Summary

The chemical shifts of the α carbons in the pentamethylene heterocycles are influenced primarily by the electronegativity of the heteroatom, with further perturbations dependent on the nature and orientation of the 1 substituents. Although heteroatom electronegativity is an important determinant of the chemical shift of the β carbons, this shift is especially sensitive to the presence of axial substituents at the 1 position and hence is of considerable utility in conformational analysis. Changes in the chemical shift of the γ carbon, like those of the α carbon, are due primarily to the electronegativity of the heteroatom. The ratio of the slopes of the plots of chemical shift vs. heteroatom electronegativity is about $1.0/-0.05/-0.1$ for the $\alpha/\beta/\gamma$ positions. The change of sign and large decrease in magnitude from carbon α to carbon β are consistent with the Pople-Gordon (alternating) model for charge polarization,[24] provided that both shifts result from the same or similar shielding mechanisms.

References and Notes

(1) Supported in part by the National Science Foundation (Grant No. MPS-72-05006).
(2) Except for piperidine the names for all the pentamethylene heterocycles discussed in this paper are constructed from the root (-ane or -inane) plus the appropriate prefix designating the heteroatom. The extra syllable -in- is included in some cases to differentiate the heterocycle from the parent hydride: silinane (not silane), germinane, and phosphorinane, but arsenane, antimonane, oxane, thiane, selenane, and tellurane. The trivial name piperidine is retained for historical reasons, although azane is not unreasonable.
(3) The conformational properties have been reviewed recently: J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).
(4) For reviews, see (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 269–277; (b) D. A. Netzel, Ph.D. Dissertation, Northwestern University, 1975.
(5) S. I. Featherman, S. O. Lee, and L. D. Quin, *J. Org. Chem.*, **39**, 2899 (1974).
(6) (a) G. Ellis and R. G. Jones, *J. Chem. Soc., Perkin Trans. 2*, 437 (1972); (b) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **95**, 165 (1973); H. Booth and D. V. Griffiths, *J. Chem. Soc., Perkin Trans. 2*, 842 (1973).
(7) F. G. Riddell, *J. Chem. Soc. B*, 331 (1970).
(8) For the study on relaxation times, see J. B. Lambert and D. A. Netzel, *J. Am. Chem. Soc.*, following paper in this issue.
(9) Thiane oxides: J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).
(10) Piperidines: J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).
(11) Thianes, selenanes, telluranes: J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Am. Chem. Soc.*, **89**, 5921 (1967).
(12) *N*-Chloropiperidine: J. B. Lambert, W. L. Oliver, Jr., and B. S. Packard, *J. Am. Chem. Soc.*, **93**, 933 (1971).
(13) Phosphorinanes: J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron*, **27**, 4245 (1971).
(14) Thiane and selenane dihalides: J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *J. Am. Chem. Soc.*, **94**, 8172 (1972).
(15) Selenanes and telluranes: J. B. Lambert, C. E. Mixan, and D. H. Johnson, *J. Am. Chem. Soc.*, **95**, 4634 (1973).
(16) P. Mazerolles, *Bull. Soc. Chim. Fr.*, **29**, 1907 (1962).
(17) J. B. Lambert and H.-n. Sun, to be published. Details may be found in H.-n. Sun, Ph.D. Dissertation, Northwestern University, 1975.
(18) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).
(19) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).
(20) E. L. Eliel and F. W. Vierhapper, *J. Am. Chem. Soc.*, **97**, 2424 (1975).
(21) S. I. Featherman and L. D. Quin, *J. Am. Chem. Soc.*, **97**, 4349 (1975).
(22) P. E. Peterson, B. R. Bonazza, and P. M. Henrichs, *J. Am. Chem. Soc.*, **95**, 2222 (1973).
(23) H. G. Kuivila (State University of New York at Albany, private communication) has recorded the carbon-13 resonances of 1,1-dimethylstanninane: α (10.8), β (28.6), γ (32.8), CH_3 (−11.4). The points for the α and γ carbons fall very close to the lines for the neutral, methylated systems in Figures 1 and 2. The β carbon continues the trend set by $(CH_3)_2Si$ and $(CH_3)_2Ge$ in Figure 3. In fact, the point falls essentially on the line determined by CH_3CH and CH_3N. The through-space effect of the axial methyl group must be entirely lost because of the long C–Sn bonds, but the through-bond effect of the equatorial methyl group is still present. We are grateful to Professor Kuivila for permission to mention these data.
(24) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(25) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).
(26) M. W. Duch, Ph.D. Dissertation, University of Utah, 1970.
(27) Reference 4a, pp 128–139.
(28) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975).

