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Observation of a plastic crystalline phase in solid MBBA

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Abstract. Wideline and high resolution NMR studies have been carried out in MBBA in its isotropic, nematic and solid phases. Isotropic and nematic spectra correspond to what has been reported earlier. In the solid phase, contrary to expectations, very intense narrow signals similar to signals of the isotropic phase have been observed for the first time at temperatures close to the solid ↔ nematic phase transition temperature. This indicates rapid reorientational or translational motion in the system. X-ray results however confirm the existence of translational order. The results are interpreted as indicative of the existence of a plastic crystalline phase in MBBA.

Keywords. Liquid crystals; MBBA; plastic crystals; nuclear magnetic resonance.

1. Introduction

The mesomorphic and solid state polymorphic behaviour of liquid crystals $nO \cdot m$ ($C_nH_{2n+1}OPhCHNPhC_mH_{2m+1}$) series of compounds have recently attracted a great deal of attention (Leadbetter *et al* 1979). In particular, the compound 10·4 (N-*p*-methoxybenzylidene-*p*-*n*-butylaniline-MBBA) has been shown to exhibit complex polymorphic behaviour below its 'melting temperature' of 22°C. Through adiabatic calorimetry, Mayer *et al* (1972) and Janik *et al* (1975), measured the temperature dependence of the specific heat of MBBA and interpreted their results as indicative of the existence of a metastable crystalline state in addition to a stable crystalline state and a glassy nematic phase (Kumagai *et al* 1981). X-ray powder pattern of Lydon and Kessler (1975) show anomalous behaviour around 15°C, in that the diffraction peak at $2\theta = 5{\cdot}2°$ gains intensity before finally losing it. The authors offer two possible explanations for this behaviour, in terms of (a) a monotropic metastable crystal → nematic transition followed by the formation of the stable crystalline form, or (b) the possibility of a monotropic smectic phase and the nematic phase. A large number of other experimental investigations such as calorimetry and dielectric studies (Moscicki *et al* 1977), infrared (Janik *et al* 1973; Kirov and Simova 1973) and Raman spectroscopy (Borer *et al* 1971; Vergoten 1972; Destrade and Gasparoux 1975; Arendt *et al* 1981), positron life-time measurements (Walker 1978; Jain and Kafle 1980), neutron diffraction (Dolganov *et al* 1980), ESR spin probe (Spielberg and Gelerinter 1982; Stillman *et al* 1978) and some NMR studies (Kronberg and Gilson 1977; Heinze *et al* 1978; Heinze and Grande 1978; Froix and Pochan 1978; Ito *et al* 1981; Kumagai *et al* 1981) have been directed towards understanding the nature of the polymorphism in

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MBBA. Even though there is general agreement among these reports regarding the occurrence of a number of distinct phases in solid MBBA, the nature of these phases is not yet unambiguously established.

We undertook wideline proton NMR studies at ambient pressure and under high hydrostatic pressure, high resolution NMR and x-ray powder diffraction studies of MBBA to clarify its rather complex behaviour below its nematic phase. The analysis of these results presented below lead us to the conclusion that MBBA exhibits a plastic crystalline state just below its nematic phase. To the best of our knowledge this is the first report of the occurrence of a plastic crystalline phase in a substance which also exhibits liquid crystalline order. A preliminary account of this work has been published earlier (Arumugam *et al* 1983).

2. Experimental

2.1 *Sample*

MBBA has the tendency to absorb moisture and decompose into anisaldehyde and *p*-butylaniline (Denat *et al* 1973) and the nematic to isotropic transition temperature (T_{NI}) decreases drastically in the presence of such molecules. In the present studies MBBA was repeatedly distilled under vacuum of about 0·1 torr. The experiments were all carried out almost immediately after the distillation after sealing the sample in a tube. The temperature T_{NI} for the sample was 45·8°C and was measured both by DSC and proton NMR. Further distillation did not increase the transition temperature T_{NI}.

