Long-range Proton Hyperfine Splittings in the EPR Spectra of Cyclohexyl and Alkylcyclohexyl Radicals: Ring Inversion in the Cyclohexyl Radical

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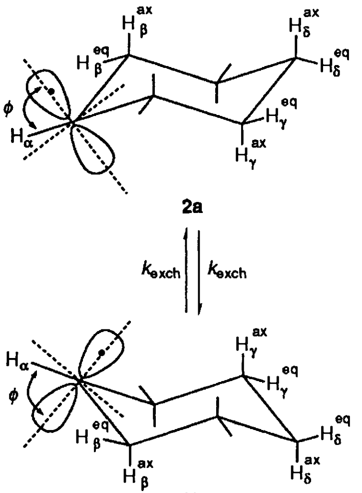
The cyclohexyl radical has been studied by EPR spectroscopy in liquid cyclopropane at low temperatures and hyperfine splittings from the γ-protons have been observed for the first time. The temperature-dependent EPR spectra have been computer simulated, taking account of β-, γ- and δ-proton exchange, to afford a new Arrhenius rate expression [eqn. (A)] for chair-to-chair interconversion in this radical ($\theta = 2.303\,RT$ kJ mol^{-1}).

$$\log_{10}(k_{\text{exch}}/\text{s}^{-1}) = (13.5 \pm 0.3) - (23.5 \pm 1.1)/\theta \qquad \text{(A)}$$

The 4-*tert*-butylcyclohexyl radical is conformationally locked by the equatorial *tert*-butyl group and its EPR spectrum does not exhibit temperature-dependent lineshape effects or resolvable splitting from the axial δ-proton. The *cis*-3,5-dimethylcyclohexyl radical is also locked in a chair conformation and its EPR spectrum shows long-range splittings from two axial γ-protons and from the equatorial δ-proton. *Ab initio* and semi-empirical (AM1) molecular orbital calculations predict a slightly non-planar equilibrium configuration at C_α in the cyclohexyl radical; H_α prefers equatorial placement, but the energetic cost of planarisation is very small.

In their classic paper,[1] published nearly 30 years ago, Fessenden and Schuler described the isotropic EPR spectrum of the cyclohexyl radical **1**, produced by electron irradiation of cyclohexane. The EPR data, taken as a whole, were considered to be most consistent with the chair conformation **2**, in which the geometry at the radical centre is close to planar[1-3] (*i.e.* Φ, the angle between the C_α–H_α bond and the perpendicular to the $C_\beta C_\alpha C_\beta$ plane, is near to 90°). The spectrum of **1** exhibits pronounced temperature-dependent lineshape effects and the Arrhenius rate expression [eqn. (2)] was obtained[3] for the degenerate chair-to-chair interconversion $\mathbf{2a} \rightleftharpoons \mathbf{2b}$ in solid cyclohexane. It was assumed that the observed lineshape effects arose solely from exchange of the pairs of highly non-equivalent axial and equatorial β-protons and any contributions which might arise from simultaneous corresponding exchanges of the γ- and of the δ-protons were neglected.



2a

2b

(1)

$$\log_{10}(k_{\text{exch}}/\text{s}^{-1}) = 12.7 - 20.5/\theta \qquad (2)$$
$$(\theta = 2.303\,RT\,\text{kJ mol}^{-1})$$

In liquid cyclohexane at 283 K, when the EPR spectrum of **1** showed narrow lines ($\Delta B_{\text{peak-peak}}$ *ca.* 0.15 G), a long-range triplet splitting of 0.71 G was resolved and was assigned to the two δ-protons, which are rendered magnetically equivalent by rapid ring inversion at this temperature.[1,3] However, no splitting from the γ-protons was detected and thus the average of the coupling constants for these two pairs of protons must be <0.15 G at 283 K.[3]