Carbon-13 Spin–Lattice Relaxation Times of the Pentamethylene Heterocycles

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Abstract: Spin–lattice relaxation times (T_1) have been measured by the inversion-recovery method for the ring and 1-substituent carbons in the pentamethylene heterocycles of groups 4, 5, and 6. The relaxation rates for the α carbons are directly proportional to the molecular weight, with the exception of piperidine, which is partially associated. Anisotropic tumbling with a preferred axis of rotation from the heteroatom to C-4 was indicated for the heterocycles from groups 4 and 5 by the consistently smaller value of T_1 (faster relaxation rate) for the γ carbons (C-4). The temperature dependence of T_1 was investigated for 1-methylpiperidine (1-methylazane), tetrahydropyran (oxane), 1-methylarsenane, and selenane. The monotonic rise of T_1 with temperature for oxane and the azane, with only a small curvature in the plot of ln T_1 vs. $1/T$, is consistent with predominant relaxation by the dipole–dipole mechanism. The relative magnitude of the CH_3 relaxation time, in comparison to that of CH_2, indicates that rotation about the C–CH_3 and N–CH_3 bonds is somewhat hindered, but that rotation about the Si–CH_3, P–CH_3, and As–CH_3 bonds is more nearly free.

Few studies have been reported on the relaxation of carbon-13 in simple saturated heterocycles: 1,4-dioxane,[2a] 2,4,6-trimethyltrioxane,[2b] 2,3,5,6-tetramethylpiperazine,[2b] 1,2,2,3,4,4-hexamethylphosphatane oxide,[2c] among others. No studies have been reported on the fundamental pentamethylene heterocycles, that is, those with six members, one heteroatom, and a substituent, if any, only at the 1 position, $(CH_2)_5X$. This family of heterocycles[3] includes piperidine (azane[4]), tetrahydropyran (oxane), thiane, and phosphorinane. Relaxation times have been found to be useful probes for the investigation of molecular structure, conformation, motion, and interactions.[6] This study was initiated to define the relaxation mechanisms present in the pentamethylene heterocycles, to determine the effects of the heteroatom and of 1 substituents on the relaxation time, to ascertain whether overall motion of the molecules is isotropic or anisotropic, and to learn

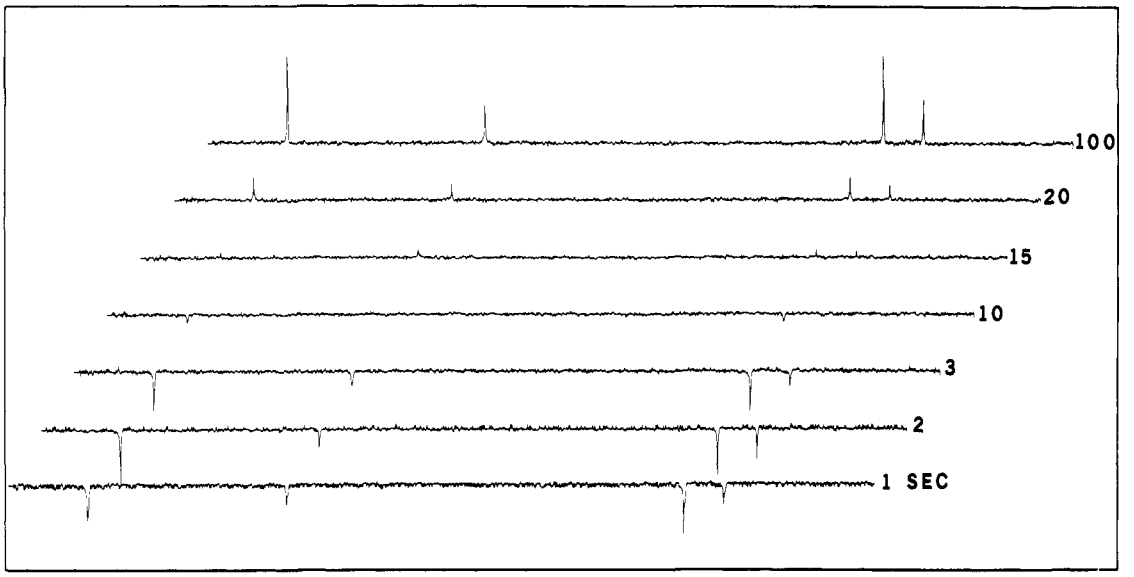

Figure 1. The frequency-domain carbon-13 spectra of 1-methylpiperidine at 90°. Each spectrum results from a 180° pulse, a variable interval τ, and a 90° pulse. The spectra are illustrated as a function of the pulse interval τ in seconds. The sweep width is 1000 Hz, and a single pulse sequence was used to obtain each spectrum. For the lowermost spectrum (τ = 1 s), the pulse interval is so short that almost all the spins remain inverted, whereas for the uppermost spectrum (τ = 100 s), the interval is sufficiently long to effect almost complete recovery. The resonances from left to right correspond to the α, CH_3, β, and γ carbons.