2.2 *Wideline NMR*

Wideline NMR experiments were performed at 10 MHz using a home-made oscillator-detector system with a Varian magnet. Temperature variation was carried out by passing cold nitrogen gas through a glass Dewar wherein the sample was kept. Above the room temperature, the nitrogen gas was heated and passed on to the sample. One junction of the copper-constantan thermocouple was kept right inside the sample and the other junction in a reference ice-bath. Very low amplitude for modulation was used to avoid modulation broadening and it was possible to see in the spectrum the structure at the centre of the signal in the nematic phase. For studies at high pressures a beryllium-copper (Be-Cu) lock-nut type (Ramanathan and Srinivasan 1978) pressure vessel which can withstand a pressure of 14 kbars was used. The sample was kept inside a teflon tube which was placed inside the radio frequency coil which in turn was kept in another teflon tube. The space was filled with silver chloride which acted as a pressure transmitting medium. Pressure experiments were carried out upto 5 kbars. At ambient pressure, only the smaller teflon tube was used, wherein the sample was transferred quickly and tightly sealed so that no moisture could get in. In these experiments the accuracy in temperature measurement was ± 1°C. To start with, the experiment was carried out in the temperature region -196°C to 50°C and later it was concentrated in the region of nematic phase and just below it.

2.3 *High resolution NMR*

Spectra were recorded using a Bruker WH-270 spectrometer operating in the FT mode. ^{1}H, ^{13}C and ^{2}H resonances were recorded with the frequencies of operation being 270,

67·89 and 41·44 MHz respectively. Both ^{13}C and ^{2}H spectra were recorded with broad-band decoupling of proton resonances being employed. A sample tube (5 mm dia.) was used for recording ^{1}H spectra and a 10 mm dia sample tube was used for recording ^{2}H and ^{13}C spectra. Temperature variation was carried out using Bruker B-ST 100/700 temperature controller. The readings of the controller were also calibrated by directly measuring the sample temperature in a separate experiment. The accuracy in measuring the temperature was $\pm 1°C$. The experiments were carried out in the isotropic phase, nematic phase and below the nematic phase down to $-60°C$.

3. Results

3.1 *NMR studies*

In the wideline NMR experiment, first the sample was heated to 48°C and the PMR spectrum corresponding to the isotropic phase was observed. The sample was cooled slowly and just below the isotropic ↔ nematic transition wings started appearing and these wings were moving out on further cooling the sample. These observations are in accordance with the results reported earlier (Lee *et al* 1973). While cooling, the wings were present down to 13°C. Further cooling of the sample resulted in the sudden appearance of a sharp signal at the centre and the disappearance of the wings. Proceeding further, it was observed that the intensity of the central sharp signal reduced drastically down to −5°C and slowly thereafter and finally disappeared at −40°C. With higher modulation it could be observed with a much reduced intensity on a broad background signal. At −68°C even this disappeared completely and further cooling of the sample resulted in broadening of the entire signal. Figure 1 shows the wideline NMR spectra recorded in the isotropic and nematic phases and at temperatures just below and well below the nematic phase. While heating from −196°C the strong sharp signal appeared again and was present till 19°C. Above this temperature this disappeared and signal, characteristic of nematic phase, appeared. These results are quite unexpected since the solid phase being an ordered phase all translational motions are expected to freeze. Consequently the NMR line is expected to be broader in the solid phase than in the nematic phase due to increased dipolar couplings. However, the observation in the solid phase of an intense sharp line and the absence of wings which were present in the nematic phase indicates that in the phase below the nematic phase there is a high degree of reorientational motion of the molecules.

When MBBA was subjected to 1·5 kbar of hydrostatic pressure, the sharp signal which appeared at low temperature and at ambient pressure, appeared at room temperature itself. The nematic and isotropic phases were reached by heating the sample to about 55°C and 76°C respectively. At 3 kbar and at room temperature, the sharp signal was still present but with reduced intensity. At this pressure we did not attempt to reach the isotropic phase, because heating the Be-Cu pressure cell will weaken the material. At 5 kbar pressure the sharp signal was not present even at room temperature.

