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Liquid Crystals

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A diffraction and spectroscopic study of the solid states of EBBA

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The solid states and phase transitions were studied in the nematogen EBBA. Differential scanning calorimetry, neutron diffraction and Raman scattering provided well-correlated results on the structure and dynamics of the solid phases. It was concluded that (*a*) EBBA has four different solid phases, (*b*) there is a difference between the dynamics, viz. the coherence length of phonons in the rapidly-cooled phases of MBBA and EBBA, (*c*) the molecular shape in the nematic phase can be determined by using the solid state structures.

1. Introduction

Liquid crystals have many interesting features and have been intensively studied for many years [1]. Comparatively recent work on liquid crystals, particularly on the well-known nematogen 4-methoxybenzilidene-4′-*n*-butylaniline (MBBA), has shown that their investigation at low temperatures provides a new and attractive field in solid state research [2–4]. In particular, rapid cooling of the liquid crystal phase may provide different solid states which are intermediate (solid mesophases) between ordinary glassy and crystalline materials in the sense of molecular structure and dynamics.

In the case of rapidly-cooled MBBA a sequence of polymorphic modifications has been found [3], viz. an increase of ordering and the evolution of the coherence of the phonon states, as a consequence of the gradual structural relaxation, has been followed from the initial glassy state to a final crystalline one. It was possible to realize this by simultaneously recording the structural (neutron diffraction) and the spectral (Raman scattering) data on the same sample during the phase transitions and the subsequent recooling to low temperatures of the metastable states after they had been produced by heating from the previous modification.

Other rapidly-cooled liquid-crystalline materials have also been investigated by various methods [2]. D.S.C. and spectral measurements have been reported [5, 6] on a few solid phases of 4-ethoxybenzilidene-4′-*n*-butylaniline (EBBA)—which is analogous to MBBA—and, in addition, the structure of one of its crystalline modifications has been determined by X-ray diffraction [7].

In the present paper we report a detailed study of the phase transitions and solid polymorphism of EBBA. Differential scanning calorimetry (D.S.C.), neutron diffraction and Raman scattering were used to measure the structural and dynamic properties of different solid states under various conditions of heating and cooling.

2. Experimental conditions

To carry out the neutron diffraction and Raman scattering measurements on the same sample, EBBA was placed into a thin aluminium (1 × 23 × 45) mm^3 container equipped with a quartz window 8 mm in diameter. The sample container was fixed on the cold finger of a cryostat to enable the low temperature light scattering measurements through two quartz windows (forming an angle of 45°) as well as neutron diffraction with a solid angle of 315°. The rapidly-cooled state was produced by dipping the sample into liquid nitrogen, in this way a cooling rate of $\sim 200\,\mathrm{K\,min^{-1}}$ was achieved. Measurements were made between 77 K and 320 K; the accuracy of the temperature control was 0·1 K.

Neutron diffraction patterns were measured in the interval $2\theta = 10$–24° (the monochromatic neutron beam of $\lambda = 1{\cdot}3116\,\text{Å}$ wavelength was obtained from a zinc monochromator on the triple-axis spectrometer at the Budapest WWR–M reactor; the resolution was 0·3°). Raman spectra were recorded on a Ramanor HG2S (Jobin–Yvon) spectrometer using the light source of an argon–ion laser ($\lambda = 5145\,\text{Å}$) at Eötvös Loránd University, Budapest. The spectral range of 5–1700 $\mathrm{cm^{-1}}$ was studied with a 3 $\mathrm{cm^{-1}}$ resolution.

Separate measurements were carried out on a D.S.C.–2 Perkin-Elmer calorimeter. The qualitative analysis of the phase transitions were made in the 110–380 K temperature range. The maximum cooling rate of 320 $\mathrm{K\,min^{-1}}$ of the temperature programme was used for rapid cooling. Special quenching was attempted by putting the sample, that is the aluminium container with ~2 mg EBBA, in the nematic state on the cold platform (~80 K) of the calorimeter. The minimum cooling rate was estimated to be $5 \times 10^3\,\mathrm{K\,min^{-1}}$.

