

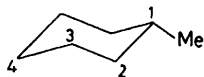
## Conformational Equilibria in Cyclohexanol, Nitrocyclohexane, and Methylcyclohexane from the Low Temperature $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra

By OLEG A. SUBBOTIN and NICKOLAY M. SERGEYEV\*

(N.M.R. Laboratory, Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R.)

**Summary** The relative integral intensities in low-temperature  $^{13}\text{C}$  n.m.r. spectra have been used to determine the conformational energies for cyclohexanol ( $A$  1.02 kcal mol $^{-1}$ ), nitrocyclohexane ( $A$  1.27 kcal mol $^{-1}$ ), and methylcyclohexane ( $A \geq 1.8$  kcal mol $^{-1}$ ).

RECENTLY  $^{13}\text{C}$  n.m.r. spectroscopy has been actively applied in conformational studies of substituted cyclohexanes.<sup>1-4</sup> However, for high-energy conformations that require low integral intensities to be measured, difficulties are encountered in the application of  $^{13}\text{C}$  (also  $^1\text{H}$ , see ref. 5) n.m.r.



(III)

spectroscopy because of the low intensity of the n.m.r. signals. We now present the results of conformational studies of cyclohexanol (I), nitrocyclohexane (II), and methylcyclohexane (III), all of which prefer<sup>2,3,5</sup> the equatorial conformer. Measurements were made on a Varian XL-100 spectrometer (25.16 MHz for  $^{13}\text{C}$  nuclei) in the pulsed Fourier-transform mode using complete proton

decoupling. Low-temperature integral intensity measurements were used for the determination of  $A$  values, as

TABLE I

$^{13}\text{C}$  chemical shifts<sup>a</sup> of individual conformers for cyclohexanol (I) nitrocyclohexane (II), and methylcyclohexane (III), and the conformational energies ( $A$  values)<sup>b</sup>

Conformation	Carbon atoms				Other carbons ( $\delta$ scale)	$A$ /kcal/mol $^{-1}$	
	$\alpha$	$\beta$	$\gamma$	$\delta$			
(I) <sup>d</sup>	$eq^c$	42.59	8.51	-1.65	-1.03	—	1.02
	$ax^c$	37.92	5.28	-6.73	-0.61	—	$\pm 0.1$
	$\langle \delta \rangle^e$	42.57	8.46	-2.38	-1.07	—	—
(II) <sup>d</sup>	$eq^c$	57.59	3.88	-2.78	-2.41	—	1.27
	$ax^c$	54.02	1.10	-5.85	-1.26	—	$\pm 0.2$
	$\langle \delta \rangle^e$	56.90	3.73	-2.93	-2.13	—	—
(III) <sup>g</sup>	$eq^f$	6.07	8.48	-0.14	-0.54	23.98	$\geq 1.8$
	$ax^f$	—	—	—	—	—	—
	$\langle \delta \rangle^e$	5.81	8.34	-0.49	-0.60	23.23	—

<sup>a</sup> Chemical shifts were measured in  $\text{CS}_2$  solution relative to  $\text{CS}_2$ , but are reported in p.p.m. relative to  $\text{C}_6\text{H}_{12}$  [ $\delta(\text{C}_6\text{H}_{12}) = 27.50$  p.p.m. on the  $\text{Me}_4\text{Si}$  scale]; positive values represent downfield shifts. <sup>b</sup>  $A = -\Delta G^\circ = -RT \ln K$  ( $T$  183 K),  $K = I_{eq}/I_{ax}$  where  $I_{eq}$  and  $I_{ax}$  are averaged integral intensities of the signals for the equatorial and axial conformers. <sup>c</sup> At 183 K. <sup>d</sup> (I) or (II) :  $\text{CS}_2 = 1:10$  (v/v). <sup>e</sup> At 300 K. <sup>f</sup> At 173 K. <sup>g</sup> (III) :  $\text{CS}_2 = 1:4$  (v/v).

previously reported.<sup>4</sup> The results are summarized in Table 1.

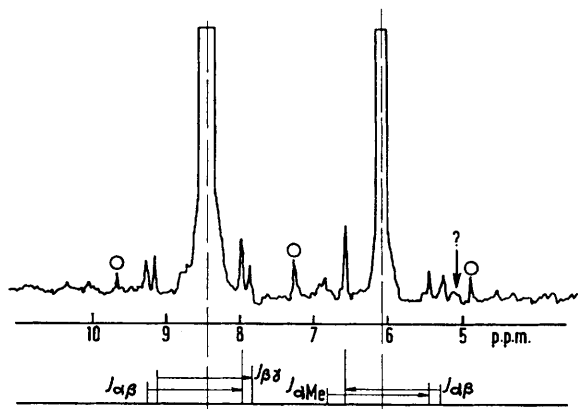


FIGURE. Proton decoupled  $^{13}\text{C}$  n.m.r. spectrum of methylcyclohexane at 173 K (5 to 10 p.p.m. region, relative to  $\text{C}_6\text{H}_{12}$ ). Two intense signals from  $\alpha$ (C-1) and  $\beta$ (C-2 and C-6) atoms are marked by dotted lines; weak signals marked by circles are assigned as folded signals or modulation side bands. The  $^{13}\text{C}$ - $^{13}\text{C}$  splittings are given below with the arrows directed towards the centres of the AB quartets. The signal at *ca.* 5.1 p.p.m. marked (?) is tentatively assigned to the  $\beta$ -carbon atom of the axial conformer (see text).