High resolution proton magnetic resonance spectrum recorded in the isotropic phase of MBBA is shown in figure 2(a). The assignment of the spectrum has already been reported in the literature (Lee *et al* 1973). The spectral width in this case was 5000 Hz. In the nematic phase three broad peaks covering a spectral range of about 41500 Hz was observed (figure 3). As the sample was cooled further, at 15°C, the broad peaks completely disappeared and four sharp lines covering a spectral range of only 5000 Hz

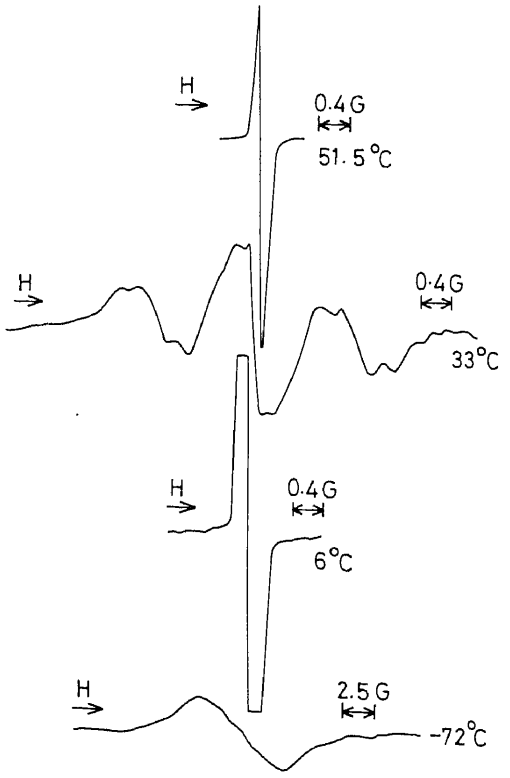

Figure 1. ^{1}H wideline NMR spectra of MBBA at different temperatures.

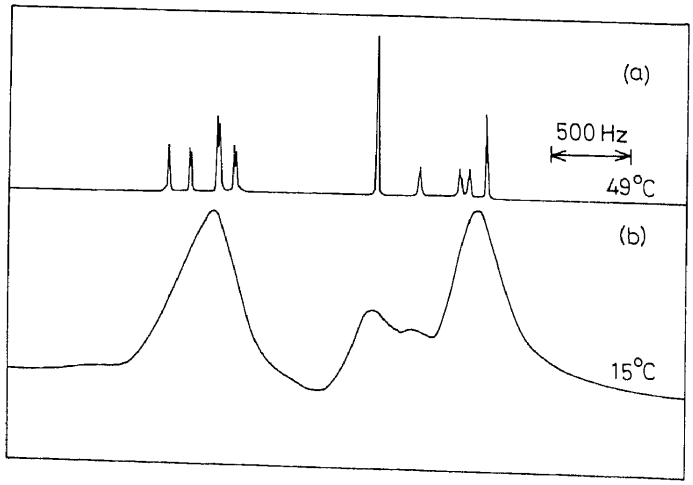

Figure 2. ^{1}H high resolution NMR of MBBA (**a**) in the isotropic phase and (**b**) in the phase just below the nematic phase.

appeared. These lines were broader than the lines of the isotropic spectrum, but each line could be identified with different groups of lines of the isotropic spectrum as seen in figure 2(b). On further cooling these sharp lines persisted, but as the temperature was lowered they tended to become broader. At $-40°C$ the spectrum appears to consist only of two lines because of broadening and finally around $-60°C$ all lines completely disappear leaving a broad background signal (figure 4). As the sample is warmed up from low temperatures the spectral pattern reverses, with the exception that the solid to nematic transition is observed at 19°C. Numerical integrated intensity over the region of the sharp lines in the low temperature phase as compared to that of the nematic phase spectrum recorded under identical conditions of spectrometer settings indicates that the bulk of the material contributes to these sharp signals. There are strong indications that on cooling to the new phase from the nematic, the entire intensity resides in the narrow lines at the transition point; on cooling an increasing fraction of the molecules contribute to the broad signal. This continues till about $-60°C$ when the entire spectrum is broad.

