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Carbon-13 Chemical Shifts of the Pentamethylene Heterocycles

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Abstract: Carbon-13 chemical shifts have been measured for the pentamethylene heterocycles from groups 4, 5, and 6. The chemical shifts of the α and γ carbons are governed almost entirely by the electronegativity of the heterogroup at the 1 position, with small direct perturbations due to substituents on the heteroatom. The chemical shift of the β carbons also depends on the heteroatom electronegativity, but the orientation of the substituent at the 1 position (axial or equatorial) provides another major contribution. Thus the β chemical shift is a useful determinant for the conformational preference at the 1 position. Increased heteroatom electronegativity causes a downfield shift for the α carbon but an upfield shift for the β and γ carbons, in the ratio $20/-1/-2$, as derived from the slopes of the chemical shift vs. electronegativity plots. Thus polarization of charge apparently reverses sign between the first (α) and second (β) carbons, with a large dropoff in magnitude, in agreement with the Pople–Gordon theory that requires an alternation of sign. The increase in magnitude of the shift without change of sign between the second (β) and third (γ) carbons is the result of a direct (steric) γ interaction similar to that between a 1-axial group and the β carbon.

Among the pentamethylene heterocycles (1) are found the fundamental building blocks for many alkaloids (piperidine) and for the pyranose sugars (oxane[2] or tetrahydropyran).

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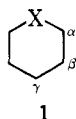
The series provides an outstanding platform for the study of conformational, structural, and electronic effects by variation of the atom X.[3] Although there have been many studies of the carbon-13 spectra of saturated heterocycles,[4] no investigation has centered on the parent heterocycles, with substituents only on the heteroatom. Systematic studies have been reported on some phosphorinanes,[5] piperidines,[6] and 1,3-dioxanes.[7] With so few data, there have been no attempts to compare effects from group to group and from row to row in the periodic table. This study was designed to survey the full range of pentamethylene heterocycles, with silicon and germanium as representatives from group 4, nitrogen, phosphorus, and arsenic from group 5, and oxygen, sulfur, selenium, and tellurium from group 6. The objective was to assess the factors that influence the chemical shifts of the ring carbons. Changes in bond lengths and bond angles alter the overall shape of the ring. Substituents on the heteroatom influence the ring reversal conformational equilibrium (eq 1). Inductive effects depend

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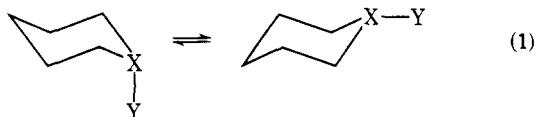
on the electronegativity of X and of its substituent(s) Y. The presence of axial substituents on X can affect the shielding of

the β carbon. We have gathered chemical shift and relaxation time[8] data and report herein on the interpretation of the shielding parameters.

Experimental Section

Carbon-13 chemical shifts were measured on a Bruker HFX-90 nuclear magnetic resonance spectrometer operating at 22.628 232 MHz in a single-coil, pulsed mode. Hexafluorobenzene provided a fluorine-19 heteronuclear lock. A Schomandl frequency synthesizer Model ND30M produced the carbon-13 frequency. Pulses were obtained from a Bruker B-SV2 power amplifier, and a second Bruker B-SV2 power amplifier was used for broadband and off-resonance decoupling of protons. Frequency offsets were measured with a Hewlett-Packard Model 5216A frequency counter. A pulse width of 7 μs was found to be optimal for a frequency range of 5000 Hz.

The free induction decay signal was stored in a Fabri-tek (Nicolet) 1074 signal averager with 4095 channels. The dwell time per channel was normally set at 100 μs with zero delay. The 4K free induction decay signal was converted by Fourier transformation to a 2K frequency domain spectrum by a Digital PDP-8/L computer with 4K memory. Data were recorded as the magnitude spectra.

Some carbon-13 spectra were obtained on 5-mm samples fitted by two spacers into 10-mm tubes containing the external lock C_6F_6. The lower Teflon spacer also served as a vortex plug. When sufficient sample was available, the roles were reversed, and the sample was placed in the 10-mm tube and the lock signal in the 5-mm tube. All chemical shifts were referred to internal tetramethylsilane, with allowance for sample geometry.

