Evidence from the Kerr Effect for Hydrogen-bonding of Fluoroform and Chloroform with Benzene

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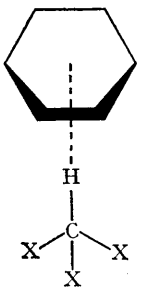
VARIOUS studies[1-4] have suggested the existence of bonding involving the π-electrons of benzene and the proton of chloroform. Stereospecific interaction of this type would produce a species (I) in which the dipole moment lies perpendicular to the directions of maximum polarisability, and any tendency towards formation of such a complex would result in an apparent molar Kerr constant *more negative* than that of the free haloform molecule.

The molar Kerr constants at infinite dilution, ${}_{\infty}({}_{m}K_2)$, of fluoroform and chloroform[5] as solutes in benzene at 25° are -33×10^{-12} and -41×10^{-12}, respectively. Molar Kerr constants for the vapours ${}_{m}K_g$, are recorded[6,7] as $-5{\cdot}3 \times 10^{-12}$ and $-25{\cdot}8 \times 10^{-12}$ at 25°. For fluoroform the ratio of ${}_{\infty}({}_{m}K_2)$ to ${}_{m}K_g$ is much greater than for any other substance for which data are available.

We have found that the n.m.r. spectrum of fluoroform (mole fraction 0·005) in deuterobenzene at 40° consists of a quartet ($\delta = 5{\cdot}26$, $J = 80$ c./sec.) which represents a high-field shift of 1·0 p.p.m. relative to cyclohexane as solvent.[8] This large shift also indicates specific interaction, but thermodynamic studies would be necessary to compare the strength of this association with that observed for chloroform.[3]

We conclude that the Kerr effect provides a method for investigation of hydrogen-bonding with benzene.



(I) X=F,Cl

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