3. Results

The D.S.C. measurements provided the following results. Crystalline EBBA kept at room temperature for several hours melts at 309 K. The nematic–isotropic phase transition can be detected at about 350 K. By decreasing the temperature slowly (for example, 1·25 $\mathrm{K\,min^{-1}}$) the nematic phase can be supercooled and crystallization occurs at about 285 K. Slow heating leads to melting into the nematic phase at 309 K. The situation is completely different when the nematic phase is rapidly cooled, viz. a metastable solid modification is formed. The solidification is marked by an exotherm at approximately 270 K. On heating this quenched phase, the D.S.C. thermogram shows a minimum (cf. figure 1) whose position depends on the heating rate

Heating rate/K $\mathrm{min^{-1}}$	1·25	2·5	10
Position/K	264	266	280

This phase transition is somewhat blurred, the process of transformation begins at about 240 K. For relatively fast heating (10 $\mathrm{K\,min^{-1}}$) the sample melts at 307 K (cf. figure 1), but if the temperature is maintained at 300 K for several hours the solid–nematic transition can be recorded again at 309 K. This means that a slow solid–solid transition takes place between the solid modifications. In figure 1 the solid line observed above 300 K was recorded, when the sample was kept at 300 K for 1 hour and the double endotherm with peaks at 307 K and 309 K indicates the melting of two different modifications (stable and metastable). This shows that the transition between these phases was incomplete after 1 hour. When the sample was quenched at a rate of over 5000 $\mathrm{K\,min^{-1}}$ a further phase transition was observed on reheating, since at about 235 K an endotherm, then at 260 K another one can be obtained

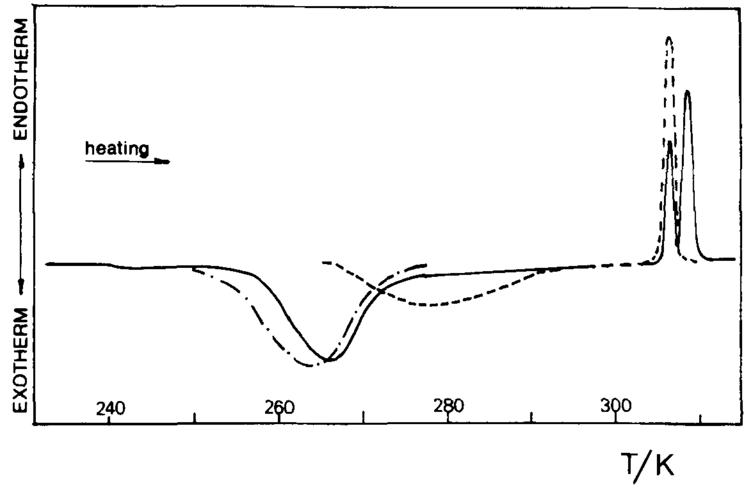

Figure 1. D.S.C. thermograms of EBBA samples produced by rapid-cooling at 160 K min^{-1}. ——, heating rate 2·5 K min^{-1}; —·—·—, 1·25 K min^{-1}; ....., 10 K min^{-1}.

(the heating was stopped at 290 K). Repeated cooling and heating do not provide further phase transitions. At relatively fast heating (10 K min^{-1}) the sample melts at 307 K. This procedure proves that the very fast cooling provides one more metastable phase, D.S.C. results thus show that there are four solid modifications of EBBA with the solid–solid phase transitions being characterized by rather long relaxation times.

In order to search for a glass transition with characteristic T_g the D.S.C. measurements were repeated several times under different conditions, for example, samples of three different origins as well as two subsequent purifications (recrystallization from alcohol) were studied. Precisely the same results were obtained in each case without finding a glassy transition, in contrast to the results of [5] where a glassy-like transition was recorded with T_g of 219 K. It should be noticed, that no disagreement was found in the nematic–isotropic and crystal–nematic transition temperatures, measured at 350 K and 309 K, respectively.

Figure 2 shows the diffraction patterns from the nematic phase at 320 K. The broad maximum centred at $2\theta = 16{\cdot}8^\circ$ corresponds to an average intermolecular distance of approximately 4·5 Å. The size of the domains of coherent scattering with a correlation length L_{corr} was estimated from the peak width on the basis of Hosemann's model [8] as $L_{\mathrm{corr}} \sim 5l$ where l is the molecular length.