The number of pulses necessary to obtain a good spectrum varied from 128 to 8000, depending on the concentration of the sample. Time between pulses was normally 0.5 s, but for some samples with long relaxation times the delay time was extended to 20 s.

Most of the samples were available from previous work, or were prepared according to reported procedures.[9-15] Details may be found elsewhere.[4b] 1,1-Dimethylsilinane was obtained from Aldrich. 1,1-Dimethylgerminane was prepared by the method of Mazerolles.[16]

Details of the preparation of the arsenanes will be recorded in a subsequent report.[17]

Results

With broadband decoupling, all of the ring carbon spectra were expected to consist of three peaks, the α, β, and γ, in the ratio 2/2/1, respectively. Additional peaks could arise from solvent and from substituents on X. For the most part, the β and γ resonances did appear in the expected 2/1 ratio, but the α resonance was less intense than the β. In addition to intensity considerations, a number of other procedures were utilized to assign the resonances: (1) specifically deuterated materials (changes in relaxation times associated with introduction of deuterium at the β or γ positions caused loss in the intensity of the resonance of the attached carbon); (2) $^{13}C-^{31}P$ coupling constants;[5] (3) off-resonance decoupling; (4) obvious considerations of electronegativity, which often made assignment of the α carbon self-evident. The specific criteria used in each case have been enumerated in detail elsewhere[4b] and will not be repeated here. The results of the chemical shift measurements and assignments are given in Table I. Consistent and unambiguous assignments were achieved in almost every case. Those for which there is still some uncertainty are pointed out in the table. Most of the literature values for these or other pentamethylene systems are also included in the table. Our values were in excellent agreement with the available data, and no reassignments of reported resonances resulted from our observations.

Discussion

The α Carbon. Changes in the carbon-13 chemical shift of the ring carbon adjacent to the heteroatom are due primarily to alterations in the electron density at carbon caused by changes in the electronegativity of the heteroatom. The influence of the inductive/field effect can be seen by plots of the carbon-13 chemical shift as a function of the Allred-Pauling electronegativities[18] (Figure 1).

The group 6 heterocycles represent an ideal case for the examination of electronegativity effects, since the heteroatom carries no substituent. The center line in Figure 1, with a slope of about 50 ppm/electronegativity unit, shows that the correlation is quite good. Piperidine and cyclohexane have been included, since they carry only hydrogen substituents. On the Allred scale, sulfur (2.58) and selenium (2.55) have essentially the same electronegativity, yet the chemical shifts of the α carbons differ by 9 ppm. Either the electronegativity is not known accurately for sulfur, which appears to be the deviant point, or there is another factor that contributes modestly to the α chemical shift in thiane alone.

The left-hand plot in Figure 1 contains data for the dimethyl group 4 and the monomethyl group 5 heterocycles. This plot is displaced from that of the group 6 and unmethylated groups 4 and 5 heterocycles in the middle because of the "β effect" of the methyl substituents, which results in a downfield shift of a few ppm (compare NH with NCH$_3$). Otherwise, the behavior is quite similar to that of group 6, the plot having a slope of about 40 ppm/electronegativity unit. It is interesting that the dimethyl compounds appear to lie comfortably on the same plot with the monomethyl compounds. The downfield β effect of an axial methyl group is slightly smaller than that of an equatorial methyl group, and the geminal arrangement of methyls produces a small but offsetting upfield shift.[19] The effect of nonalkyl substituents is often much larger and will be discussed in a later section. There is no manifestation of the fact that the methyl group in piperidine is entirely equatorial[20] and those of phosphorinane[21] and arsenane[17] have substantial contributions from axial conformers.