whether conformational information such as the orientation of the 1 substituent could be derived from relaxation times. We report herein the determination of the spin-lattice relaxation times for pentamethylene heterocycles of groups 4, 5, and 6. To help define the mechanisms of relaxation, the phenomenon has been studied as a function of temperature for 1-methylpiperidine, 1-methylarsenane, oxane, and selenane.

Experimental Section

Spin-lattice relaxation measurements were performed on a Bruker HFX-90 NMR spectrometer operating in a single-coil, pulsed mode. A fluorine-19 lock was provided by hexafluorobenzene sealed in a capillary tube. Proton coupling was removed with broadband double irradiation. The inversion-recovery technique (180°-τ-90°-t) was utilized for measurement of the relaxation times (a 180° pulse for inversion of spins, a variable amount of time τ for recovery through relaxation, a 90° pulse for determination of the extent of magnetization remaining after τ, and finally a time t to permit reestablishment of equilibrium before initiation of another pulse sequence). The pulse width and the interval between pulses (τ) were controlled by a pulse programmer built locally by J. G. Larsen. The 180° pulse width was set by a hardwired program at twice the length of the experimentally determined 90° pulse width. To determine the 90° pulse width of undegassed benzene, the maximum height of a single-pulse free induction decay (fid) was plotted against the pulse width in microseconds. A maximum was obtained at 23 μs, a minimum at 46 μs, and another maximum of smaller intensity at 67 μs, corresponding to 90, 180, and 270° pulses. A similar experiment with the heterocycles indicated a setting of about 25 μs for the 90° pulse.

A dwell time of 200 μs was used to expand the frequency range to 2500 Hz and to increase the number of data points per resonance peak. The fid signal was stored in a Fabri-tek (Nicolet) 1074 signal averager with 4095 channels, and the Fourier transformation was carried out on a PDP-8/L computer with 4K memory. For determination of the spin-lattice relaxation time, the digital intensity of each resonance signal obtained from the magnitude spectrum of the transformed fid signal was measured as a function of the pulse interval τ. Figure 1 depicts a stack of spectra[7] obtained in this fashion for 1-methylpiperidine at 90°. A single pulse sequence was used to obtain the intensity of the resonance lines for each value of τ. The spin-lattice relaxation time, T_1, was computed from eq 1, in which A_∞ is the intensity at time ∞ (after a single 90° pulse), A_τ is the intensity at time τ, and τ is the pulse interval time in seconds.

$$\ln (A_\infty - A_\tau) = \ln 2A_\infty - \tau/T_1 \quad (1)$$

Calculations were carried out on a Nova 840 computer with a program DNT1CAL, a listing of which is given elsewhere.[8,9] The program, written in Basic, computes the best exponential curve for the data points according to the least-squares criterion by adjusting A_∞, A_0 (intensity after the 180° pulse), and T_1. The only input data are the signal intensities A_τ and the pulse interval times τ. The program lists the spin-lattice relaxation time, the calculated intensity at each value of τ, the difference between the observed and calculated intensities, the standard deviation for the best fit, the 90% error on T_1, and the value of A_∞. The program does not plot the data. The major advantage of this program is its independence from an experimentally measured value of A_∞.

The inversion-recovery method does not depend on complete inversion of the nuclear spin magnetization on application of the 180° pulse for valid T_1 determinations. The actual degree of inversion can be computed by comparing the theoretical intercept of eq 1, $\ln 2A_\infty$, with the observed intercept found from the best straight-line fit of the data. For benzene the degree of inversion was found to be 99%, but for the heterocycles it was less (85% for thiane). Since the same pulse width (25 μs) was used throughout the study, either the 90° pulse width varies with the compound or one or more of the instrumental components are not entirely stable.

Spin-lattice relaxation times were measured as a function of temperature for several samples. Analysis of these data required a plot of the logarithm of T_1 against reciprocal temperature. A polynomial regression program DNBB05,[9] a listing of which is given elsewhere,[8] used an input of T_1 and T and produced a best fit for a given polynomial order. Second-order plots provided the best fit in all cases. The same program was used to plot the $\ln (A_\infty - A_\tau)$ vs. τ data for visual inspection.

