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LINE BROADENING IN THE NMR SPECTRA OF THE METHYL PROTONS ON PIPERIDINE RINGS

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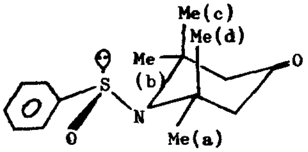
In NMR spectra of 2,2,6,6-tetramethyl-4-oxopiperidine (I) and its N-methyl derivative (II), the C-3 and C-5 methylene protons and the C-2 and C-6 methyl protons have been found to give single sharp lines (TABLE I) resulting from the rapid ring-inversion at room temperature$^{1)}$.

However, it was found that four methyl groups of 1-benzenesulfinyl-2,2,6,6-tetramethyl-4-oxopiperidine (VII) (FIG. 1) gave rise to two broad absorptions[*1] indicative of magnetic nonequivalence. One signal was very broad and the other was just slightly broadened, while the C-3 and C-5 methylene protons appeared as a singlet, as shown in FIG. 2-b and TABLE I.

FIG. 1



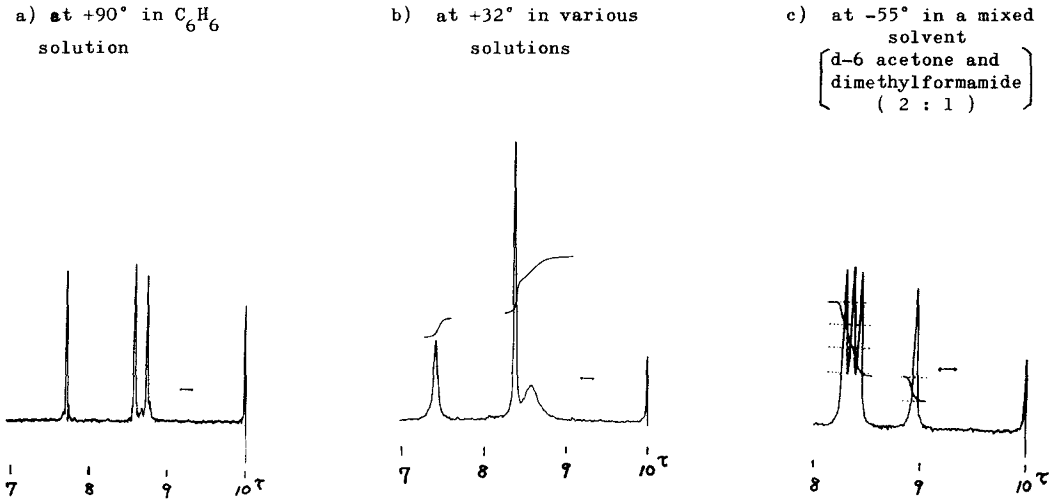
[*1] The spectra were ordinally recorded, unless otherwise stated, at 32° in $CDCl_3$ solution on a Varian A-60 spectrometer with tetramethylsilane as internal standard. Solution concentrations in this study were ca. 4-10%(wt./vol.).

Solvent effects on the spectrum of VII were investigated with three kinds of solvents. The overall shape of the spectra was the same as FIG. 2-b, whereas the chemical shifts of the methylene and methyl protons showed expected solvent effects (TABLE I).

The temperature dependence of the spectrum of VII is shown in FIG. 2-a,b,c. The signals at τ 8.80 (broad), 8.66 and 7.79 in benzene solution (TABLE I) became sharp and shifted to τ 8.75(6H), 8.60(6H) and 7.72(4H) respectively (FIG. 2-a). Furthermore, four peaks at τ 8.30(3H), 8.36(3H), 8.44(3H) and 8.96(3H) are observed at -55° (FIG. 2-c). Since this shows the existence of the four kinds of methyl groups, the line broadening of the methyl protons shown in FIG. 2-b would be rationalized as the combination of the moderately slow configurational inversion of the nitrogen atom in the piperidine-ring and the nonequivalence of four methyl groups arising from the molecular asymmetry[2)3)] as shown in FIG. 1. The structure depicted is one of the stable conformers at lower temperatures. The coalescence temperature(Tc) of VII was about 30° as shown in FIG. 2-b.