Methylation of the groups 5 and 6 heterocycles provides the right-hand plot in Figure 1. As with the α protons, increased
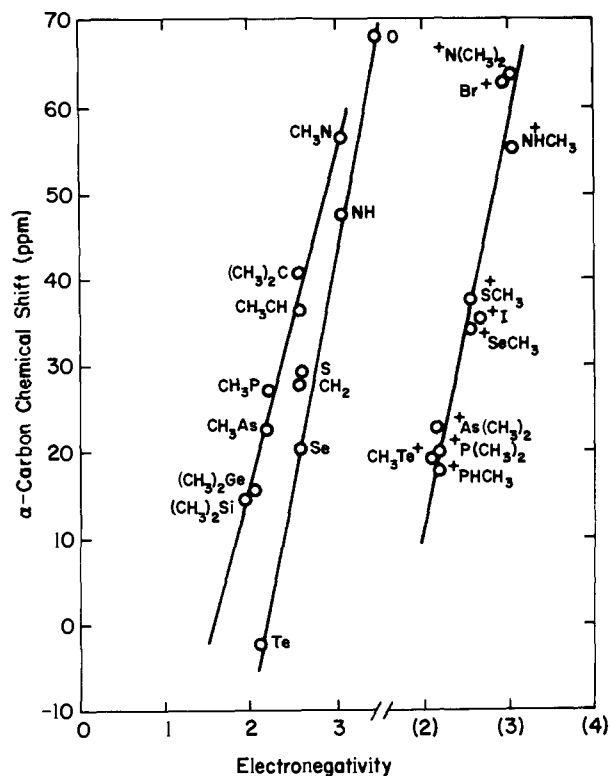

Figure 1. The chemical shift of the α carbon as a function of electronegativity for the pentamethylene heterocycles of groups 4 and 5 (left), for those of group 6 plus piperidine and cyclohexane (center), and for the positively charged heterocycles of groups 5, 6, and 7 (right).

electronegativity causes a downfield effect. The electronegativities of the uncharged heteroatoms have been used for the x axis. Introduction of the positive charge will make the atoms more electronegative, but it is assumed that the increase is a constant amount for all the atoms. The actual plot would simply be translated further to the right. The linearity of the plot appears to justify the usage. Also included on the plot are the data of Peterson for the group 7 heterocycles.[22] The slope of the plot is about 45 ppm/electronegativity unit. In most of the systems, methylation brings about a downfield shift, e.g., NH to N$^+$HCH$_3$ or S to S$^+$CH$_3$, as is expected for introduction of a positive charge and a β methyl group.[19,23]

The Methyl Carbon. The methyl carbon chemical shifts follow essentially the same pattern as do the α carbons. A plot of the methyl chemical shifts vs. electronegativity for the neutral silicon, germanium, arsenic, phosphorus, carbon, and nitrogen compounds is linear with a slope of about 45 ppm/electronegativity unit.[4b] Effects due to the presence of more than one methyl group and to their axial or equatorial orientation do not show up in this gross plot. Formation of a positively charged species through methylation results in downfield shifts for the nitrogen, sulfur, selenium, tellurium, and arsenic compounds, but an upfield shift for phosphorus. The plot of chemical shift vs. electronegativity is still quite linear for the charged series. A difference of 9 ppm between the methyls on sulfur and selenium again cannot be explained in terms of the Allred electronegativities.

The γ Carbons. Electronegativity also provides the most important effect on the chemical shifts of the γ carbons. A plot of electronegativity vs. the carbon-13 chemical shift is linear, with a negative slope (Figure 2). The line for heteroatoms with a methyl substituent is displaced upfield (downwards) by about 0.5 ppm with respect to the line for heteroatoms with no substituent or with only hydrogen. This small displacement corresponds to a "δ effect", which is about the same size as in

Table I. Carbon-13 Chemical Shifts of the Pentamethylene Heterocycles (1)