All liquid samples were distilled, degassed by three or four freeze-thaw cycles, and vented with N_2 gas. The sample was placed in a 10-mm tube with a sealed 4-mm coaxial tube containing the standard C_6F_6. A vortex plug was placed 2 cm above the bottom of the tube, which was then capped. The bottom of the tube (lower end of the sample) and the bottom of the plug (upper end of the sample) extended only slightly beyond the receiving coil so that diffusion of spins was minimal. Sources of materials have been given elsewhere.[5]

Results

Table I lists the relaxation times measured in this study. For each compound, the α, β, γ, and 1-substituent (if any) carbons were examined. Representatives are present from groups 4, 5, and 6. Substituents were admitted only at the 1 position, with the 1-methyl group 5 series extending from nitrogen through

Table I. Spin–Lattice Relaxation Times in Pentamethylene Heterocycles[a]

X	T, °C	$T_1(\alpha)$, s	$T_1(\beta)$, s	$T_1(\gamma)$, s	$T_1(CH_3)$, s
			Group 4		
$C(CH_3)_2$[b]	30	11.9 ± 0.6	11.3 ± 0.6	10.4 ± 0.5	8.4 ± 0.9
$Si(CH_3)_2$	30	9.6 ± 0.6	9.0 ± 0.5	8.8 ± 0.6	11.6 ± 0.6
			Group 5		
:NH	30[c]	8.0 ± 1.4	7.6 ± 1.1	6.9 ± 1.1	
	30[c]	8.0 ± 0.8	8.1 ± 0.9	7.3 ± 0.9	
$:NCH_3$	5	7.4 ± 0.7	7.3 ± 0.9	6.4 ± 0.6	6.1 ± 1.5
	19	7.9 ± 1.2	7.6 ± 0.9	7.3 ± 0.9	6.5 ± 1.2
	30	12.8 ± 0.9	12.6 ± 1.1	11.0 ± 1.3	9.7 ± 0.9
	50	12.7 ± 2.6	12.7 ± 0.6	10.7 ± 1.2	10.3 ± 1.8
	60	15.0 ± 2.2	14.6 ± 2.3	12.3 ± 1.5	11.6 ± 1.5
	71	14.5 ± 2.3	14.6 ± 2.0	12.8 ± 1.5	12.1 ± 2.1
	89	17.0 ± 2.4	17.8 ± 2.7	15.3 ± 2.4	14.0 ± 1.7
$:PCH_3$	30	8.1 ± 1.1	7.9 ± 0.9	7.0 ± 0.8	8.2 ± 1.1
$:AsCH_3$	5	3.8 ± 0.5	3.8 ± 0.5	3.2 ± 0.4	7.3 ± 0.3
	30	9.5 ± 0.8	9.0 ± 0.8	8.9 ± 0.9	13.5 ± 1.1
	72	10.0 ± 1.0	9.6 ± 1.0	8.8 ± 1.5	12.5 ± 1.2
			Group 6		
O	5	10.4 ± 1.3	9.4 ± 1.2	9.5 ± 1.1	
	30	14.4 ± 2.8	13.8 ± 0.7	14.5 ± 0.7	
	71	18.3 ± 2.6	18.4 ± 1.3	19.1 ± 1.8	
S	30	8.6 ± 0.8	9.1 ± 1.3	9.0 ± 1.0	
Se	20[d]	4.5 ± 0.4	4.2 ± 0.5	4.2 ± 0.5	
	30	7.1 ± 0.9	7.7 ± 0.9	7.6 ± 0.9	
	90[d]	12.1 ± 2.2	12.3 ± 2.3	11.8 ± 2.7	
Te	30	4.2 ± 0.5	4.5 ± 0.6	4.4 ± 0.7	
:SO[e]	30	2.9 ± 0.4	3.1 ± 0.5	2.7 ± 0.4	
SO_2[f]	30	2.6 ± 0.4	2.6 ± 0.3	2.5 ± 0.3	

[a] Neat samples unless otherwise noted. [b] The T_1 of the quaternary carbon was measured to be 70.0 ± 0.6 s. [c] Separate, independent runs on the same sample, to determine reproducibility. [d] Measured from data taken at the University of Chicago with the assistance of Dr. W. W. Conover. [e] 6.9 M $CDCl_3$ solution. [f] 4.3 M $CDCl_3$ solution.

arsenic. The unsubstituted group 6 series was complete from oxygen to tellurium. Thiane was also studied as the oxide and dioxide. Only carbon and silicon in the 1,1-dimethyl forms were studied for group 4, although abortive attempts were made with the germanium compound. Errors were generally in the range 10–15%.