In figures 2 and 3 results of the neutron diffraction and Raman scattering measurements taken from the rapidly-cooled state labelled C_1 are presented. This phase was found to be stable below 230 K; above this temperature a transition into another phase, C_2, takes place. This latter phase can be considered as a metastable phase since it can be recooled and reheated without further transitions. The curves in figures 2 and 3 were recorded at 80 K and the C_2 state was produced at 240 K after waiting 1 hour. Both neutron diffraction patterns and Raman spectra show considerable differences as indicated in the table by the main diffraction peaks (Q) and phonon frequencies (ν) for the low frequency region.

The C_2 phase was found to be stable up to 290 K, then it transforms into phase C_3 or C_4. If the C_2 to C_3 transition took place, the C_3 transforms into C_4 at 300 K.

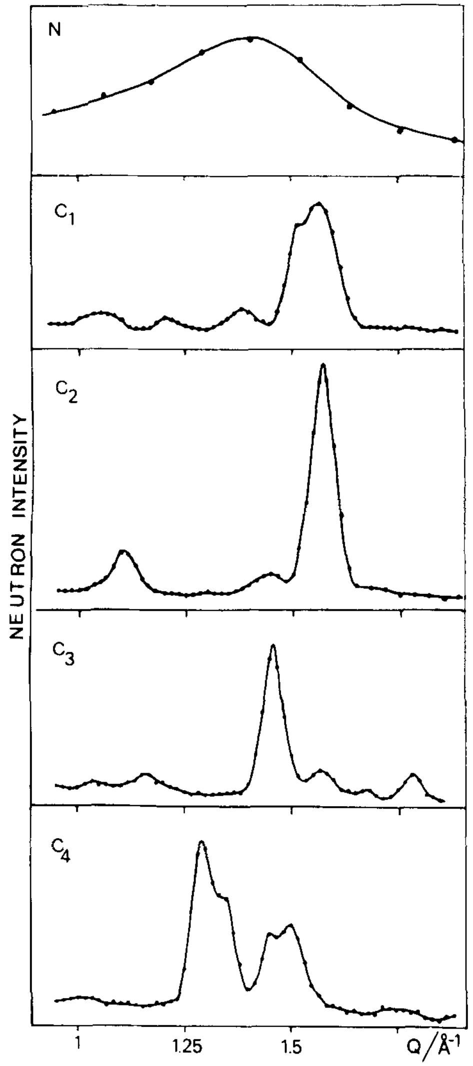

Figure 2. Neutron diffraction patterns of the nematic (measured at 320 K) as well as the solid (80 K) phases of EBBA. $Q = (4\pi \sin \theta)/\lambda$; 2θ is the scattering angle, and λ is the neutron wavelength.

Neutron diffraction peak positions (Q) with the corresponding lattice spacings (d) and the low frequency Raman lines (ν) for the solid phases of EBBA.

	C_1	C_2	C_3	C_4
$Q/\text{Å}^{-1}$	1·515, 1·565	1·57, 1·11	1·46, 1·78	1·29, 1·34, 1·45 1·49
$d/\text{Å}$	4·15, 4	4, 5·66	4·31, 3·53	4·86, 4·68, 4·33 4·19
ν/cm^{-1}		24, 32, 42 53, 60, 68 82, 90, 100 110, 121, 136 149, 156, 178	28, 36·5, 51·5 61, 69, 76 86, 92, 101 107, 126, 138 143, 164	16·5, 37, 52 58, 65, 76 87, 94, 118 125, 146, 161·5, 170