^{2}H and ^{13}C spectra were also recorded in the isotropic, nematic and phase just below the nematic phase. It was observed that in these cases also the low temperature phase spectrum consisted of narrow lines similar to the isotropic phase whereas the nematic phase spectrum consisted of much broader lines. In figure 5, ^{13}C spectra in the three phases are shown.

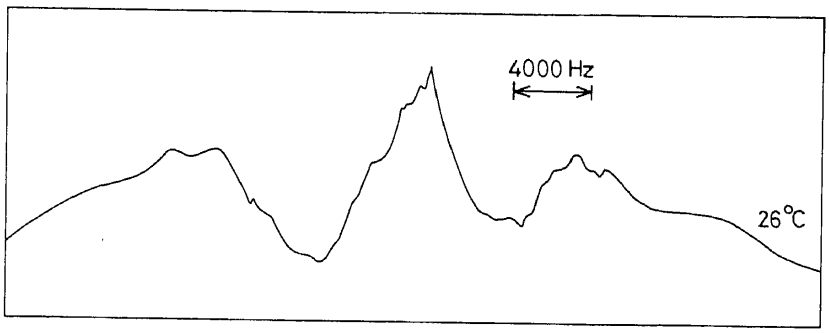

Figure 3. ^{1}H high resolution NMR spectrum of MBBA in the nematic phase.

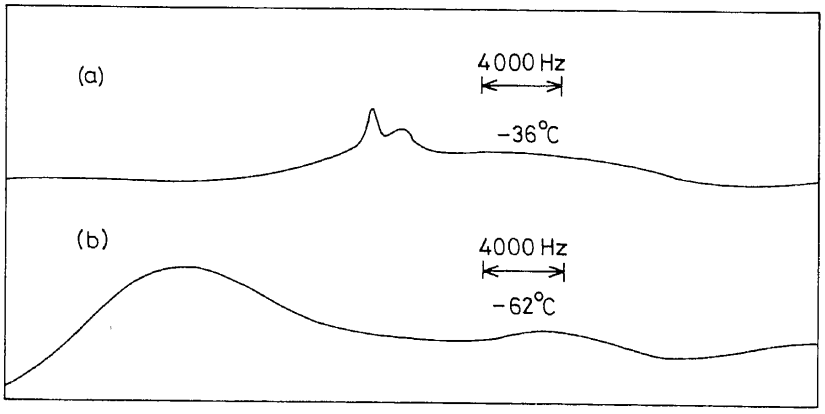

Figure 4. ^{1}H high resolution NMR spectra of MBBA in the solid phase.

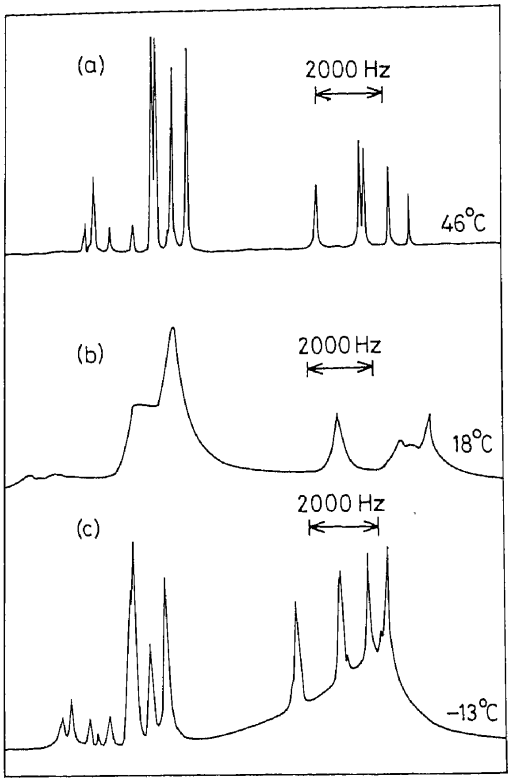

Figure 5. ^{13}C high resolution NMR spectra of MBBA at different temperatures.