Relaxation times were measured as a function of temperature for 1-methylpiperidine, 1-methylarsenane, oxane, and selenane to determine whether spin-rotation contributes to the relaxation process. Figure 2 presents a plot of the logarithm of the spin-lattice time vs. reciprocal temperature for the γ carbon of 1-methylpiperidine. The remaining carbons gave similar plots, which have been recorded elsewhere.[8] The analogous plots for oxane, although based on more limited data, appeared to have essentially the same form. For 1-methylarsenane and selenane, however, the plots fell off more rapidly with increased temperature or even gave an apparent maximum. The shapes were poorly defined, since only three points were available.

Discussion

Of the possible mechanisms of spin-lattice relaxation (dipole-dipole, spin-rotation, chemical shift anisotropy, and scalar coupling), we can expect that dipole-dipole relaxation will provide the dominant effect because each carbon carries directly bonded protons. For an isotropic, rigid molecule tumbling rapidly in solution, the rate R_1 of dipole-dipole relaxation is given by eq 2,

$$R_1(\mathrm{DD}) = \frac{1}{T_1(\mathrm{DD})} = \frac{n\hbar^2\gamma_C^2\gamma_H^2\tau_c}{r^6} \qquad (2)$$

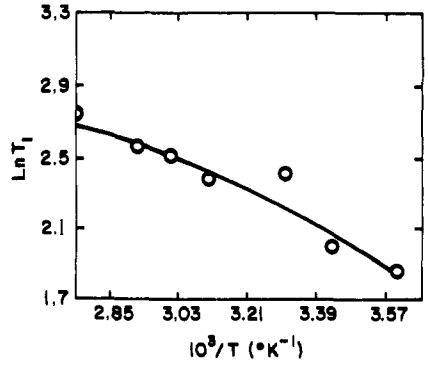

Figure 2. The logarithm of the spin-lattice relaxation time of the γ carbon of 1-methylpiperidine as a function of reciprocal temperature (Arrhenius plot). The line represents the best least-squares fit to a second-order polynomial.

in which n is the number of protons directly bonded to the carbon, the γ's are the gyromagnetic ratios for carbon-13 and hydrogen, τ_c is the molecular correlation time, and r is the directly bonded C–H distance.[6] Although this equation is valid only in the case of "extreme narrowing", most nonviscous organic compounds realize this condition. Many molecules, however, are not rigid and are not isotropic in their tumbling. We will examine the consequences of the breakdown of these assumptions. The correlation time τ_c in eq 2 can be related to the diffusion constant D by eq 3.[10]

$$\tau_c = 1/6D \qquad (3)$$

The diffusion constant in turn can be related to the temperature T, the molecular radius a (assuming a spherical molecule), and the viscosity η by eq 4,

$$D = kT/8\pi a^3\eta \qquad (4)$$

in which k is the Boltzmann constant. Equation 4 is sometimes modified to include a correction for microviscosity. The radius to the third power is equivalent to a volume dependence, which can be replaced by molecular weight (M) divided by density (ρ), as in the proportionality of eq 5,

$$D \propto \rho/M\eta \qquad (5)$$

which is expressed at constant temperature. The inverse relationship between the diffusion constant and the molecular correlation time (eq 3) therefore leads to the proportionality of eq 6.

$$R_1(\mathrm{DD}) = \frac{1}{T_1(\mathrm{DD})} \propto \frac{nM\eta}{\rho} \qquad (6)$$

At constant temperature, the dipole-dipole relaxation rate is seen to vary directly with the number of attached protons n, the molecular weight M, and the viscosity η, and inversely with the density. For the solutions we are studying, changes in density should be small. Changes in viscosity, however, may be significant. The phenomenon of dipole-dipole relaxation can therefore be approached by examining the effect of temperature and viscosity, of the number of attached protons, or of the overall molecular weight. Any conclusions drawn from the proportionality of eq 6 must be tempered by recognition that its derivation required the assumption of isotropic motion of rigid, spherically shaped molecules. Woessner[11] has explored the dipolar spin-lattice relaxation rate for ellipsoidal molecules undergoing anisotropic rotational diffusion. Our results will be examined qualitatively in terms of this model. The assumption that the molecule is rigid may be good for most of this series of molecules. Ring reversal ($E_a \sim 10$ kcal/mol) is very slow with respect to overall molecular reorientation. Rotation about the CH_3–X bond in the groups 4 and 5 het-