X	Solvent	$\delta(\alpha)^a$	$\delta(\beta)^a$	$\delta(\gamma)^a$	$\delta(S)^{a,b}$	Source[c]
			Group 4			
CH_2	None	27.7	27.7	27.7		d
$CHCH_3$	None	36.4	27.1	27.0		d
$C(CH_3)_2$	None	40.4	23.2	27.3	29.4	d
$Si(CH_3)_2$	None	14.3	24.4	30.1	−3.3	
$Ge(CH_3)_2$	None	15.4	25.9	30.6	−3.9	
			Group 5			
:NH	None	47.5	27.2	25.5		
	None	47.7	27.5	26.1		e
:NCH$_3$	None	56.7	26.3	24.3	47.0	
	None	56.7	26.2	24.3	46.9	e
	None	57.0	26.6	24.6	47.2	f
:N-t-C$_4$H$_9$	None	46.9	26.0	27.1	53.2, 25.2	
:NCl	CH_2Cl_2	64.0	27.8	23.2		
$^+NH_2$ I$^-$	H_2O	45.8	23.2	22.4		
	H_2O	45.5	23.1	22.6		e
$^+NHCH_3$ I$^-$	H_2O	55.9	24.1	21.7	44.3	
	H_2O	55.2	23.7	21.8	45.1	e
$^+N(CH_3)_2$ I$^-$	H_2O	63.7	20.5	21.0	52.7	
	H_2O	63.3	20.6	21.0	52.7	e
$N(O)CH_3$	C_6H_6	66.1	21.1^g	21.7^g		e
:PCH$_3$	None	27.0	23.5	28.6	11.3	
	None	26.7	23.4	28.3	11.3	h
:PC$_6$H$_5$	None	24.6	23.4	27.9		h
$P(O)CH_3$	$CDCl_3$	29.9	23.6	27.1	14.4	
$P(S)CH_3$	$CHCl_3$	32.7	22.4	26.2	18.5	h
$^+PHCH_3$ I$^-$	$CHCl_3$	17.6	22.8	24.9	5.3	
$^+P(CH_3)_2$ I$^-$	H_2O	19.9	21.2	24.8	6.9	
:AsCH$_3$	None	22.4	23.9	29.3	5.1	
:AsC$_6$H$_5$	CCl_4	22.8	24.7	29.4		
$As(O)CH_3$	$CDCl_3$	33.0	25.5	27.8	14.6	
$As(S)CH_3$	CS_2	34.0	24.9	28.2	17.5	
$As(Se)CH_3$	C_6H_6	32.1	23.1	26.6	18.6	
$AsCH_3Cl_2$	CCl_4	51.1	23.9	52.0	22.4	
$AsCH_3Br_2$	$CDCl_3$	47.2^g	24.2	47.2^g	22.2	
$^+As(CH_3)_2$ I$^-$	H_2O/DMSO-d_6	22.8^g	22.8^g	25.8	6.4	
			Group 6			
O	None	68.0	26.6	23.6		
	None	69.7	27.9	25.1		i
S	None	29.3	28.2	26.9		
:SO (average)	$CDCl_3$	49.0	19.3	25.3		
:SO-ax^j	CD_2Cl_2	45.1	15.5	24.7		k
:SO-eq^j	CD_2Cl_2	52.1	23.3	24.7		k
SO_2	$CDCl_3$	52.6	25.1	24.3		
SBr_2	CH_2Cl_2	34.7	22.9	27.6		
SI_2	CH_2Cl_2	33.3	25.9			
:S$^+$H FSO$_3^-$	FSO_3H	31.2	24.1	21.8		
:S$^+$CH$_3$ I$^-$	H_2O	37.8	20.5	22.7	22.4	
	$SO_2{}^l$	37.8	20.2		22.1	
Se	None	20.2	29.1	28.4		
:SeO (average)	CH_2Cl_2	42.1	18.6	26.3		
:SeO-ax^m	CH_2Cl_2	39.4	16.8	25.1		
SeO_2	CH_2Cl_2	57.5	25.1	24.9		
$SeBr_2$	CH_2Cl_2	51.2	20.9	22.9		
SeI_2	CH_2Cl_2	29.7	25.7^g	26.0^g		
:Se$^+$H FSO$_3^-$	FSO_3H	41.8	23.8	22.5		
:Se$^+$CH$_3$ I$^-$	H_2O	34.1	20.5	23.9	15.7	
	$SO_2{}^l$	34.0	20.1		15.2	
Te	None	−2.1	29.9	30.9		
$TeBr_2$	CH_2Cl_2	36.9	20.3	25.9		
TeI_2	CH_2Cl_2	33.2	21.4	25.5		
:Te$^+$H FSO$_3^-$	FSO_3H	24.0^g	25.0^g	25.8^g		
:Te$^+$CH$_3$ I$^-$	H_2O		20.7	27.7^g		
	$SO_2{}^l$	17.7	19.9		−0.6	
^+Br	SO_2	62.9	25.4	22.6		n
^+I	SO_2	35.4	24.8^g	25.4^g		n