More recent EPR spectroscopic investigations have led to basically similar conclusions regarding the preferred conformation and fluxional behaviour of **1**, although until now γ-proton splitting has never been observed.[4,5] The temperature-dependent spectrum of **1**, trapped in the channels of crystalline thiourea, has been simulated and the Arrhenius rate expression [eqn. (3)] was obtained.[5]

$$\log_{10}(k_{\text{exch}}/\text{s}^{-1}) = 11.6 - 17.0/\theta \qquad (3)$$

Although the average γ-proton splitting is close to zero, we felt that the individual splittings should be resolvable in the low-temperature spectrum of **1** in fluid solution. The value of *a*(Hγ) for an alkyl radical is known[6-9] to be highly dependent on stereoelectronic factors and can be either positive or negative, suggesting that for **1** the axial and equatorial γ-proton coupling constants could be nearly equal in magnitude, but of opposite sign. Furthermore, since no previous lineshape analysis has taken into account the effects of exchanging the γ- and the δ-protons, we considered that the temperature dependence of the EPR spectrum of **1** was worthy of reinvestigation in the liquid phase.

Results and Discussion

Cyclohexyl radicals were generated in cyclopropane solvent by UV irradiation of solutions containing di-*tert*-butyl peroxide (DTBP) (*ca.* 15% v/v), bromocyclohexane (*ca.* 1 mol dm^{-3}), and either triethylsilane[10] (*ca.* 1.5 mol dm^{-3}) or trimethylamine–butylborane (TMBB)[11] (*ca.* 0.8 mol dm^{-3}) [eqns. (4)–(6); $M^\bullet$ = $Et_3Si^\bullet$ or $Me_3N\rightarrow\dot{B}HBu$]. Spectra obtained using TMBB were

Table 1 EPR parameters for the cyclohexyl radical **1** and for the 4-*tert*-butylcyclohexyl radical **4** in cyclopropane

			Hyperfine splittings^{a,b}/G									
Radical	T/K	g Factor	$1H_\alpha$	$2H_\beta^{ax}$	$2H_\beta^{eq}$	$\langle 4H_\beta\rangle^c$	$2H_\gamma^{ax\,d}$	$2H_\gamma^{eq}$	$\langle 4H_\gamma\rangle^{c,e}$	$1H_\delta^{ax}$	$1H_\delta^{eq}$	$\langle 2H_\delta\rangle^c$
	145	2.0027(7)	21.37	41.47	5.30	23.29	−0.90	1.10	0.10	(0.03)^f	1.25	(0.64)
1	187		21.34	(41.05)	(5.48)	23.05	(−0.98)	(1.03)	(0.03)^f	(0.19)	(1.15)	0.67
	240		21.18	(40.05)	(5.82)	22.94	(−1.06)	(0.95)	(−0.06)^f	(0.38)	(1.02)	0.70
	145	2.0027(4)	21.17	42.66	6.20	24.43	−0.55	1.10	0.28	f	—	—
4	187		21.17	42.16	6.35	24.25	−0.64	1.08	0.22	f	—	—
	240		21.17	41.15	6.68	23.92	−0.71	1.06	0.18	f	—	—

^{a} Corrected to second-order. ^{b} Values in parentheses are calculated from the relationships given in the text. ^{c} Mean values. ^{d} Negative sign assumed (see text). ^{e} Calculated on the assumption that $a(H_\gamma^{eq})$ is positive and $a(H_\gamma^{ax})$ is negative. ^{f} Not resolved.