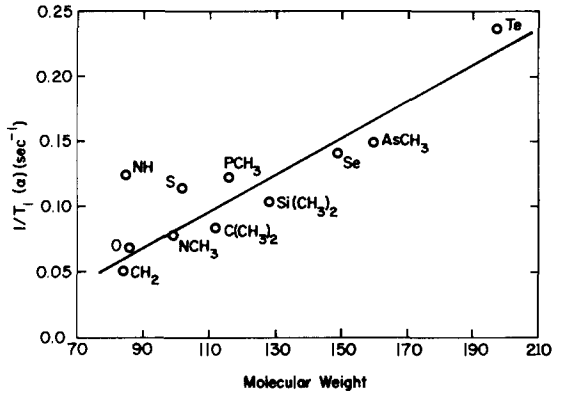

Figure 3. The relaxation rate (reciprocal relaxation time) as a function of molecular weight for the pentamethylene heterocycles of groups 4, 5, and 6, plus cyclohexane and 1,1-dimethylcyclohexane.

erocycles, however, may lead to a breakdown in this assumption for methyl relaxation.

At higher temperatures, as the dipole–dipole mechanism becomes less important, spin–rotation provides a compensating mechanism for relaxation. Hence Arrhenius plots (Figure 2) can give an indication of the importance of spin–rotation relaxation.[6]

The plot of the relaxation rate as a function of molecular weight at constant temperature gives quite a good straight line for the entire set of data obtained in this study. Figure 3 illustrates this plot for the relaxation rate at 30° of the α carbons, all of which have two attached protons. The small amount of scatter can be due to variations in density or viscosity or to different degrees of anisotropy in tumbling. The goodness of the overall correlation, however, confirms that the major mechanism of relaxation is dipolar. The most prominent deviation from the plot is piperidine. It is known that this molecule is associated in solution through intermolecular hydrogen bonds.[12] Such a phenomenon would have a strong effect on the molecular correlation time. A higher effective molecular weight would put the piperidine point on the line. The relationship between relaxation rate and molecular size has been noticed in many other systems, such as the cycloalkanes.[13] No other homologous series, however, has been able to illustrate the effect with such a plot.

Comparison of the α-, β-, and γ-carbon relaxation times for a given heterocycle (Table I) shows that there is anisotropic tumbling of the molecules. For all the groups 4 and 5 heterocycles, the γ-carbon relaxation time is slightly shorter than those of the α and β carbons. The effect is similar to, but not so large as that in monosubstituted benzenes.[14] The preferred axis of molecular rotation therefore is that between the heteroatom and C-4. For the group 6 heterocycles, which have no substituent on X, the relaxation times are almost the same for all the carbons. Tumbling may be essentially isotropic for this entire series.

If the methyl groups are a rigid part of an isotropically tumbling molecule, the methyl/methylene relaxation time ratio should be 2/3 (eq 6). For rapid internal rotation about the CH_3–X bond, however, the ratio should be 6.[6] The observed methyl relaxation times are intermediate between 2/3 and 6 times the methylene relaxation times (Table I). For carbon and nitrogen, the methyl relaxation times are less than those of the ring carbons and hence are nearer the extreme of 2/3. Although detailed conclusions cannot be drawn because of anisotropic motion, the methyl–X rotation for C and N must be less than free, so that the molecule approaches the rigid model. Further down the periodic table, the relative values reverse, so that for silicon and particularly arsenic the methyl relaxation times are significantly longer. Less hindered rotation must be permitted by the longer bond lengths. These results agree with what is known about torsional barriers, with the CH_3–N barrier higher than the CH_3–P barrier, and the CH_3–C barrier higher than the CH_3–Si barrier.[15]

In general, the spin–lattice relaxation times increase with temperature for the four systems studied (Table I), as expected for predominant dipolar relaxation. There is some curvature in the Arrhenius plots (Figure 2), which, although slight for oxane and 1-methylazane, is quite pronounced for selenane and 1-methylarsenane. Thus at higher temperatures spin–rotation relaxation probably becomes more important. Differentiation of the equation defining the line in Figure 2 and setting the result equal to zero gives the temperature at which contributions from dipole–dipole and spin–rotation relaxation become equal (neglecting contributions from other mechanisms). For 1-methylpiperidine, this temperature was found to be about 165° (the average for the four carbons). Only three points were obtained for each of the other three systems studied by variation of temperature, so that an accurate 50/50 temperature could not be determined. The plots gave the appearance that spin–rotation relaxation was proportionately more important at lower temperatures for the third row heterocycles than for those of the first row. More definitive data could be obtained from nuclear Overhauser experiments. For the azane and the arsenane the methyl and ring carbon relaxation times showed no qualitative difference in their temperature dependences, so a spin–(internal rotation) contribution is not important at these temperatures.