^{a} In ppm, downfield from internal TMS; taken at 30° unless otherwise noted. ^{b} Substituent on X. ^{c} This work, unless otherwise specified. ^{d} Reference 19; also see ref 4a, p 64. ^{e} Reference 26; also see ref 4a, pp 272 and 273. ^{f} Reference 6a. ^{g} Assignments are uncertain. ^{h} Reference 5. ^{i} G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965). ^{j} Taken at −93 °C. ^{k} Reference 28. ^{l} The material was γ deuterated. ^{m} Taken at −98 °C; also see ref 4b, p 61. ^{n} Reference 22.
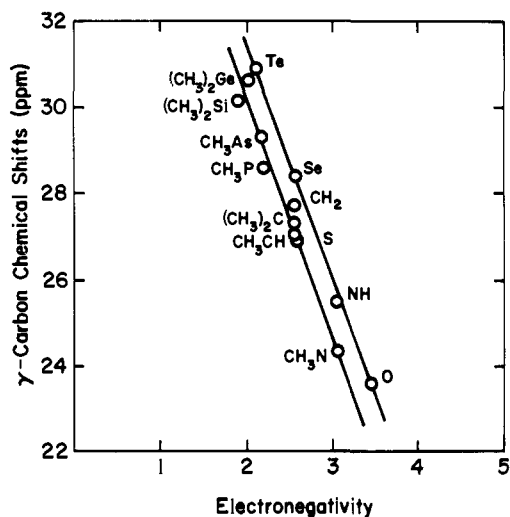
Figure 2. The chemical shift of the γ carbon as a function of electronegativity for the pentamethylene heterocycles of groups 4 and 5 (left) and for those of group 6 plus piperidine and cyclohexane (right).

methyl-substituted cyclohexanes (−0.1 to −0.3 ppm).[19] Thus the dominant effect for the γ carbon is the electronegativity, with small δ-effect perturbations from the substituents on X. It is noteworthy that the monomethyl and dimethyl compounds fall on the same (left-hand) plot in Figure 2. The effect of the second methyl group must be compensated by a geminal effect in the opposite direction. Once again, the sulfur case is well off the plot, suggesting an inadequacy in the reported electronegativity. The displacement of cyclohexane from the line determined by the group 6 heterocycles may indicate that there is a small substituent effect of hydrogen with respect to a lone pair.

The large influence of the X group on the γ resonance is strictly analogous to the well-known effect of a 1-axial group on a β carbon (the γ-axial effect), some examples of which are given in the next section. The relationship between the X group and the γ carbon or between a 1-methyl group and the β carbon is gauche. Grant and Cheney[25] proposed that the mechanism for the shielding of a carbon by a γ-gauche substituent is steric polarization of the valence electrons, whereas that by an α substitution is charge polarization. Minor changes in electron densities cause major perturbations in the paramagnetic term. Our results show that this sterically induced γ effect closely follows the electronegativity of the perturbing X group. Although all these carbon-13 shifts appear to have a paramagnetic origin,[25] the mechanisms can differ. Thus if the α shift is primarily charge polarization and the γ shift steric polarization, the relative magnitudes of the shifts do not reflect charge densities in a parallel fashion.

The positively charged methylated heterocycles exhibit similar behavior to that of the neutral methyl-substituted heterocycles. There is a general shift to higher field as a result of the presence of the positive charge. The plot of the γ carbon chemical shift vs. electronegativity (values for the neutral heteroatom) has some scatter, but is basically a straight line with a negative slope (about −8 ppm/electronegativity unit) for CH_3S^+, CH_3Se^+, CH_3Te^+, $(CH_3)_2N^+$, $(CH_3)_2P^+$, and $(CH_3)_2As^+$.[4b] Thus the situation is essentially the same as with the neutral groups 4, 5, and 6 compounds, with increased electronegativity causing an upfield shift.