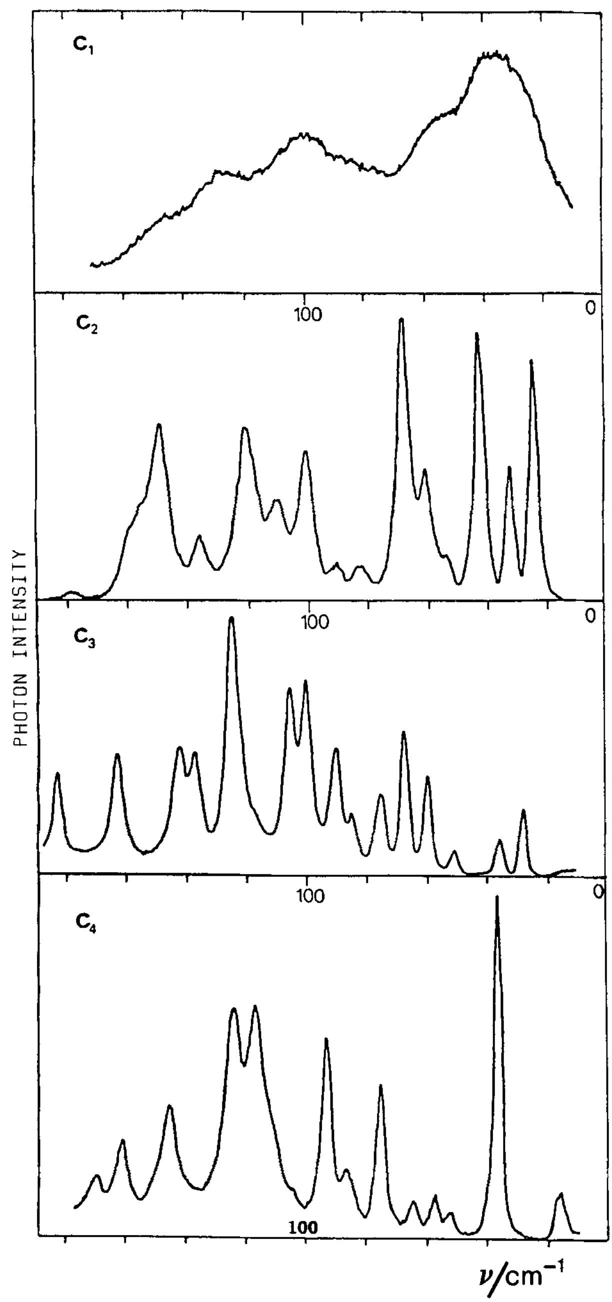

Figure 3. Low frequency Raman spectra of the solid phases of EBBA (80 K).

The neutron diffraction patterns and Raman spectra of these states are also shown in figures 2 and 3; the characteristic neutron diffraction peaks and spectral lines are listed in the table.

Phase C_1 was produced by quenching at a minimum rate of $1\,\mathrm{K\,s^{-1}}$. Slower cooling usually results in crystallization, however, solidification into a non-ordered structure is possible judging from the Raman spectrum (cf. the lower curve in

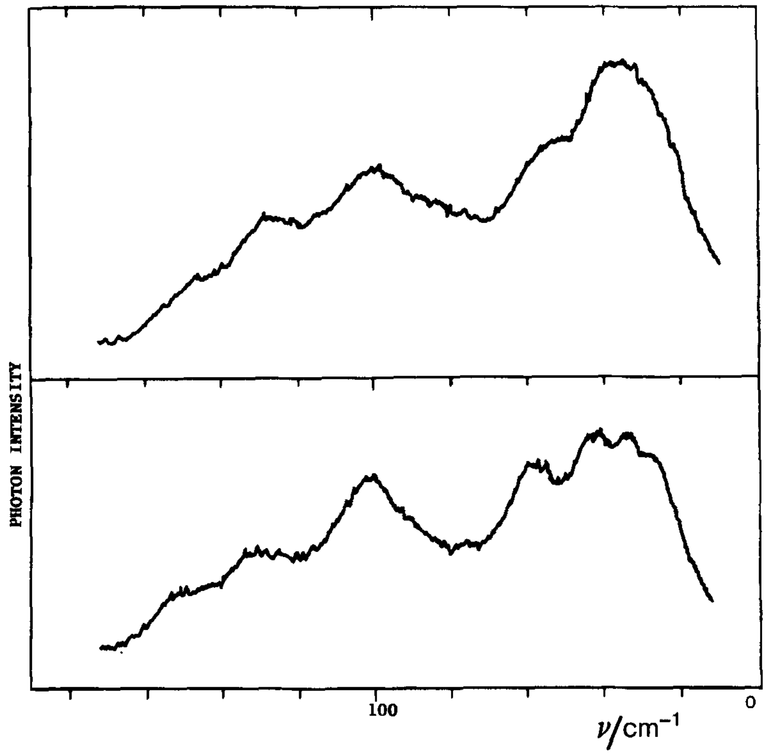

Figure 4. Raman spectra of EBBA solid phases produced by different cooling rates (rapid cooling: 160 K min^{-1} (upper curve); medium cooling rate: 10 K min^{-1} (lower curve).

figure 4) which shows somewhat more expressed lines of the optical phonons compared with the C_1 spectrum.