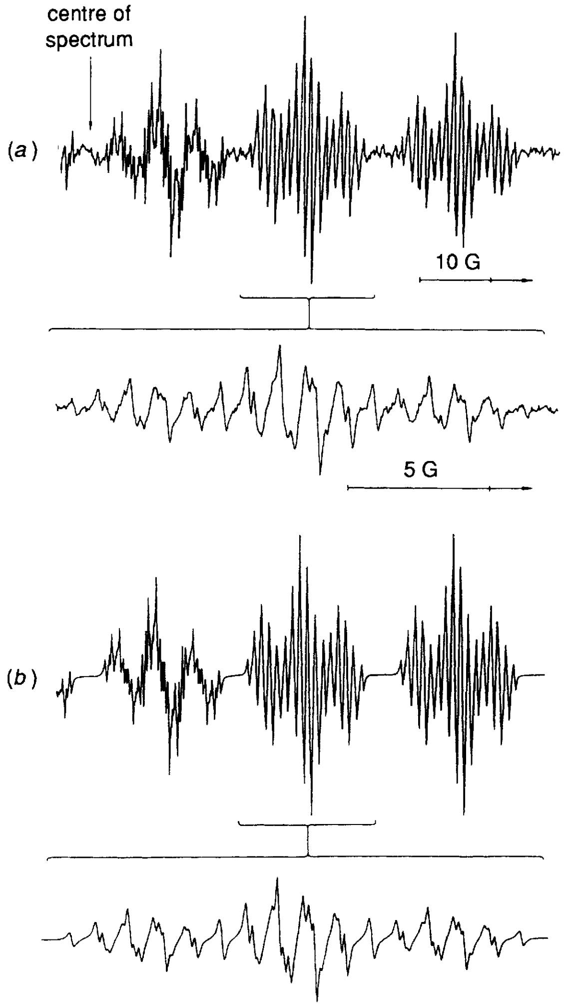


Fig. 1 (*a*) EPR spectra of the cyclohexyl radical, generated by photolysis of DTBP in the presence of bromocyclohexane and TMBB, at 145 K in cyclopropane; an expansion is shown inset. (*b*) Computer simulations of the spectra shown in (*a*), obtained using the parameters given in Table 1.

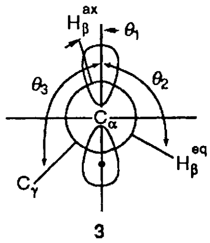
somewhat stronger, especially at the lower temperatures. With the amine–borane, chlorocyclohexane also gave rise to good quality EPR spectra of **1** at low temperatures.[11] The spectrum shown in Fig. 1(*a*) was obtained at 145 K and is ascribed to the cyclohexyl radical, when this is undergoing ring inversion slowly on the EPR timescale. γ-Proton splittings are clearly resolved and the spectrum can be analysed and computer simulated [Fig. 1(*b*)] on the basis of the coupling constants given in Table 1.

$$Bu^tO_2Bu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \qquad (4)$$

$$Bu^tO^\bullet + MH \longrightarrow M^\bullet + Bu^tOH \qquad (5)$$

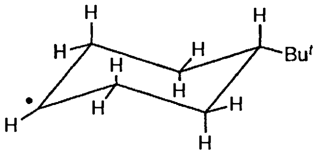
$$M^\bullet + RHal \longrightarrow MHal + R^\bullet \qquad (6)$$

The assignments of the axial and equatorial γ-proton splittings are tentative and are based on the results of *ab initio* molecular orbital calculations for the propyl radical reported by Ellinger *et al.*[7] If the dihedral angles θ_1 and θ_2 (see structure **3**) are taken to be *ca.* 11° and 109°, respectively, as estimated by Hori *et al.*,[5] then θ_3 will be *ca.* 131°. The dihedral angles $H_\gamma C_\gamma C_\beta C_\alpha$ will be about ±60° for H_γ^{ax} and 180° for H_γ^{eq}, and inspection of the splittings calculated for γ-protons in comparable positions in the propyl radical suggests that $a(H_\gamma^{eq})$ will be positive and larger in magnitude than $a(H_\gamma^{ax})$, which will be negative.