The β **Carbons.** The β carbons also show a significant response to the electronegativity of X, but the effect of 1 substituents is of considerable importance for the first time. The group 6 atoms, together with piperidine and cyclohexane, show the substituent-free effect (Figure 3, uppermost curve). Like that of the γ carbons, the chemical shift of the β carbons for
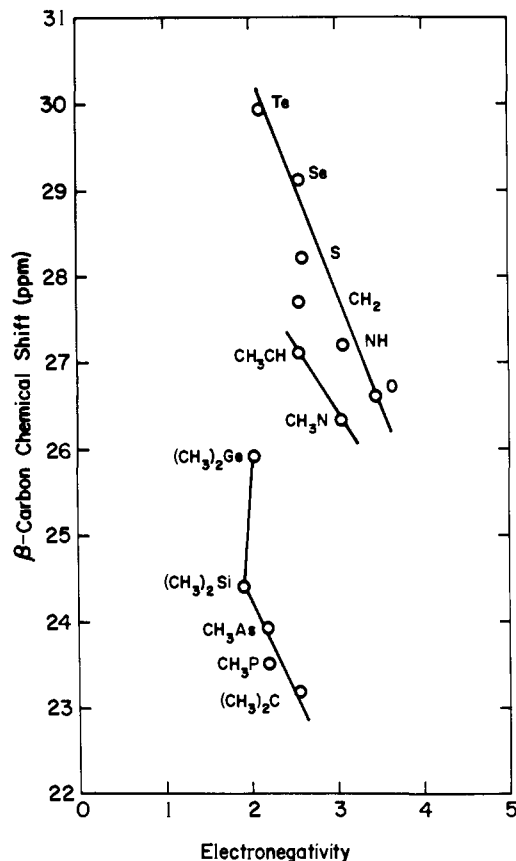

Figure 3. The chemical shift of the β carbon as a function of electronegativity for the pentamethylene heterocycles of groups 4 and 5 (lowermost), for methylcyclohexane and 1-methylpiperidine (center), and for those of group 6 plus piperidine and cyclohexane (uppermost).

the group 6 and related systems goes upfield with an increase in electronegativity. With one minor exception (tellurane) each of these systems has the β-carbon resonance at lower field than that of the γ carbon, so that the chemical shifts follow the pattern of α lower than β lower than γ. The electronegativity effect on the β and γ carbons is much attenuated with respect to that on the α carbons, the slopes of the lines in Figures 2 and 3 being −5 (γ) and −2.5 (β) ppm/electronegativity unit, compared to about 50 (α) in Figure 1. The Pople–Gordon alternation of sign for charge polarization (2), with a large

$$X\text{—}C\text{—}C$$
$$\overset{\delta-}{} \quad \overset{\delta+}{} \quad \overset{\delta\delta-}{}$$
2
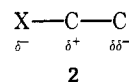
drop-off in magnitude with increased distance,[24] adequately explains the shielding behavior of the α and β carbons, and the traditional monotonic drop-off (3) is in disagreement. This

$$X\text{—}C\text{—}C$$
$$\overset{\delta-}{} \quad \overset{\delta+}{} \quad \overset{\delta\delta+}{}$$
3
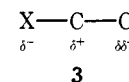
conclusion is based on the assumption that both the α and β shifts are paramagnetic and of similar mechanism. Until the mechanism of the β shift is clarified,[25] the conclusion that **2** rather than **3** is the correct mechanism for charge polarization must be regarded as tentative.