The spin–lattice relaxation times for the oxides of thiane are much smaller (rates faster) than could be explained in terms of molecular weight alone (Figure 3). The molecules may be associated, or there may be a dipolar interaction with the solvent, since these were the only systems studied in a solvent.

Summary

The relaxation rate for the ring carbons of the pentamethylene heterocycles of $Si(CH_3)_2$, NCH_3, PCH_3, $AsCH_3$, O, S, Se, and Te is directly proportional to the molecular weight at constant temperature. Dimethylcyclohexane and cyclohexane fall on the same line (Figure 3). The deviation of NH (piperidine) from this line is consistent with its known associative nature. The remarkable linearity of this plot over a molecular weight range of more than 100 is consistent with the dominance of the dipole–dipole mechanism for relaxation at 30°. A consistently lower relaxation time for the γ carbon in groups 4 and 5 indicates that the molecules tumble anisotropically, with the principal rotational axis along the line between the heteroatom and C-4. Tumbling is more nearly isotropic for the group 6 heterocycles, since all three carbon atoms have essentially the same relaxation times. The methyl relaxation times in groups 4 and 5 indicate some rotational constraint for the first row systems (C and N) but increasingly less hindered rotation on passing to the lower rows (Si, P, As). For the first row systems, the methyl relaxation time is shorter than the methylene relaxation times, as expected for nearly rigid systems. For the lower rows, the methyl relaxation time is faster, as would be expected for a more nearly free rotation. The increase in the relaxation time with temperature is consistent with a predominant dipole–dipole mechanism, although curvature at higher temperatures indicates that spin–rotation relaxation probably becomes significant.

References and Notes

(1) Supported in part by the National Science Foundation (Grant No. MPS-72-05006).
(2) (a) I. M. Armitage, H. Huber, D. H. Live, H. Pearson, and J. D. Roberts, *J. Magn. Reson.*, **15**, 142 (1974); (b) H. Jaeckle, U. Haeberlen, and D. Schweitzer, *ibid.*, **4**, 198 (1971); (c) G. A. Gray and S. E. Cremer, *ibid.*, **12**,

5 (1973). The list is not exhaustive. Carbon relaxation has also been studied in complex natural products that contain saturated heterocyclic rings, e.g., stachyose, A. Allerhand and D. Dodderell, *J. Am. Chem. Soc.*, **93**, 2777 (1971).
(3) For a review, see J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).
(4) Nomenclature has been discussed in the previous paper.[5]
(5) J. B. Lambert, D. A. Netzel, H.-n. Sun, and K. K. Lilianstrom, *J. Am. Chem. Soc.*, preceding paper in this issue.
(6) For reviews, see E. Breitmaier, K.-H. Spohn, and S. Berger, *Angew. Chem., Int. Ed. Engl.*, **14**, 144 (1975); J. R. Lyerla, Jr., and G. C. Levy, *Top. Carbon-13 NMR Spectrosc.*, **1**, 79 (1974).
(7) This stack of real spectra was obtained with the assistance of Dr. W. W. Conover of the University of Chicago. All reported data unless otherwise noted were obtained at Northwestern University from magnitude spectra. A comparison of T_1 obtained from the real and the magnitude spectra showed no differences.
(8) D. A. Netzel, Ph.D. Dissertation, Northwestern University, 1975.
(9) We thank Dr. W. W. Conover for the program DNT1CAL and Dr. R. J. Bastasz for the program DNBB05 and their adaptation to the Nova 840.
(10) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948); also see, J. R. Lyerla, Jr., PhD. Dissertation, University of Utah, 1971.
(11) D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom, *Mol. Phys.*, **14**, 265 (1968); D. E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962).
(12) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).
(13) S. Berger, F. R. Kreissl, and J. D. Roberts, *J. Am. Chem. Soc.*, **96**, 4348 (1974).
(14) G. C. Levy, *J. Chem. Soc., Chem. Commun.*, 47 (1972).
(15) See Table II in ref 3.

