N.M.R. Evidence for a Transition between Isotropic and Anisotropic Thermal Motion of *nido*-Decaborane in an Aromatic Solvent

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Summary The temperature dependence of the ^1H and ^{11}B longitudinal relaxation times and of the ^1H nuclear shieldings in *nido*-decaborane ($B_{10}H_{14}$), in $C_6D_5CD_3$ solution indicate that there is a transition between anisotropic and essentially isotropic molecular tumbling between *ca.* −35 and +25 °C; this transition has not previously been observed in solution.

WE have measured the proton longitudinal relaxation times $T_1(^1H)$ at 100 MHz for decaborane ($B_{10}H_{14}$) in $C_6D_5CD_3$ solution. Plots of $\ln[T_1(^1H)]$ *vs.* $1/T$ for the various protons are linear and parallel above *ca.* +25 °C. The gradient of the plots implies[1] an activation energy E_a of 9·4 kJ mol^{-1} for a single angular step in the molecular rotational diffusion. The parallelism of the plots implies that this motion is isotropic. Between *ca.* +25 and −35 °C, however, the plots are curved, and become linear again (though non-parallel) only below *ca.* −35 °C (*e.g.* Figure, A). The mean of the gradients at lower temperatures implies a value for E_a of *ca.* 15·9 kJ mol^{-1}. Analogous behaviour is observed for $T_1(^{11}B)$. The increase in E_a is considered to arise from an inhibition of molecular motion