The substituent chemical shifts of the individual conformers given in Table 1 together with the values previously reported for a number of substituents<sup>3,4,6</sup> form a set of additive parameters useful in predicting the carbon chemical shifts in polysubstituted cyclohexanes.<sup>7,8</sup> The averaged chemical shifts,  $\langle\delta\rangle$ , obtained in the spectra at ambient temperatures, although they may reflect some perturbation effects (temperature dependence of the chemical shifts, effects of media, solvation, *etc.*), lead (by using the Eliel equation,  $p_{eq} = \langle\delta\rangle - \delta_{ax}/\delta_{eq} - \delta_{ax}$ ) to quite reasonable estimates. By excluding the carbon chemical shifts of the  $\alpha$ - and  $\delta$ -atoms in a manner similar to that given in ref. 4 the following  $p_{eq}$  values are obtained: 0.98 and 0.87 for (I), and 0.94 and 0.95 for (II), from the  $\beta$ - and  $\gamma$ -carbon shifts, respectively. These values can be compared with the low-temperature data (Table 1) of 0.94 for (I) and 0.97 for (II). The  $A$  values obtained from the  $^{13}\text{C}$  n.m.r. spectra (Table 1, see also data in refs. 3 and 4) are systematically greater than the best  $A$  values proposed by Jensen and Bushweller<sup>5</sup> by *ca.* 20%.

It was difficult to obtain data for the axial conformer of methylcyclohexane. Previous estimates of the conformational energy made by Anet and his co-workers led to values of *ca.* 1.6 kcal mol<sup>-1</sup>, ref. 2 (from continuous-wave spectra, some saturation effects being possible<sup>9</sup>) and 1.76 kcal mol<sup>-1</sup>, ref. 9 (from pulsed Fourier transform spectra).

Our search for signals arising from the axial conformer in the low-temperature spectra (173 K) included a careful study of weak signals by using reference signals of known intensity. We used the intensities of  $^{13}\text{C}$ - $^{29}\text{Si}$  satellites from the internal  $\text{Me}_4\text{Si}$  [ $J(^{13}\text{C}$ - $^{29}\text{Si})$  50.6 Hz] added in amounts which gave a signal of 2% intensity, and we also studied the  $^{13}\text{C}$ - $^{13}\text{C}$  satellites from which signals of 0.5% intensity were obtained. A part of the low-temperature  $^{13}\text{C}$  n.m.r. spectrum of (III) is shown in the Figure. After distinguishing the folded signals and the rotation side bands we identified almost all the  $^{13}\text{C}$ - $^{13}\text{C}$  satellites. The corresponding  $^{13}\text{C}$ - $^{13}\text{C}$  couplings (Table 2) are typical of  $sp^3$ -

TABLE 2

Coupling constants  $^1J(^{13}\text{C}$ - $^{13}\text{C})$  for the equatorial conformer of methylcyclohexane (III) (in Hz)

Position of $^{13}\text{C}$ isotopes	Carbon	Splittings $^1J(^{13}\text{C}$ - $^{13}\text{C})$	$\Delta(\text{exp.})$ /Hz <sup>a</sup>	$\Delta(\text{calc.})$ /Hz <sup>b</sup>
Me and C-1	Me	36.0	-0.5	-0.7
	$\alpha$	36.0	+0.5	+0.7
C-1 and C-2	$\alpha$	33.5	-4.5	-4.2
	$\beta$	33.5	+4.5	+4.2
C-2 and C-3	$\beta$	32.8	+1.5	+1.1
	$\gamma$	33.0	-1.0	-1.1
C-3 and C-4	$\gamma$	$30 \pm 10^c$	—	—
	$\delta$	$30 \pm 10^c$	—	—

<sup>a</sup> The frequency difference between the centre of the  $^{13}\text{C}$ - $^{13}\text{C}$  satellite and the  $^{13}\text{C}$ - $^{12}\text{C}$  signal (accuracy  $\pm 0.3$  Hz). <sup>b</sup>  $\Delta(\text{calc.}) = \frac{1}{2} [\sqrt{J^2 + \delta^2} - \delta]$ . <sup>c</sup> Calculated on the basis of the chemical shifts in Table 1 and the experimental central AB-quartet frequencies determined with an accuracy of  $\pm 0.5$  Hz.

hybridized carbon atoms.<sup>10</sup> Finally, at least two of the remaining weak signals (at *ca.* 5.1 and *ca.* -6.2 p.p.m., relative to  $\text{C}_6\text{H}_6$ ) may be tentatively assigned, respectively, to  $\beta$ -(C-2 and -6) and  $\gamma$ -(C-3 and -5) carbon atoms of the axial conformer. These two signals were not identified in the spectra obtained at ambient temperature, which supported their assignment to the axial conformer. Although this assignment is also supported by Dalling and Grant's estimates<sup>6</sup> and the experimental data reported by Anet,<sup>9</sup> the signal-to-noise ratios for these signals (see Figure) are too small for the assignment to be unambiguous. The signals show noticeable broadening, probably owing to slow ring inversion still taking place at 173 K. The relative integral intensities of these weak signals may be estimated roughly, giving the proportion of the axial conformer as 0.5% or lower, corresponding to  $A$  values of 1.8 kcal mol<sup>-1</sup> or higher.

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