Studies on the ^1H and ^{13}C Contact Shifts for σ-Bonded Molecules.[1] Stereospecific Electron Spin Transmission in Cyclic and Bicyclic Amines

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Abstract: ^1H and ^{13}C NMR contact shifts induced by nickel acetylacetonate ($Ni(AA)_2$) have been observed for various cyclic and bicyclic amines. These contact shifts are well reproduced by INDO molecular orbital calculations of spin densities on the proton 1s and carbon 2s atomic orbitals for the corresponding hydrocarbon σ radicals. It is shown that the proton contact shifts follow the stereospecificity established for nuclear spin–spin coupling constants. The importance of the *through-space* spin transfer in the rigid σ-bonded skeleton is also proposed to account for the nonalternating feature of ^{13}C contact shifts for planar zigzag arrangement of the σ skeleton. This mechanism is also discussed in relation to the long-range H–H coupling constant across four σ bonds.

We have currently been interested in the stereospecificity of the mode of electron spin distribution through the σ skeleton in view of elucidation of the σ-electronic structures. We have previously reported[2] the proton and carbon-13 contact shifts for N-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate ($Ni(AA)_2$).[3,4] In these studies it has been demonstrated that the relative contact shifts of various protons and carbons definitely depend on the conformation or configuration of the intervening σ-bonds connecting these and the nitrogen atoms. A linear correlation between the Ni-$(AA)_2$-induced *NMR contact shift* and the ESR *hyperfine coupling constant* (hfsc) in an organic free radical with the corresponding isoelectronic structure has recently been demonstrated.[2,5,6] It has also been shown that NMR contact shifts are quite useful to probe the mechanism of intramolecular electron spin transmission because it is quite sensitive to a small quantity and a sign of the induced spin density.[2]

The correlation between *hyperfine coupling constant* (hfsc) of a σ-type radical and the NMR nuclear *spin–spin coupling constant* (J) for protons has been pointed out theoretically[7-9] and experimentally.[8] The correlation between the *contact shifts* and the *nuclear spin coupling constants* (J) has also been studied.[10,11] The studies on the stereospecific electron spin transmission through the σ skeleton seem to serve as an aid in understanding the electronic structure of σ-bonded molecules. For this purpose, we have extended here our NMR contact shift studies to the various cyclic and bicyclic amines. Our concern in this study is to find the conformational or configurational dependence of electron spin distribution and to elucidate the mechanism of intramolecular electron spin transmission in relation to hfsc's and nuclear spin–spin coupling constants associated with the corresponding σ skeleton.

Experimental Section

Materials. Piperidine (**1**), 4-methylpiperidine (**2**), 3-methylpiperidine (**3**), *N*-methylpiperidine (**4**), and quinuclidine (**7**) were obtained from commercial sources. 1,4-Dimethylpiperidine (**5**) and 1,3-dimethylpiperidine (**6**) were prepared by N-methylation of **2** and **3**, respectively.[12] 1-Azaadamantane (**8**) was provided by Dr. W. N. Speckamp. 3,3,4-Trimethyl-2-chloro-1-azabicyclo[2.2.1]heptane (**9**) was provided by Professor P. G. Gassman. 7-Chloromethyl-1-azabicyclo[3.2.1]octane (**10**) was a gift from Dr. C. F. Hammer. $Ni(AA)_2$ was dried in vacuo over 30 h at 60 °C before use.

Proton NMR Measurements. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer in our department. Me_4Si was used as an internal standard. The samples were made in 10% v/v $CDCl_3$ solutions for piperidine derivatives (**1–6**), in ca. 0.1 M $CDCl_3$ solutions for **7** and **8**, and in 0.5 M $CDCl_3$ solution for **10**. Assignment of proton signals was made by referencing the spectral patterns, the europium dipivalomethane ($Eu(dpm)_3$), and cobalt acetylacetonate ($Co(AA)_2$) induced pseudocontact shifts. The variation of the spectral patterns were also referred. Signal assignments of **10** remain somewhat speculative.

^{13}C NMR Measurements. Completely proton decoupled ^{13}C NMR spectra were obtained at 25.15 MHz on a JEOL-JNM-PFT-100 system. After the ~100–30000 accumulations of the free induction decays induced by the 45° pulses with the interval of 2–4 s, the Fourier-transformed spectra were recorded. The ^{13}C spectra were obtained from a $CDCl_3$ solution of **9** in 0.5 M, **10** in 3 M, and **3** in 50% v/v. The spectra were taken at room temperature (24°) in the presence of varying amounts of $Ni(AA)_2$ as in the case of ^1H NMR measurements. The ^{13}C chemical shifts were measured with respect to internal Me_4Si or $CDCl_3$ (77.1 ppm from Me_4Si). The assignments of ^{13}C NMR spectra were made by referring the shifts of related compounds[2d,f,13] and by the use of the stereospecific ^{13}C contact shift induced by $Ni(AA)_2$.[2b-e] The half-decoupled technique was used to help the signal assignment of the ^{13}C NMR spectra.