3

The 4-*tert*-butylcyclohexyl radical **4** was generated in a similar way from the corresponding chloride[12] (93% *cis* + 7% *trans*), using TMBB as the source of halogen-abstracting radicals. The EPR spectrum of **4** at 145 K is shown in Fig. 2 and the computer simulation was obtained using the parameters given in Table 1. The coupling constants are similar to those found for the unsubstituted cyclohexyl radical, although no δ-proton splitting is evident. Since the *tert*-butyl group would be expected to occupy an equatorial site in **4**, this result clearly indicates that it is H_δ^{eq} which gives rise to the resolvable splitting in the low-temperature spectrum of **1**.



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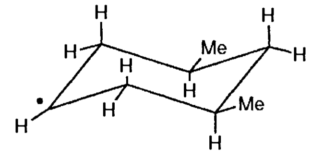

5

The *cis*-3,5-dimethylcyclohexyl radical **5** was generated (using TMBB) by halogen-atom abstraction from isomerically-pure *trans,trans*-1-chloro-3,5-dimethylcyclohexane. The EPR spectrum at 190 K was readily analysed in terms of $a(1H_\alpha)$ 21.42, $a(2H_\beta^{ax})$ 39.85, $a(2H_\beta^{eq})$ 4.78, $a(2H_\gamma^{ax})$ 1.17 and $a(1H_\delta^{eq})$ 1.17 G. The splittings from the pair of axial γ-protons and the

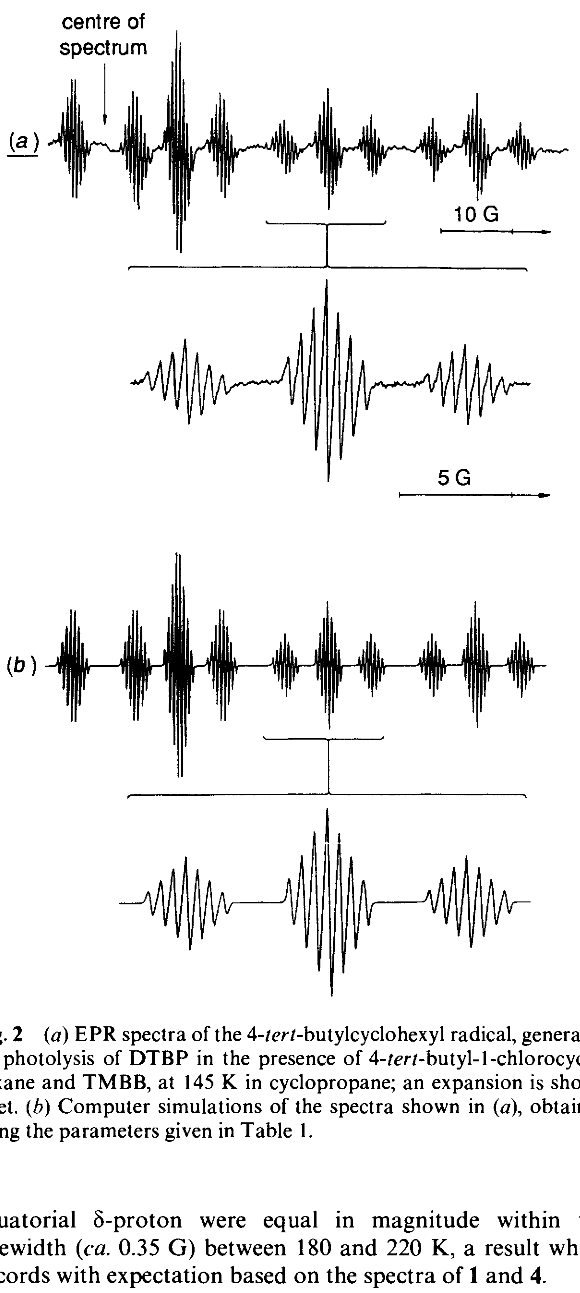

Fig. 2 (*a*) EPR spectra of the 4-*tert*-butylcyclohexyl radical, generated by photolysis of DTBP in the presence of 4-*tert*-butyl-1-chlorocyclohexane and TMBB, at 145 K in cyclopropane; an expansion is shown inset. (*b*) Computer simulations of the spectra shown in (*a*), obtained using the parameters given in Table 1.

equatorial δ-proton were equal in magnitude within the linewidth (*ca.* 0.35 G) between 180 and 220 K, a result which accords with expectation based on the spectra of **1** and **4**.

