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J. Shashidhara Prasad [a]
[a] Department of Physics, University of Mysore, Manasagangotri, Mysore, 570 006, India
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Orientational Order Parameter in 4-4′Bis(pentyloxy)azoxy Benzene

J. SHASHIDHARA PRASAD

Department of Physics, University of Mysore, Manasagangotri, Mysore 570 006. India†

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Dipole–dipole splitting and order parameters for 4-4′bis(pentyloxy)azoxy benzene obtained from the wide line NMR study are communicated. The values of order parameters are compared with those obtained by the optical studies.

In a nematic liquid crystal the long molecular axes are preferentially oriented in a particular direction. Due to thermal oscillations, a particular molecular axis will be inclined at an angle ξ to the direction of preferred orientation. This oscillation is then decomposed into two opposing rotations. In such a case one defines the order parameter S, which describes the fluctuation of the molecular axis from the direction of preferred orientation of the molecule by

$$S = \tfrac{1}{2}(3\cos^2\xi - 1).$$

For complete order $\cos^2\xi = 1$ and $S = 1$ as in the case of the crystal, whereas for complete disorder $\cos^2\xi = \frac{1}{3}$ and $S = 0$ representing an isotropic liquid. The order parameter of the nematic phase will be between 0 and 1. By a knowledge of the optical anisotropy of the molecules, the orientational order parameter can be calculated from the refractive index data of nematic compounds. In principle one can obtain optical anisotropy from the birefringent data of the crystalline phase by Neugebauer's relation.[1–3] One can also obtain the order parameters from wide line NMR spectra, using the doublet splitting arising from the dipole–dipole interaction of the adjacent ring protons.

† Present address: Department of Chemical Crystallography, Oxford University, 9, Parks Road OXFORD OX1 3PD, UK.

Presently, dipole–dipole splittings and order parameters of 4-4′bis(pentyloxy)azoxy benzene are communicated, and the order parameters obtained by the wide line NMR studies are compared with those obtained from the measurements of refractive indices and densities of the same in the crystalline, liquid crystalline, and liquid phases.

The commercially available yellow compound of 4-4′bis(pentyloxy)azoxy benzene (supplied by Eastman Organic Chemicals, USA) was purified by successive recrystallization from its solution in toluene to obtain fine transparent flakes. The solid-nematic and nematic-isotropic temperatures of the purified crystal were determined to be 78°C and 122°C respectively. The wide-line spectra were recorded at different temperatures in the NMR set up fabricated in the laboratory. The NMR arrangement consisted of a water cooled magnet with pole diameter of 12″ and with a gap of 2″. A current stabilizer designed by Cook, George and Grant[4] was adopted with some modifications. A variable frequency oscillator-detector of the Robinson[5] type was used. A Hewlett-packard strip chart recorder was made use of to record the signals. The temperature was varied by immersing the probe

