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^{13}C-N.M.R. studies of discotics

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^{13}C-N.M.R. studies of discotics

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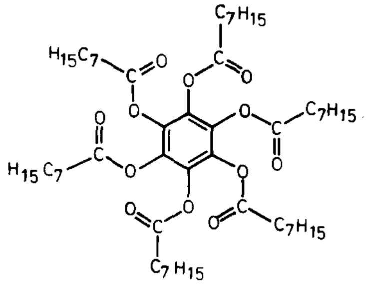
^{13}C-N.M.R. spectra of benzene-hexa-*n*-octanoate (a discotic liquid-crystalline material) show significant differences in the isotropic, mesomorphic and solid states. The presence of four molecules per asymmetric unit is required to explain the results in the solid state.

The discotic liquid-crystalline phases first discovered in 1976 [1] have subsequently received considerable attention [2, 3]. N.M.R. studies of such materials in the mesomorphic phase and the molecules dissolved therein have been undertaken mostly by ^{2}H-N.M.R. [4, 5] though ^{1}H and ^{13}C-N.M.R. investigations have been reported with a view to investigate the molecular order and the dynamics [6, 7]. In the present communication, we report the proton decoupled ^{13}C-spectra of a discotic compound in the isotropic, liquid-crystalline and solid states with a view to study the phase transitions and the differences in the structure of the three phases.



(1)

The compound studied was benzene-hexa-*n*-octanoate (structure 1). It was prepared by the standard procedure reported in the literature [8]. Compounds of this type were the first disc-like materials where mesomorphic behaviour was observed [1]. The spectra were recorded at 75·5 MHz frequency on a Bruker MSL-300 spectrometer equipped with high power decoupling and Magic Angle Sample Spinning

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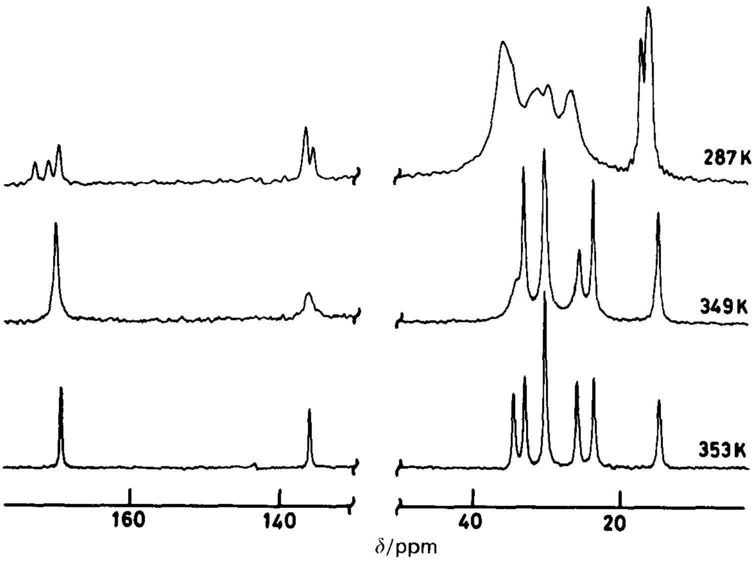

^{13}C-N.M.R. spectra of benzene-hexa-*n*-octanoate at various temperatures. The isotropic phase spectrum (bottom trace) was obtained by accumulating 45 transients, with a relaxation delay of 5 s. The spectrum in the liquid-crystalline phase (middle trace) was obtained with 200 transients with a relaxation delay of 5 s and the MASS at 4100 Hz. For the spectrum in the solid state (upper trace), 300 transients were accumulated with a relaxation delay of 10 s and MASS at 4100 Hz.

(MASS) accessories. Typical proton decoupled spectra in the three phases are shown in the figure along with the other relevant experimental details. The spectra in the liquid-crystalline and the solid states were recorded with high power proton decoupling and MASS. The chemical shifts were measured with repect to external tetramethylsilane (TMS) as the reference.

It may be mentioned that the reported transition temperatures for the compound are isotropic $\xleftarrow{(81\cdot5^{\circ}C)}$ mesomorphic $\xleftarrow{(79\cdot8^{\circ}C)}$ crystalline. Our values as determined from the N.M.R. spectral changes were different by about 2°C compared to these. This might well be due to the difference in calibration of our variable temperature unit and the fact that its precision was only ± 1°C. The molecular symmetry axis of the phase is on the average tilted with respect to the columnar axis and is referred to as tilted discotic (Dt).

The spectra in each phase exhibit three distinct regions. The carbonyl carbons appear around 170 p.p.m. The aromatic carbons resonate at nearly 136 p.p.m. and the alkyl chain carbons between 14 and 36 p.p.m. The terminal methyl carbon which appears at the highest frequency is well separated from the rest. The methylene carbons appear within a small range of 10 p.p.m. and hence their resonances were not well resolved particularly in the spectrum in the solid state. It was, therefore, difficult to draw definite conclusions about the individual methylene carbons. The information reported, herein, was consequently derived exclusively from the spectra of the carbonyl, aromatic and the methyl carbons.

The differences in the spectra in the three phases can be clearly seen in the figure. The carbonyl, aromatic and methyl carbons show single lines each with nearly equal intensity and width in the isotropic phase (figure, bottom trace). However, in the mesomorphic phase, the line from the aromatic carbons is broader and smaller in intensity (figure, middle trace). This difference in the intensity and width of the lines under discussion may be attributed to different relaxation effects, intercolumnar jumps [9] and other types of motions. The spectrum in the solid state (figure, upper trace) shows three separate lines for the carbonyl carbons with the intensity ratio of 1 : 1 : 2, two lines for the aromatic carbons having intensity ratios of 3 : 1 and three lines (clearly seen on expansion) for the terminal methyl carbons with the intensity ratio of 1 : 1 : 2. If one looks into the conformational structure of the molecule with six-fold symmetry, it is not possible to interpret the above intensity distribution. The solid state structural effects have, therefore, to be incorporated in order to understand the spectra. The differences in the spectra of the liquid and the solid states have in other cases been reported [10] and interpreted in terms of such effects.

The three distinct lines for the carbonyl and the methyl carbons suggest that there should be at least three types of molecules per non-equivalent unit. However, the observed intensity distribution of 1 : 1 : 2 for a molecule with six-fold symmetry would require four molecules per asymmetric unit. It is, therefore, concluded that benzene-hexa-*n*-octanoate has four molecules per asymmetric unit. The relative chemical shift differences between the non-equivalent molecules are larger for the carbonyl carbons than for the methyl since two of the lines in the latter case are nearly overlapping. They are even smaller for the aromatic carbons with the result that only two lines with the intensity ratio of 3 : 1 could be resolved indicating an overlap of the two lines with intensity ratio of 1 : 2 to provide the more intense line. In the absence of X-ray crystal structure data on the molecule, it is difficult to draw more information on the packing and the number of molecules in the unit cell. Work on these lines, on other homologues and different discotic materials is in progress.

The experiments clearly demonstrate the utility of MASS for the study of phase transitions and structural differences in the materials exhibiting liquid-crystalline behaviour.

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