The groups 4 and 5 heterocycles have one or two methyl groups on the heteroatoms. In all cases except 1-methylpiperidine and methylcyclohexane, the β-carbon resonance is at higher field than that of the γ carbon, in contrast to the group 6 heterocycles. This reversal of the β and γ positions appears to be associated with the presence of an axial substituent at the 1 position. The "γ effect" for an axial methyl group in cyclo-

Table II. Substituent-Induced Shifts (ppm)^a

Change in X	$\Delta\beta$ (at the α carbon)	$\Delta\gamma$ (at the β carbon)	$\Delta\delta$ (at the γ carbon)
$CH_2 \rightarrow CHCH_3{}^b$	+8.7	−0.6	−0.7
$NH \rightarrow NCH_3$	+9.2	−0.9	−1.2
$CHCH_3 \rightarrow C(CH_3)_2{}^b$	+4.0	−3.9	+0.3
$^+NHCH_3 \rightarrow {}^+N(CH_3)_2$	+7.8	−3.6	−0.7
$^+PHCH_3 \rightarrow {}^+P(CH_3)_2$	+2.2	−1.6	−0.1
$^+NH_2 \rightarrow {}^+NHCH_3$	+10.1	+0.9	−0.7
$NH \rightarrow {}^+NH_2$	−1.7	−4.0	−3.1
$NH \rightarrow {}^+NHCH_3$	+8.4	−3.1	−3.8
$^+SH \rightarrow {}^+SCH_3$	+6.6	−3.6	+0.6
$^+SeH \rightarrow {}^+SeCH_3$	−7.7	−3.3	+1.4
$^+TeH \rightarrow {}^+TeCH_3$	−4.8	−4.3	+1.9
$S \rightarrow {}^+SH$	+1.9	−4.1	−5.1
$Se \rightarrow {}^+SeH$	+21.6	−5.3	−5.9
$Te \rightarrow {}^+TeH$	+26.1	−4.9	−5.1
$S \rightarrow {}^+SCH_3$	+8.5	−7.7	−4.5
$Se \rightarrow {}^+SeCH_3$	+13.9	−8.6	−4.5
$Te \rightarrow {}^+TeCH_3$	+21.9	−9.2	−3.2
$NCH_3 \rightarrow {}^+N(CH_3)_2$	+7.0	−5.8	−3.3
$PCH_3 \rightarrow {}^+P(CH_3)_2$	−7.1	−2.3	−3.8
$AsCH_3 \rightarrow {}^+As(CH_3)_2$	+0.4	−1.1	−3.5
$NH \rightarrow NCl$	+16.5	+0.6	−2.3
$S \rightarrow SO$ (ax)	+15.8	−12.7	−2.2
$S \rightarrow SO$ (eq)	+22.8	−4.9	−2.2
$Se \rightarrow SeO$ (ax)	+19.2	−12.3	−3.3
SO (av) $\rightarrow SO_2$	+3.6	+5.8	−1.0
SeO (av) $\rightarrow SeO_2$	+15.4	+6.5	−1.4
$NCH_3 \rightarrow N(O)CH_3$	+9.4	−5.2	−2.6
$PCH_3 \rightarrow P(O)CH_3$	+2.9	−0.1	−1.5
$AsCH_3 \rightarrow As(O)CH_3$	+10.6	+2.3	−1.5

^{a} A positive sign denotes a downfield shift. ^{b} Reference 19.

hexane is about −5 ppm. Indeed, the plot for the β chemical shifts of dimethylcyclohexane, dimethylsilinane, 1-methylphosphorinane, and 1-methylarsenane is displaced downwards (upfield) from that of the group 6 heterocycles (including unmethylated piperidine and cyclohexane) by about 5 ppm. The carbon and silicon systems by necessity have an axial methyl group, and other evidence has shown that the 1-methyl group on phosphorus[21] and arsenic[17] is predominantly axial. In methylated piperidine and cyclohexane, however, the large shift is absent because the 1-methyl group is essentially all equatorial.[20] *Thus the substituent-induced γ effect of the 1-methyl group on the β carbon should be a useful predictor of the conformational preference of the methyl group.*

Two other aspects of the plots in Figure 3 are of interest. The dimethylgerminane shift does not lie on the line defined by the C, P, As, and Si systems. The longer distances involved with germanium (and for that matter, but to a lesser extent, with arsenic and silicon) must attenuate the shielding effect of the axial methyl group. The second point to note is that the methylcyclohexane and 1-methylpiperidine β shifts are about