We believe that this is the first report of an observation of a narrow line NMR spectrum in MBBA in the solid phase though similar observation has been made in stearic acid in its crystalline form earlier (Cyr *et al* 1967). We have taken up x-ray studies to characterise this phase of MBBA and to understand the unusual behaviour described above.

3.2 *X-ray diffraction studies*

A sample of MBBA was cooled to 0°C so that it is in the solid form. Powder x-ray diffractograms were taken of this sample while slowly warming it, using a Philips powder x-ray diffractometer. A typical diffractogram is shown in figure 6 which indicates the crystalline nature of the sample. The pattern is also similar to the ones obtained by Janik *et al* (1975) and Lydon and Kessler (1975).

4. Discussion

The NMR results obtained just below the nematic phase are obviously contrary to what is expected. Whereas one would expect in this phase a signal much broader than the signal in the nematic phase, appearance of sharp, intense and narrow signals is clearly anomalous.

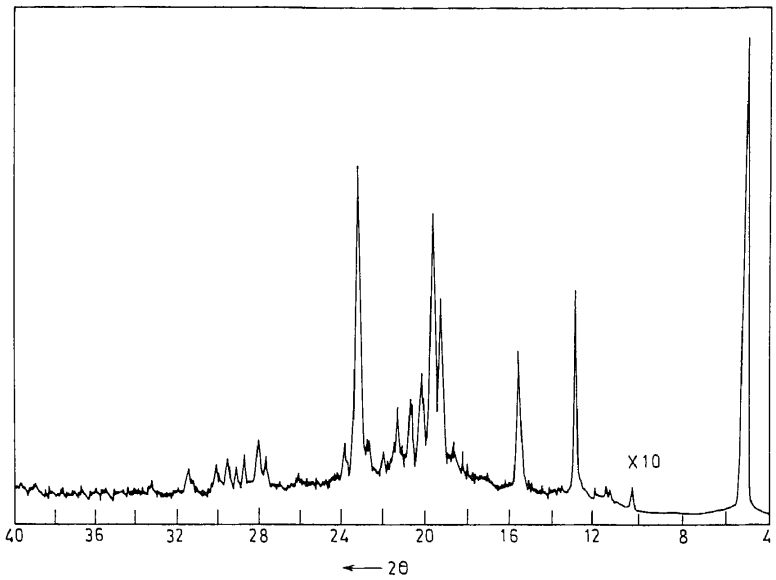

Figure 6. X-ray powder diffraction pattern of MBBA just below the nematic phase.

It must be pointed out at this stage, that anomalous behaviours have been observed in MBBA before in many other studies like x-ray diffraction (Lydon and Kessler 1975), spin-spin relaxation measurements (Ito *et al* 1981), ESR spin probe study (Stillman *et al* 1978), absorption spectra (Sciesinska *et al* 1974), IR and Raman studies (Witko and Janik 1978; Le Brumant *et al* 1976; Kirov *et al* 1980), dielectric studies (Moscicki 1976; Agarwal *et al* 1977), time-of-flight neutron spectroscopy (Bielushkin *et al* 1981) and Mossbauer study (La Price and Uhrich 1979). Most of these have been explained as due to increased mobility of various parts such as tails or the rings of the molecules of the substance in a proposed metastable state of MBBA. Further, in the majority of the studies this behaviour is reported to be monotropic, occurring while warming up of a rapidly frozen sample. We wish to emphasize the fact that what we observe is independent of the direction of change of temperature, of time and of the thermal history of the sample and whether the sample is cooled outside the magnet or within it. Therefore we conclude that what we see is a stable phase of MBBA. This conclusion is also borne out by the fact that the powder x-ray diffraction pattern just below the nematic phase as shown in figure 6 is very similar to that of 'stable' phase as observed by Janik *et al* (1975). Moreover, the isotropic liquid like very narrow (width 0.06 G) nature of the NMR lines can be accounted for only by assuming that the entire molecule is rapidly tumbling almost isotropically on the NMR time scale and not by allowing motion of just part of the molecule, either the segmental or the ring protons. Thus on the basis of the x-ray diffraction results indicative of crystalline order and the NMR results indicating rapid tumbling, we conclude that MBBA goes into a plastic crystalline state just below its nematic phase.

