A Direct Determination of the Position of Equilibrium in *trans*-1,2-Dimethylcyclohexane

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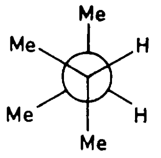
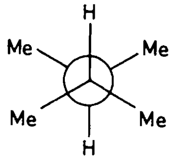
The ^{13}C n.m.r. spectrum of *trans*-[1-*methyl*-^{13}C]-1,2-dimethylcyclohexane at 169 K reveals a signal due to the methyl carbons of the *trans*-diaxial conformation (equilibrium constant *ca.* 3 655; $-\Delta G^{\circ}_{aa\rightarrow ee}$ *ca.* 2.75 kcal mol^{-1}), whilst studies of the broadening of the natural abundance ^{13}C signals in the range 195—240 K yield a more accurate value for $-\Delta G^{\circ}_{aa\rightarrow ee}$ of 2.58 ± 0.05 kcal mol^{-1}, in good agreement with calculations by Allinger.

Three studies[1–3] using force-field calculations have concluded that the 2,3-dimethylbutane conformations (**1**) and (**2**), which apparently differ by 1 *gauche* butane interaction, have nevertheless almost identical enthalpies. This result is in keeping



(1)



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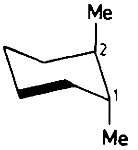

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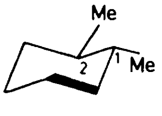

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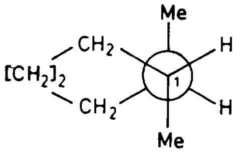

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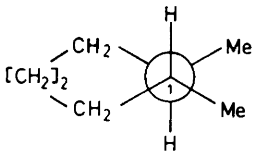

(6)

with the classic work of Sheppard and Szasz,[4] and more recent findings,[5] both utilising variable temperature Raman spectroscopy. Moreover, the ^{13}C n.m.r. spectrum[6,7] of 2,3-dimethylbutane at 93 K gave for (**1**) and (**2**) a ratio of 2 : 1 ($\Delta G^\circ_{1\rightarrow 2}$ 0.13 kcal mol^{-1}†), as expected if $\Delta H^\circ = ca.$ 0 and $\Delta S^\circ_{1\rightarrow 2} = -2\ln 2$ [(**1**) exists as a pair of enantiomers]. The possibility that a qualitatively similar effect might apply to the *trans*-1,2-dimethylcyclohexane conformations (**3**) and (**4**) [*cf.* Newman projections (**5**) and (**6**) respectively], which apparently differ by 3 *gauche* butane-type interactions, led us to investigate the equilibrium (**3**) $\rightleftharpoons$ (**4**), which has hitherto been studied only indirectly.[8] We now report a direct analysis of the equilibrium (**3**) $\rightleftharpoons$ (**4**) by ^{13}C n.m.r. spectroscopy.

The ^{13}C n.m.r. spectrum (62.87 MHz) of a mixture‡ of 33% *cis*- and 67% *trans*-[1-*methyl*-^{13}C]-1,2-dimethylcyclohexane at 169 K revealed a weak signal at 18.36 p.p.m., close to the intense signal (20.61 p.p.m.) due to the methyl carbons of the diequatorial conformation (**4**). The equilibrium constant of 3655 ± 650 is equivalent to a $-\Delta G^\circ$ value of 2.75 ± 0.11 kcal mol^{-1}. The assignment of the weak signal to the methyl carbons of the diaxial conformation (**3**) rests on its chemical shift (*cf.* ref. 8), on its increased width at 193 K, and on its disappearance at 203 K. However, the possibility that the weak signal is due to an impurity, itself undergoing exchange with a hidden signal, is one which cannot be eliminated. Consequently, studies of the broadening[9] of the ^{13}C spectral lines were undertaken on a non-enriched sample of the pure *trans*-1,2-dimethylcyclohexane in the range 195—240 K. A 5 mm sample tube was employed, and high accuracy in band width measurements ($W_{\frac{1}{2}}$) was ensured by the use of 32 K data points over a spectral width of 4000 Hz. The measured signals had signal to noise values of between 72 and 300, and the half-intensity widths (W_0) for Me$_4$Si were in the range 0.31—0.42 Hz. Calculations of conformer proportions required ^{13}C chemical shift values for ring carbons in (**3**) and (**4**); the values for (**4**) were the shifts *observed* at 169 K whilst those for the diaxial conformation (**3**) were *calculated* from the ^{13}C chemical shift parameters[10] for an axial methyl substituent in cyclohexane (shift 27.0 p.p.m.). The signal for carbons 3,6 (chemical shift difference of 9.52 p.p.m. for $\delta_{aa} - \delta_{ee}$) showed a maximum for ($W_{\frac{1}{2}} - W_0$) of 1.75 ± 0.05 Hz at 222 ± 3 K, giving 341 ± 10 for the equilibrium constant K and a $-\Delta G^\circ$ value of 2.58 ± 0.05 kcal mol^{-1}, equivalent to 3 *gauche* butane-type interactions. Confirmation of this result was provided by similar measurements on the signals for C-4,5 (maximum $W_{\frac{1}{2}} - W_0$ of 1.07 ± 0.05 Hz at 218 ± 3 K, $-\Delta G^\circ$ 2.55 ± 0.06 kcal mol^{-1}) and on the signal for C-1,2 (maximum $W_{\frac{1}{2}} - W_0$ of 1.00 ± 0.05 Hz at 218 ± 3 K, $-\Delta G^\circ$ 2.52 ± 0.06 kcal mol^{-1}). The line broadening study also gave the activation energy for ring inversion $\Delta G^*_{ee\rightarrow aa}$ as 11.8 ±0.2 kcal mol^{-1}.

To the extent that the 4 *gauche* butane-type interactions in (**3**) are expected to total 3.50 ± 0.10 kcal mol^{-1} (*cf.* ref. 11), the diequatorial *gauche* interaction in (**4**) can be concluded to amount to 0.92 ± 0.15 kcal mol^{-1} (*cf.* Manoharan and Eliel's value[8] of 0.74 ± 0.09 kcal mol^{-1}).

The value of 2.58 kcal mol^{-1} for $\Delta G^\circ_{aa\rightarrow ee}$ shows good agreement with that of 2.69 kcal mol^{-1} calculated by Allinger *et al.*[1] Relief of steric repulsions in (**1**) is due to a widening of the CH$_3$–C–CH$_3$ bond angle and alterations in torsional angles along CH–CH and CH$_3$–C bonds (*cf.* refs. 1 and 2); evidently these factors are less likely to occur in (**3**), probably owing to constraints imposed by the ring system.

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† 1 cal = 4.184 J.

‡ Synthesised from 2-methylcyclohexanone by a Wittig reaction, followed by hydrogenation of [*methylene*-^{13}C]-1-methyl-2-methylenecyclohexane over Pd/C in ethanol.

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