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SOLVENT SHIFT INDUCED BY HEXAFLUOROBENZENE IN NMR SPECTRA

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NMR solvent shifts induced by C_6F_6 have been interpreted as resulting from a dipole-quadrupole interaction.

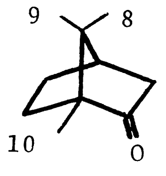
Direction of solvent-induced shifts observed in the ^1H NMR spectrum of a polar solute in C_6F_6 have been known to be opposite to that of shifts in C_6H_6.1) An electro-static interaction of dipole(solute)-quadrupole(solvent) have been reported as a principal cause of a large solvent shift in C_6H_6 in a previous paper.2)

The values of magnetic anisotropy of C_6H_6 and C_6F_6 are -89×10^{-30} and -53×10^{-30} emu, respectively.3) However, the principal values on the six-fold axis of quadrupoles of C_6H_6 and C_6F_6 are -56×10^{-27} and $+17.2\times10^{-26}$ esu, respectively.4) Remarkable is the presence of a close correlation between the sign of the principal values of the quadrupoles and the sence of the shifts.

Solvent shifts of the proton signals of three methyl groups of d-camphor in C_6H_6 and C_6F_6 have been measured and listed in Table 1.7) The observed shifts in C_6F_6 have a sign opposite to that inferred from the carbonyl plane rule5) in C_6H_6.

Table 1. The observed NMR solvent shifts of d-camphor ($\Delta\delta$ in ppm)

signal	in C_6H_6	in C_6F_6
10-methy 1	-0 07	+ 0.06
9-methy	+0.29	-0.16
8-methy	+0.21	-0.07



In order to estimate a value of a solvent shift of camphor (μ=3.10 Debye unit),6) a solute which is covered with protons has been assumed as a model (see Fig. 1). It is assumed that the orientation of C_6F_6 molecules around a camphor molecule is mainly caused by the dipole-quadrupole interaction as described in the previous paper.2) The shifts have been calculated from the magnetic anisotropy of C_6F_6 molecules oriented around the camphor.8) In Fig. 2, the calculated and the observed shifts in C_6F_6 are plotted against the angle η and compared. The observed values are in good agreement with the calculated results.

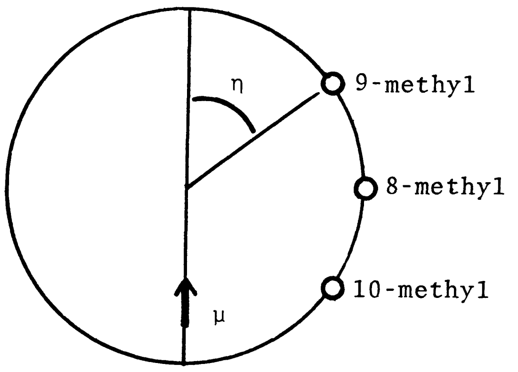


Fig. 1 The spherical molecular model for camphor.

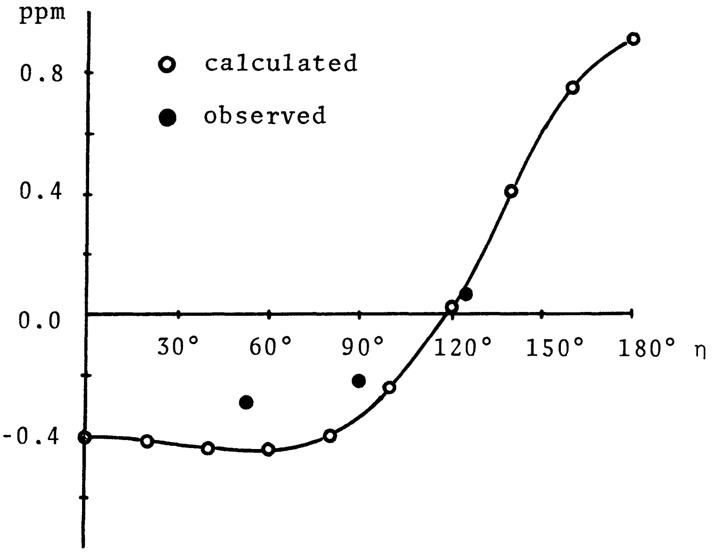


Fig. 2 The relationship between calculated and observed solvent shifts and the angle η.

Consequently, the dipole-quadrupole interaction is also concluded to be a main cause for the solvent shift in C_6F_6 as for the case in C_6H_6.

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7) Proton Chemical shifts were measured on a Hitach R-20B spectrometer at 60 MH_z using 0.1 mol% solutions with internal reference of C_6H_{12}.
Solvent shift $\Delta\delta=\delta_{C_6H_6 \text{ or } C_6F_6}-\delta_{CCl_4}$.

8) Calculations were performed at the computer center of the University of Tokyo.

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