FIG. 2

NMR spectra of VII



a) at +90° in C_6H_6 solution

b) at +32° in various solutions

c) at -55° in a mixed solvent
(d-6 acetone and dimethylformamide (2 : 1))

TABLE I

Chemical Shifts for 2,2,6,6-Tetramethyl-4-oxopiperidines (I-XI)(at 32°)

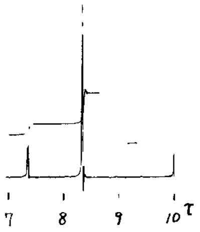
	N-Substituent	Solvent	τ -CH_2-	w (cps)	h (cm)	τ -CH_3	w (cps)	h (cm)	Tc
I	-H	$CDCl_3$ C_6H_6	7.70(4H) 7.97(")	1.0 ---	7.0 ---	8.75(12H)$^{1)}$ 9.00(")$^{1)}$	1.0 ---	22.0 ---	
II	-CH_3	$CDCl_3$ C_6H_6	7.72(") 7.95(")	--- ---	--- ---	8.75(")$^{1)}$ 8.99(")$^{1)}$	--- ---	--- ---	
III	-SO_2-C_6H_5	$CDCl_3$ C_6H_6	7.37(") 7.76(")	1.2 1.0	5.6 6.3	8.38(") 8.60(")	1.0 1.0	19.7 21.0	< -55°
IV	-SO_2-C_6H_4-OCH_3(p)	$CDCl_3$	7.37(")	1.2	6.0	8.38(")	1.0	20.8	
V	-SO-C_6H_4-NO_2(p)	$CDCl_3$	7.37(")	11.0	1.4	8.37(6H) 8.5$^{e.b}$+0.5 (")	2.7 30.0	11.6 0.7	
VI	-SO-C_6H_4-Cl(p)	$CDCl_3$	7.40(")	4.5	3.7	8.39(") 8.55(")	1.7 18.0^{b}	16.0 1.6	
VII	-SO-C_6H_5	$CDCl_3$	7.41(")	3.5	6.2	8.38(") 8.55(")	1.9 13.0^{b}	20.8 2.5	
		$(CD_3)_2CO$ DMF (2:1)	----	---	---	8.40(") 8.60(")	1.4 7.0^{b}	17.6 3.3	c.a. +30°
		C_6H_6	7.79(")	1.5	7.9	8.66(") 8.80(")	2.9 9.0^{b}	8.0 3.2	c.a. +30°
VIII	-SO-C_6H_4-CH_3(p)	$CDCl_3$	7.42(")	3.5	7.4	8.41(") 8.56(")	1.9 13.0^{b}	21.6 4.0	
IX	-SO-C_6H_4-OCH_3(p)	$CDCl_3$	7.43(")	2.2	7.0	8.40(") 8.56(")	1.5 7.0^{b}	18.7 3.4	
X	-S-C_6H_4-Cl(p)	$CDCl_3$	7.19(2H) 7.60(") (J≒13 cps)	3.0 2.9 2.0 1.7	0.7 2.4 3.0 1.0	8.65(") 8.71(")	1.6 1.6	15.2 13.2	
XI	-S-C_6H_5	$CDCl_3$	7.16(") 7.59(") (J=12 cps)	3.0 2.5 1.5 1.7	0.7 2.1 2.8 1.0	8.64(") 8.73(")	1.6 1.8	14.2 12.3	> +32°

w: full line width at half height h: height of peak
e.b: extremely broad, b: broad

The p-substituent effects on the spectrum of VII were also investigated with p-nitro-(V), p-chloro-(VI), p-methyl-(VIII) and p-methoxy-derivative(IX). In all cases the methyl protons produced similar broad signals. As shown in TABLE I, the full line width(w) at half height of the broader signal increased but the height(h) decreased, with increasing electronegativity of the substituent. Further details will be discussed in a concluding paper.

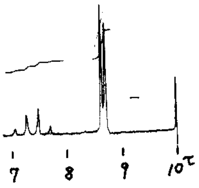
The effect of N-substituents on the spectrum of I were further studied with N-sulfonyl-(III and IV) and N-sulfenyl-derivatives (X and XI)*2. Since the spectra of III exhibited the same shape in $CDCl_3$ as in C_6H_6 solution, any accidental overlap was excluded5).

FIG. 3



NMR spectra of III and IV

FIG. 4



NMR spectra of X and XI

Therefore, inversion of the nitrogen atom was as rapid in III and IV as in I and II. On the other hand, the C-2 and C-6 methyl protons in X and XI indicated two sharp singlets, while the C-3 and C-5 methylene protons revealed an A_2B_2 spectrum (FIG. 4). Hence, inversion rate of the nitrogen atom was considered to be slower in X and XI than in I-IX. The methyl proton signal of III was not split even at -55°, while that of XI showed two sharp peaks at +32°. Thus the coalescence temperatures of III and XI were determined to be below -55° and above +32°, respectively.

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*2 It is well known3),4) that sulfonyl group and sulfenyl group operate in opposite directions with respect to the electronic states on the N-atom. Further, they have no molecular asymmetry.

These results showed that the rates of inversion decreased in the following order:

$$\mathrm{C_6H_5{-}SO_2{-}N}< \quad \text{(III)} \quad > \quad \mathrm{C_6H_5{-}SO{-}N}< \quad \text{(VII)} \quad > \quad \mathrm{C_6H_5{-}S{-}N}< \quad \text{(XI)}.$$

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