1 ppm to higher field than cyclohexane and piperidine, respectively. The short line connecting the two points in Figure 3 is intended to point out this relationship. Thus there is a small (ca. −1 ppm) equatorial "γ effect".[19]

Substituent-Induced Shifts. Table II summarizes various substituent-induced shifts observed in these heterocycles. It is unfortunate that data could not be obtained for the parent phosphorinane and arsenane, so that shifts from an unmethylated model could be measured in the phosphorus and arsenic series as well. The shifts in the nitrogen series have been discussed previously.[29] Our results are essentially the same. Replacement of the proton on nitrogen with a methyl ($NH \rightarrow$ NCH_3 or $N^+H_2 \rightarrow N^+HCH_3$) produces β, γ, and δ effects at the α, β, and γ carbons, respectively, of very similar magnitudes to those observed for methyl substitution in cyclohexane (Table I). In particular, the small value of the γ effect on the β carbon is consistent with a predominantly equatorial methyl on nitrogen. Introduction of an axial methyl on nitrogen ($N^+HCH_3 \rightarrow N^+(CH_3)_2$) produces a much larger, upfield (negative) γ effect, comparable to that in cyclohexane ($CHCH_3 \rightarrow C(CH_3)_2$).[19]

Simple protonation ($NH \rightarrow N^+H_2$, $NCH_3 \rightarrow N^+HCH_3$, $S \rightarrow S^+H$, $Se \rightarrow Se^+H$, $Te \rightarrow Te^+H$) causes a nearly constant upfield shift at the β and γ carbons (−3 to −5 ppm) in all systems. The effect on the α carbon, however, is quite irregular (−1.7 to +26.1 ppm) and is currently unexplained. Introduction of a chlorine on nitrogen causes a large downfield effect on the α carbon, because of the increased electronegativity of the NCl group. The rather small γ effect on the β carbon provides the first evidence that the chlorine substituent is equatorial. Previous studies appeared to indicate that only one conformation was present[12] but could make no assignment of the preferred form. The small γ effect is not consistent with an axial orientation of the chlorine atom, since gauche forms would be expected to cause shielding.[27]

Introduction of oxygen on the heteroatom ($NOCH_3$, $POCH_3$, $AsOCH_3$, SO, SeO) shifts the α carbon downfield, and a second oxygen (SO_2, SeO_2) causes an additional effect. The downfield shift has been found to depend on the axial or equatorial orientation of the oxygen, with the carbon of the equatorial oxygen (axial lone pair) system resonating at lower field.[28] Sulfur or selenium on phosphorus or arsenic causes a similar downfield shift. The addition of molecular halogen to sulfides, selenides, tellurides, phosphines, or arsines can have a fundamental effect on the molecular structure. Depending on the relative electronegativities of the heteroatom (X) and the halogen substituent (Y), either simple molecular complexes (**4**) or severely distorted trigonal bipyramids (**5**) can be formed.
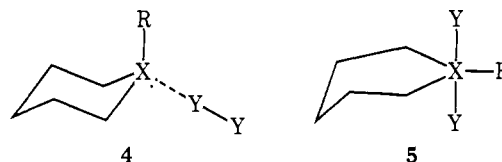
X = S, Se, Te, As; Y = Cl, Br, I; R = lone pair, CH_3

The structures of the various complexes have been determined by other means.[14,17] In all cases, addition of halogen shifts the α resonance downfield. The shift is very modest for those cases in which addition of halogen results in formation of a simple molecular complex (SBr_2, SI_2, SeI_2). Shifts of 30 ppm or more, however, are observed when the resulting structure is a trigonal bipyramid ($SeBr_2$, $TeBr_2$, TeI_2, $AsCH_3Cl_2$, $AsCH_3Br_2$), indicating greater polarization of charge in this structure. Similar downfield shifts have been observed in the proton spectra.[14] Plots of the α carbon-13 chemical shift vs. the α proton chemical shift are linear within each series: S, SI_2, SBr_2; Se, SeI_2, $SeBr_2$; and Te, TeI_2, $TeBr_2$.[4b]

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.
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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