The EPR spectra of **4** and **5** did not exhibit temperature-dependent lineshape effects below 240 K, as would be anticipated because of the equatorial preference of the alkyl substituents. In contrast, the spectrum of the parent cyclohexyl radical varied markedly with temperature, as reported previously,[1–5] and representative results are illustrated in Fig. 3.

The high-field wing regions of the spectra, which do not show second-order[13] splitting, were computer simulated on a first-order basis, using a slightly modified version of Heinzer's program ESREXN,[14] to yield rate constants for the chair-to-chair exchange process shown in eqn. (1). For these simulations, the value of $a(H_\alpha)$ was measured directly at each temperature. The individual β-proton splittings are temperature dependent[5] and their values in the intermediate exchange rate region were estimated by extrapolation from values measured in the slow exchange region. Experimental points were fitted to quadratics* in the absolute temperature T and, for temperatures in the fast exchange region, the mean value of $a(2H_\beta^{ax})$ and $a(2H_\beta^{eq})$ agreed closely with the measured average splitting (see Table 1). Assuming their signs to be opposite (see above), the mean of the values of $a(2H_\gamma^{eq})$ and $a(2H_\gamma^{ax})$, measured between 126 and 170 K, decreases with increasing temperature. By 225 K, when H_γ^{eq} and H_γ^{ax} are exchanging rapidly on the EPR timescale, the mean splitting from the four γ-protons is not resolved within the linewidth (0.13 G) and remains unresolved at much higher temperatures.[3] The individual values of $a(2H_\gamma^{eq})$ and $a(2H_\gamma^{ax})$ in the intermediate exchange region were estimated by linear extrapolation of the values measured in the slow exchange region, which indicates that $a(2H_\gamma^{eq}) = -a(2H_\gamma^{ax}) = ca.\ 1.0$ G at 225 K.† Despite the fact that the average γ-proton splitting remains unresolved at high temperatures,[3] the assumption of linearity is quite adequate for the purpose of the lineshape analysis. Values of $a(H_\delta^{eq})$ (assumed to be positive) in the intermediate exchange region were obtained by linear extrapolation from the values measured directly between 126 and 155 K. Values of $a(H_\delta^{ax})$ were calculated from $a(H_\delta^{eq})$ and the linearly-extrapolated average δ-proton splitting, derived from measurements in the fast exchange region.‡

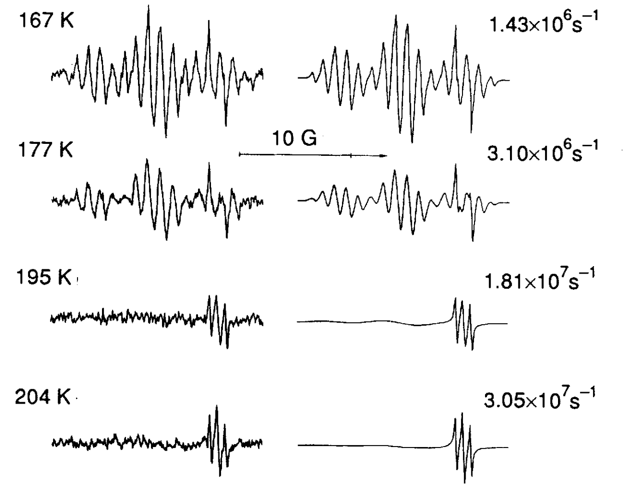

Fig. 3 The $M_I(2H_\beta^{ax}) = M_I(H_\alpha) = -1$ lines (shown expanded in Fig. 1) from the EPR spectrum of the cyclohexyl radical at the temperatures indicated. Alongside each spectrum is shown a computer simulation obtained using the parameters given in the text and the indicated values of k_{exch}.