That such a transition to a plastic crystalline state is plausible can be seen in terms of Onsager's (1949) model of onset of liquid crystalline order. In this model, it is the collision of the rod-like molecules occurring at a rate faster than a critical value which maintains the orientational order of the nematogens. Thus it is conceivable that on

cooling the substance below its nematic phase into the solid phase with translational order, the collisions between the molecules cease and thus complete reorientational disorder is established where correlation time turns out to be shorter than the NMR time scale.

It must be pointed out that, high resolution NMR spectra similar to that exhibited by MBBA below its nematic phase have been observed in a few other liquid crystalline substances. Most of them however are in amphiphilic systems (Johansson and Lindman 1974)—in their so-called viscous isotropic mesophases—where individual molecules are supposed to form globular micelles which are located on the sites of a cubic lattice and 'are undergoing thermal rotatory motion at the lattice points analogous to the thermal rotatory motion of the globular molecules at the lattice points in the optically isotropic, non-amphiphilic cubic plastic crystals (Winsor 1974)'.

Finally, an earlier ESR spin probe study (Murakami and Sohma 1979) seems to indicate the presence of the plastic crystalline phase in MBBA though the phenomenon has been interpreted as melting of frozen molecular mobility on a small scale below the temperature of the bulk melting. However, as our results clearly indicate, the mobility is present over the entire sample along with translational order, establishing that what is actually observed is a plastic crystalline state. The transition temperature from nematic to this plastic crystalline state has a positive pressure coefficient, as indicated by our high pressure NMR results and from Clausius-Clapeyron equation one can conclude that the specific volume of this phase is less than that of the nematic phase.

Preliminary study of N-(*p*-ethoxybenzylidene)*p'*-*n*-butylaniline (EBBA), a substance with an additional CH_2 group attached to the methoxy side chain of MBBA, showed similar behaviour. Figure 7 shows ^1H high resolution NMR spectra of EBBA recorded at 80°C, 40°C and 20°C in the isotropic, nematic and the plastic crystalline phases respectively. It is clear that EBBA behaves in a manner similar to MBBA and it is possible that other members of the series also show similar behaviour.

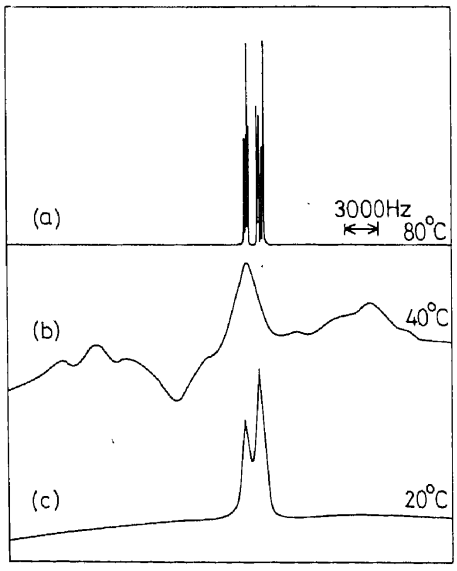

Figure 7. ^1H high resolution NMR spectra of EBBA in its (**a**) isotropic (**b**) nematic and (**c**) below nematic phase.

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