Magnetic Birefringence of Ethane

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EXPERIMENTAL VALUES for the anisotropy of the magnetic susceptibility of hydrocarbons[1-3] and other simple molecules are neither as plentiful nor as reliable as might be wished. Such information is currently of importance because of the relationship between the magnetic anisotropy associated with chemical bonds and the chemical shifts in high resolution nuclear magnetic resonance.[4-6]

Measurements of the magnetic birefringence (Cotton–Mouton effect) of gases provide important information, and suitable apparatus has been assembled for such studies. The average magnetic field available is 28,000 Oersted over a sample length of 50 cm. perpendicular to the field. The light is plane polarized at an angle $\pi/4$ to the field and the phase lag due to the birefringence is converted into an angle of rotation of this plane by means of a quarter-wave plate, and this rotation is measured on a Bendix–Ericsson recording polarimeter. With a sample of ethane at 40 atmospheres pressure the observed rotation was about $1{\cdot}4 \times 10^{-4}$ radians. The birefringence induced was proportional to the gas density and the molecular Cotton–Mouton constant for ethane, ${}_{\mathrm{m}}C$, as defined by Buckingham and Pople[7] in their equation 3·9, was found to be $(-2{\cdot}63 \pm 0{\cdot}2) \times 10^{-18}$ e.m.u. at 293°K for light of wavelength 5461Å.

Provided the temperature-independent terms can be neglected and the molecule has effectively axial symmetry then

$$ {}_{\mathrm{m}}C = \frac{4\pi \boldsymbol{N}}{405\, \boldsymbol{k}T} (\alpha_{\parallel} - \alpha_{\perp})\,(\chi_{\parallel} - \chi_{\perp}), $$

where α and χ are the molecular optical polarisability and the magnetic susceptibility in the directions parallel and perpendicular to the axis as indicated. The quantity $(\alpha_{\parallel} - \alpha_{\perp})$ is best obtained from the depolarisation ratio, ρ_0, of the Rayleigh scattering and the value[8] $\rho_0 = 1{\cdot}97 \times 10^{-2}$ at 6328Å is adopted despite the difference of wavelength; the mean polarisability at 5461Å is[9] $4{\cdot}11 \times 10^{-24}$ cm.^{3} and these values give $(\alpha_{\parallel} - \alpha_{\perp}) = \pm 0{\cdot}71 \times 10^{-24}$ cm.^{3}. The positive sign is taken as required by the empirical bond polarisabilities[10] which give $+0{\cdot}72 \times 10^{-24}$ cm.^{3}. The derived molecular magnetic anisotropy $(\chi_{\parallel} - \chi_{\perp}) = -8{\cdot}0 \times 10^{-30}$ cm.^{3}, which is equivalent to $-4{\cdot}9 \times 10^{-6}$ cm.^{3}/mole.

If the anisotropies of bond susceptibilities are truly additive properties and regular tetrahedral angles may be assumed, the ethane anisotropy can be written as

$$ (\chi_{\parallel} - \chi_{\perp})_{\mathrm{C\text{-}C}} - 2(\chi_{\parallel} - \chi_{\perp})_{\mathrm{C\text{-}H}} $$

where parallel and perpendicular now refer to the bond directions. Previous estimates of this quantity[5] were $-2{\cdot}6 \times 10^{-6}$ cm.^{3}/mole based on crystal studies[3] of long-chain acids and $-2{\cdot}0 \times 10^{-6}$ cm.^{3}/mole based on a wider survey[6] of the evidence; both these estimates are smaller in magnitude than the value $-4{\cdot}9 \times 10^{-6}$ cm.^{3}/mole found in the present work.

We thank Professor J. A. Pople for his encouragement of this work, which forms part of the programme of the Basic Physics Division of the National Physical Laboratory.

(*Received, December 29th*, 1964.)

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