Rate constants derived from spectra obtained between 167 and 212 K gave a good fit to the Arrhenius eqn. (7). Although the activation parameters for ring inversion of the cyclohexyl

$$\log_{10}(k_{exch}/s^{-1}) = (13.5 \pm 0.3) - (23.5 \pm 1.1)/\theta \quad (7)$$

radical obtained in this work are considered to be rather more accurate and soundly-based than those obtained in the early studies of Fessenden and his co-workers, the differences between the two sets of activation parameters are small and the experimental values of k_{exch} in the region of 190 ± 20 K are in good agreement.

The activation energy for ring inversion of the cyclohexyl radical (23.5 kJ mol^{-1}) is much smaller than that determined for the corresponding inversion of cyclohexane (E_a 45.2 kJ mol^{-1}),[15] but is closer to that for inversion of cyclohexanone[16] (E_a 18.8 kJ mol^{-1}, if the Arrhenius pre-exponential factor is taken to be 10^{13} s^{-1}). The ring in cyclohexanone contains a three-coordinate carbon atom at which the geometry is rigidly

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* $a(2H_\beta^{ax})/G = 40.56 + (1.934 \times 10^{-2})T - (8.942 \times 10^{-5})T^2$
$a(2H_\beta^{eq})/G = 5.23 - (2.484 \times 10^{-3})T + (2.052 \times 10^{-5})T^2$

† $a(2H_\gamma^{eq})/G = 1.33 - (1.58 \times 10^{-3})T$
$a(2H_\gamma^{ax})/G = -0.70 - (1.48 \times 10^{-3})T$

‡ $a(H_\delta^{eq})/G = 1.59 - (2.37 \times 10^{-3})T$
$a(H_\delta^{ax})/G = -0.46 + (3.50 \times 10^{-3})T$

planar. The radical centre in the cyclohexyl radical is also three-coordinate, and although probably non-planar in the equilibrium structure, it is easily planarised (see below).

Molecular Orbital Calculations.—Low-level (STO-3G) *ab initio* calculations for the cyclohexyl radical have been reported by Lloyd *et al.*[17] Using 'standard' bond lengths and angles, these authors optimised the angle Φ for the chair conformation **2** and found the radical centre to be quite strongly pyramidal (Φ *ca.* 59 *or* 122°) with little preference for axial or equatorial placement of H_α. We have carried out semi-empirical AM1-UHF calculations[18] and *ab initio* calculations at the UHF/4-31G* level[19] for the cyclohexyl radical in the chair conformation, with full optimisation of all geometrical parameters within the constraint of C_s symmetry. The AM1 calculations predict that the radical is essentially planar at C_α ($\Phi = 86.6°$, $\Delta H_f = -41.5$ kJ mol^{-1}). However, the radical centre is easily deformed from its equilibrium configuration. When Φ was fixed at 70°, 80°, 100° and 110°, and the remaining geometrical parameters were optimised, the enthalpy of formation rose only by 2.5, 0.6, 2.5 and 7.7 kJ mol^{-1}, respectively.

The *ab initio* calculations predict a somewhat greater equilibrium deviation from planarity at C_α [$\Phi = 72.7°$, E(UHF) = −233.349 204 hartree], but the energy surface is flat and optimisation with Φ fixed at 90° gave a structure less stable by only 2.3 kJ mol^{-1}.

The AM1-UHF single-determinant H-1s spin populations, in conjunction with scaling factors of 387.9 and 784.3 G per unpaired electron for α- and β-protons, respectively,[20] give $a(H_\alpha) = -22.1$, $a(H_\beta{}^{ax}) = +44.5$ and $a(H_\beta{}^{eq}) = +13.6$ G. Hyperfine coupling with γ- and δ-protons is not properly treated by the semi-empirical methods available at present.

Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz. The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) in an Oriel 1 kW housing equipped with an f 0.7 Aspherab fused silica condensing lens. The slightly-converging beam from this was focused using a fused silica lens (focal length 10 cm, diameter 7.5 cm) and directed onto the sample through a 3 cm pathlength water-cooled cell filled with an aqueous solution containing $NiSO_4{\cdot}7H_2O$ (0.38 mol dm^{-3}), $CoSO_4{\cdot}7H_2O$ (0.07 mol dm^{-3}) and sulfuric acid (0.04 mol dm^{-3}). The temperature of the sample during photolysis was determined, using the method described previously,[21] by careful measurement of the value of $a(H_\beta)$ for the isobutyl radical in cyclopropane. The temperature dependence of this splitting constant (in gauss) is given by eqn. (8).[21] The heating effect at full light intensity varied between 5 and 7 K depending on conditions.

$$T/\mathrm{K} = 2.703\,94\,a(\mathrm{H}_\beta)^2 - 198.419\,a(\mathrm{H}_\beta) + 3763.56 \qquad (8)$$

Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (3 mm i.d., 4 mm o.d.). The microwave frequency was measured using a frequency counter (Hewlett-Packard 5350B) and the magnetic field was measured with an NMR gaussmeter calibrated to account for the field difference between the sample and the NMR probe using the pyrene radical anion (g 2.002 71) as a standard.[22] Where necessary, second-order corrections were applied to g-factors and hyperfine splittings.[13]

Computer simulations of spectra were obtained using a modified version of the program ESRSPEC2,[23] adapted to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > 1/2$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian. Spectra showing lineshape effects resulting from ring inversion were simulated using the program ESREXN.[14]

Materials.—NMR spectra ($CDCl_3$ solvent) were obtained using a Varian VXR-400 instrument (400 MHz for ^1H) with tetramethylsilane as an internal standard.

Di-*tert*-butyl peroxide (Aldrich, 98%) was passed down a column of basic alumina (activity 1) and distilled (b.p. 46–47 °C at 76 Torr)* before use. Trimethylamine–butylborane was prepared by the method of Hawthorne.[24] 1-*tert*-Butyl-4-chlorocyclohexane was prepared from 4-*tert*-butylcyclohexanol (Aldrich, 80% *trans* + 20% *cis*) by treatment with triphenylphosphine in refluxing carbon tetrachloride, as described by Beckwith and Westwood.[12] The fraction with b.p. 38–40 °C at 0.5 Torr was further purified by HPLC (Kromasil silica, hexane eluent) to give 1-*tert*-butyl-4-chlorocyclohexane, which was shown by ^1H NMR spectroscopic analysis to consist mainly (93%) of the *cis*-isomer, together with a small amount (7%) of the *trans*-isomer.

1-Chloro-3,5-dimethylcyclohexane was prepared in the same way from 3,5-dimethylcyclohexanol (Aldrich; mixture of isomers, *ca.* 60% all *cis*). The product (b.p. 45–46 °C at 5 Torr, lit.,[25] b.p. 68–71 °C at 20 Torr) contained mainly (*ca.* 72%) *trans,trans*-1-chloro-3,5-dimethylcyclohexane and a pure sample of this isomer was obtained by preparative GLC (3 m × 1 cm column packed with 7% Bentone + 7% diisodecyl phthalate on Chromosorb W 85–100 mesh, ramped from 40–140 °C at 1 °C min^{-1}). The chlorine atom is axial and the two methyl groups are equatorial in the most stable conformation of this isomer [δ_H 0.87 (d, 6 H, J 7.5, Me_2)† and 4.51 (quintet, 1 H, J 2.8, CHCl)].

Other compounds used in this work were obtained commercially and were purified, if necessary, by standard methods.

Acknowledgements

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* 1 Torr = 133.322 Pa.

† J Values are given in Hz.

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