II). The apparent conclusion from this result is that the methyl groups in these compounds are relaxed *via* the overall molecular motion; that is, they are essentially "locked in" and do not undergo significant independent spinning motion on the molecular diffusion time scale. For methylcyclobutane, it was not possible to obtain a satisfactory fit either with or without consideration of the methyl group, whereas in methylcyclopropane, this kind of treatment is not possible because, here, the rigid part of the molecule provides only two ^{13}C signals. The obvious result from a comparison of the rotational diffusion tensors in Table II is that the more spherical-shaped molecules, methylcyclooctane and methylcycloheptane, undergo more or less isotropic reorientation while the smaller molecules prefer to reorient more rapidly along their long axes, where the moments of inertia are smaller and the anisotropic factors are larger than 3. As spin-rotation effects tend to become prevalent only as the motion moves into the inertia-controlled limit, these results are reasonable. The relatively high errors in the fits for methylcyclobutane and methylcyclopentane can, perhaps, be explained by the fact that the assumption of rigidity does not hold for these molecules.

Limits in the Rotational Barriers for Methyl Group Rotation. The fact that the methyl groups in methylcyclooctane through methylcyclopentane are relaxed *via* the overall molecular motion allows calculation of the lower limit of their rotational barrier. In eq 7,[4a] ρ is the spinning rate (torsional

$$\rho = \rho_0 e^{-\Delta E/RT} \qquad (7)$$

rotation) of the methyl group; ρ_0 is given by eq 8. The moment of inertia of a methyl group, I_m, in respect to its symmetry axis can be calculated to be 3.258×10^{-40} amu cm^2

$$\rho_0 = \frac{3}{2}\left(\frac{kT}{I_m}\right)^{1/2} \qquad (8)$$

which leads to a ρ_0 value of 1.7×10^{13}. Assuming that ρ can be given by eq 9, where $\bar{R}$ is the trace of the rotation

$$\rho \leq \bar{R} \qquad (9)$$

diffusion tensor, we calculated with $\rho = \bar{R}$ the lower limit of the ΔE value, and these are given in Table III. The fact that the lower limit of the barrier drops toward the smaller rings fits nicely with our observation that we have not been able to find a good fit with the program MOTION for methylcyclobutane when the methyl group was included in the minimization.

References and Notes

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(17) It should be noted that the molecular geometries used for the calculations were slightly asymmetric. The average of the calculated values for equivalent carbon atoms is given in Table II.

Fluoropyridines. Carbon-13 Chemical Shifts and Carbon–Fluorine Coupling Constants

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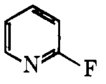
Abstract: Carbon-13 chemical shifts and all ^{13}C–F coupling constants have been determined for 2-, 3-, and 4-fluoropyridine and pyridinium ions. With the exception of C_2 in the 2-fluoro compounds, chemical shifts are derived additively from those of the corresponding carbons in pyridine, pyridinium ion, and fluorobenzene. $^1J_{CF}$ in 2-fluoropyridine is algebraically more positive than $^1J_{CF}$ in 3- and 4-fluoropyridine, consistent with a positive contribution associated with the presence of a proximate lone pair orbital. Protonation induces increases in the one-bond couplings of 2- and 4-fluoropyridine, while that of 3-fluoropyridine is unaffected. Many of the detailed trends exhibited by the coupling constants are paralleled by values of J_{CH} in pyridine and fluorobenzene, as well as some other heterocycles, although only crude overall correlations exist. A better correlation exists between corresponding values in the fluoronitrobenzenes vs. the fluoropyridinium ions. Most of the experimental coupling trends are reproduced by values calculated using finite perturbation theory in the INDO MO approximation assuming only the Fermi contact mechanism.

Our current interest in carbon-13 magnetic resonance parameters of unsaturated nitrogen compounds[2] has led us to examine a series of fluorinated pyridines. These are of interest because of the possibility that geometry-dependent interactions involving the lone-pair orbitals may affect chemical shifts and coupling constants. It has already been amply documented that nitrogen lone-pair orientation markedly affects coupling constants to nitrogen[2,3] and coupling between nuclei with different relative spatial proximity to the lone pair.[4] We report here ^{13}C magnetic resonance data on 2-, 3-, and 4-fluoropyridine (**1–3**) and the pyridinium ions.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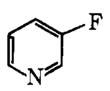
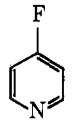

2


3

The carbon magnetic resonance parameters of these compounds display systematic variations which allow comparison with structurally related compounds and with semiempirical MO calculations. The latter have been carried out in order to determine the extent to which the Fermi contact term can account for the observed coupling constants. Earlier published work[5] did not include **2** and **3** because of their unavailability; indeed only recently has **3** been described.[6]

Experimental Section

Materials. 2-Fluoropyridine was obtained from Aldrich Chemical Co., while 3-fluoropyridine and 4-fluoropyridine hydrochloride were gifts from Olin Chemical. The hydrochlorides of **1** and **2** were precipitated upon passage of HCl gas through solutions of **1** and **2** in dry ether. 4-Fluoropyridine was obtained from the hydrochloride by addition of ice water to a cold suspension of the salt and potassium carbonate in dichloromethane, into which the free base was immediately extracted. The dried (K_2CO_3) solution was used directly for the NMR study.

NMR Spectra. Compounds **1** and **2** were run as neat liquids; **2** was also run as dilute (~10%) solutions in dichloromethane and in methanol; a small solvent effect is apparent. 4-Fluoropyridine and all the hydrochlorides were run as solutions in dichloromethane. Spectra were obtained in Fourier transform mode on a JEOL PS/PFT-100 spectrometer with the JEOL EC-100 data system. Chemical shifts were measured with respect to solvent resonances and converted to the TMS scale with the following factors:[7] δ (TMS) = δ (CH_2Cl_2) + 54.0; δ (TMS) = δ (CH_3OH) + 44.3. Resonance positions were determined using a 5-kHz range and 16K words of memory, giving a digital resolution of 0.6 Hz. Coupling constants were measured from 2-kHz spectra and 16K words of memory, with a digital resolution of 0.24 Hz. The line broadening induced by exponential smoothing of the free induction decay amounted to 0.22 Hz. The deuterium internal lock was derived from a deuteriobenzene capillary.

Method of Calculation. Coupling constants were calculated on an IBM-360/165 computer using the finite perturbation theory of Pople[8] in the INDO approximation. The geometry of 2-fluoropyridine was taken from a microwave study,[9] while those of 3- and 4-fluoropyridine were assumed the same as that of pyridine.[10] The C–F bond length of 2-fluoropyridine (1.354 Å) was used in all six calculations. The geometry of the fluoropyridinium ions was assumed to be that of pyridinium hydrochloride.[11]