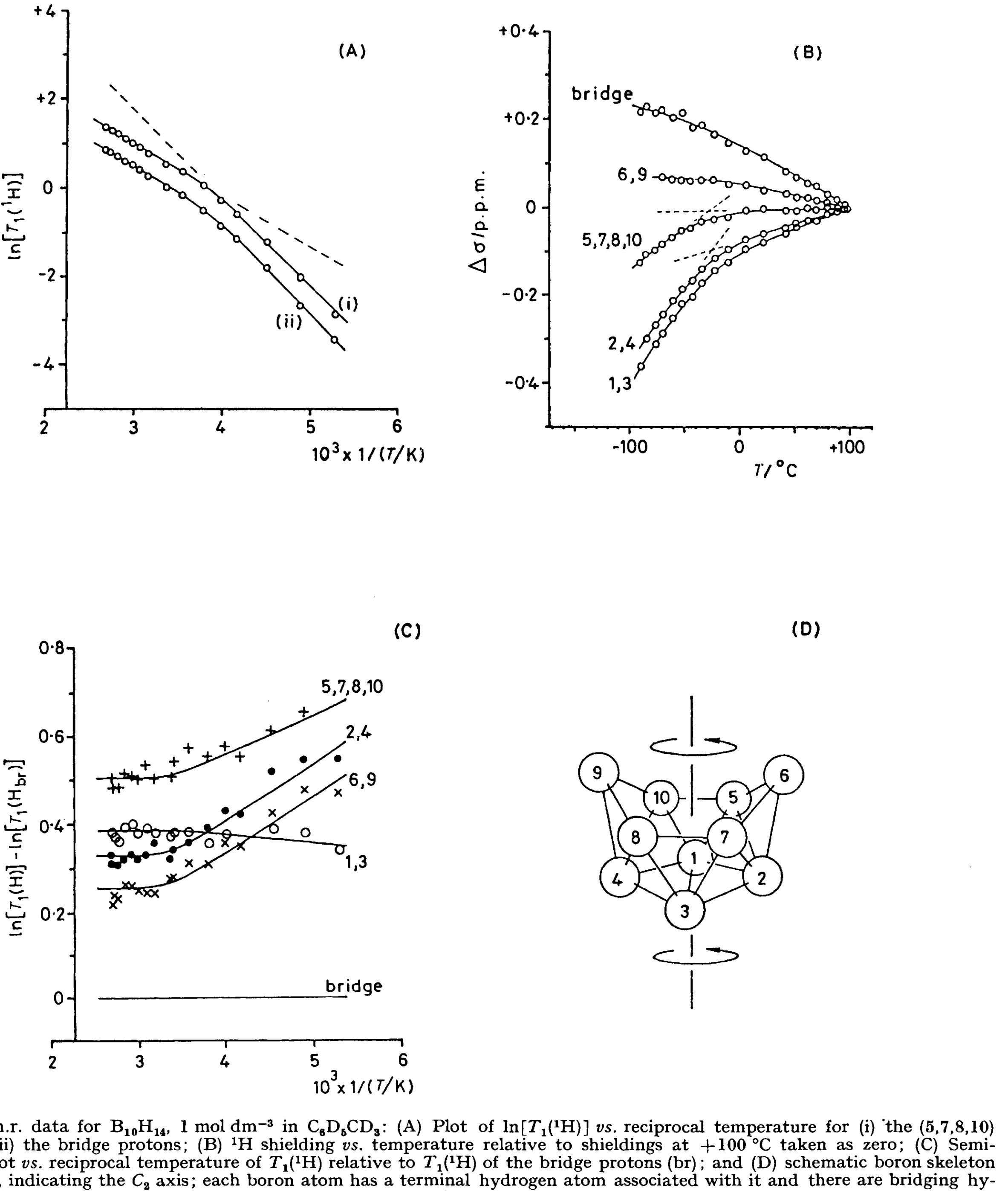

FIGURE. N.m.r. data for $B_{10}H_{14}$, 1 mol dm^{-3} in $C_6D_5CD_3$: (A) Plot of $\ln[T_1(^1H)]$ *vs.* reciprocal temperature for (i) the (5,7,8,10) protons and (ii) the bridge protons; (B) ^1H shielding *vs.* temperature relative to shieldings at +100 °C taken as zero; (C) Semi-logarithmic plot *vs.* reciprocal temperature of $T_1(^1H)$ relative to $T_1(^1H)$ of the bridge protons (br); and (D) schematic boron skeleton of decaborane, indicating the C_2 axis; each boron atom has a terminal hydrogen atom associated with it and there are bridging hydrogen atoms in the four equivalent positions (5,6), (6,7), (8,9), and (9,10).

due to increased interaction of the solute with the aromatic solvent at lower temperatures; in the non-aromatic solvent CD_2Cl_2, for example, plots of $\ln[T_1(^1H)]$ and $\ln[T_1(^{11}B)]$ *vs.* $1/T$ are parallel and linear (E_a *ca.* 10 kJ mol^{-1}) over the liquid range of the solution (measurements taken from -92 to $+40$ °C).

That this interaction with the aromatic solvent is quite specific is evident from the ^1H shieldings within $B_{10}H_{14}$ which exhibit substantial changes in their rates of variation with temperature between *ca.* $+25$ and -35 °C (Figure, B). It is also particularly apparent from the Figure, C, in which relative rates of ^1H longitudinal relaxation are compared. Above *ca.* $+25$ °C, these curves are approximately linear and parallel, confirming isotropic motion, between *ca.* $+25$ and -35 °C there is transitional behaviour, and below *ca.* -35 °C they are again approximately linear but no longer parallel. The low temperature behaviour implies anisotropic tumbling, with different effective rotational activation energies and thus correlation times for non-equivalent positions in the molecule. The individual ^1H relaxation rates will depend upon the individual components of the anisotropic rotational diffusion tensor, and on the individual dipolar and possibly scalar coupling tensors, and we are attempting a more detailed analysis. Preliminary considerations, however, suggest that the results may be interpretable in terms of relatively free rotation about the molecular C_2 axis (Figure, D), with somewhat more restricted rotation about those axes perpendicular to it, and with the C_2 axis additionally being on average approximately perpendicular to the aromatic planes of the adjacent solvent molecules. As far as we are aware, the transition between isotropic and anisotropic solute motion has not previously been observed in the isotropic solvent phase.

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[1] D. M. Doddrell, M. R. Bendall, A. J. O'Connor, and D. T. Pegg, *Austral. J. Chem.*, **1977**, **30**, **943**.