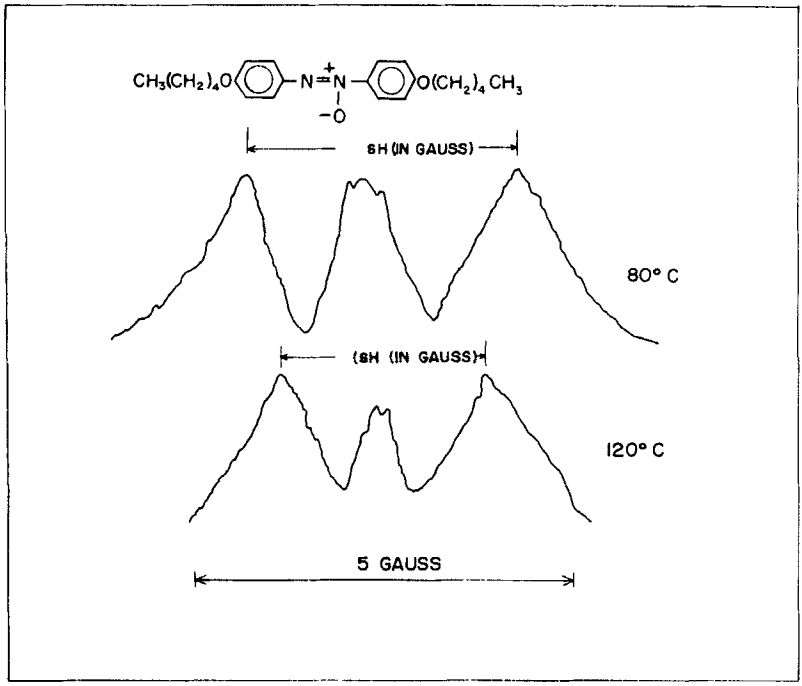

FIGURE 1 Representative wide line spectra for two temperatures and the structure of 4-4′bis(pentyloxy)azoxy benzene.

containing the sample in a bath of carbon-tetrachloride which was electrically heated. The typical representative wide line spectra are shown in Figure 1 for two temperatures along with the structure of the compound.

The doublet splitting δH arising from the dipole-dipole interaction of the adjacent ring protons was used to calculate the order parameter S by means of the equation[6–8]

$$\delta H = 4\alpha(\tfrac{3}{2}\cos^2\phi - \tfrac{1}{2})S.$$

In the above equation the interaction field parameter turns out to be 1.42×10^{-23} ERG/GAUSS, when the distance between the adjacent protons is taken to be 2.45 Å. If the angle between the para axis of a ring and the molecular axis is assumed to be zero, and taking into consideration the interaction of the alkyl chain protons the doublet split δH will turn out as

$$\delta H = 5.73\ S \text{ Gauss}.$$

Figure 2 shows the dipole–dipole splittings and the order parameter as obtained from the NMR studies and the optical studies of the sample. We notice that, there exists small difference between the order parameters calculated from the birefringence data[9] and from NMR studies, the values of the former being lower.

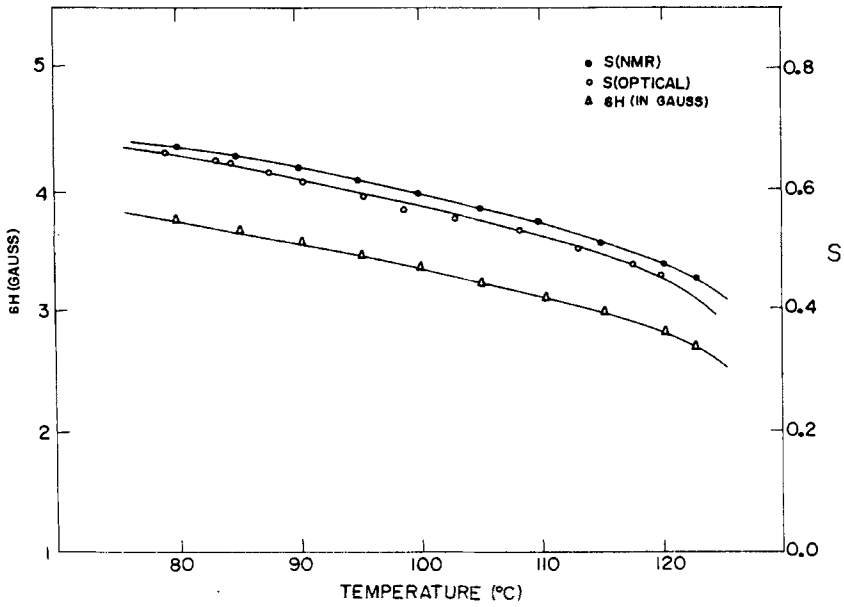

FIGURE 2 Dipole–dipole splittings and the order parameters from NMR studies and the optical studies for 4-4′bis(pentyloxy)azoxy benzene.

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