4. Discussion

In the solid phase produced by rapid cooling from the nematic state there is a considerable shift of the characteristic diffraction maximum with respect to the nematic state; moreover, the width of this maximum is much smaller. In addition, many peaks of small intensity can be seen in a wide wavevector range. This indicates that the sample does not have an amorphous structure similar to that which can be produced by quenching MBBA. In fact, if we compare the Raman spectra of rapidly-cooled EBBA and MBBA (cf. figure 5), the difference in the intermolecular dynamics is obvious. Although both spectra have a broadband nature, in the EBBA spectrum lines connected with well-defined optical phonon zones can be found in contrast to the case of MBBA. The broadened lines are due to the structure not being completely ordered, consequently the $\mathbf{k} = 0$ selection rule conditions are not fulfilled for the optical modes [9]. The low frequency maximum in the EBBA rapidly-cooled phase can be found at higher frequencies than for MBBA, and this is in good agreement with the results of inelastic neutron scattering when measuring the density of vibrational states of these substances [10]. It can therefore be concluded that all phonon states appear in the Raman spectrum. On the other hand, the presence of optical lines in the broadband spectrum is connected with ordered domains characterized by unit cells,

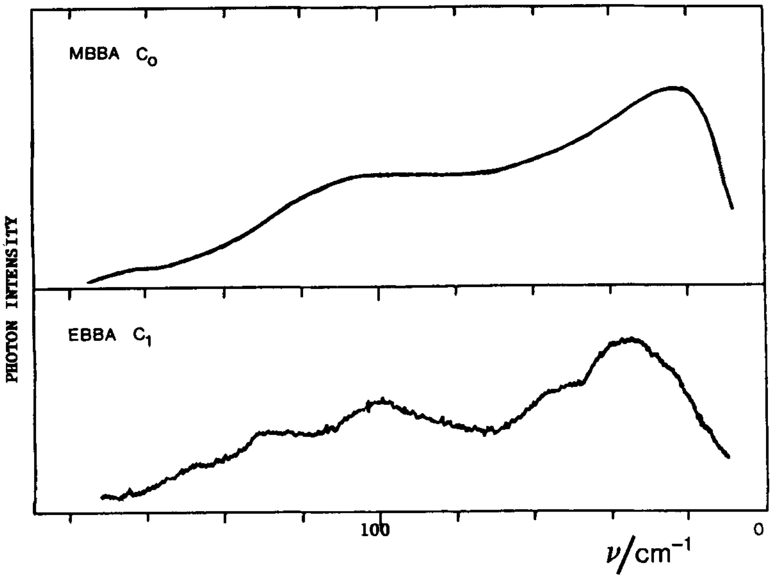

Figure 5. Low frequency Raman spectra of the fast-cooled states of MBBA [3] (upper curve); and EBBA (lower curve) at 80 K.

already formed in the C_1 phase of EBBA, and the coherence length of optical phonons is greater than in the case of usual amorphous materials.

A comparison of the Raman spectrum of the C_1 phase with the Raman scattering data published by Kirov *et al.* [5] for the rapidly-cooled state shows that these are the same states of EBBA, but it should not be classified as a glassy phase [5] in the same sense as for MBBA. This was clearly proved by the concordant results of the present D.S.C., Raman scattering and neutron diffraction measurements.

The phase transition C_1 to C_2 results in a considerable change of the structure which is expressed in both neutron diffraction and Raman scattering data. In the latter the increase of the coherence of the vibrational states is noticed since the sharp lines correspond to $\mathbf{k} = 0$ points of the phonon bands. Furthermore, most of these lines cannot be inherited from the maximum of the C_1 spectrum (cf. figure 3) by simple narrowing, i.e. new lines indicate that the increase of ordering is accompanied also by a change of the unit cell. This is supported also by comparison of the neutron diffraction patterns, where the width of the Bragg reflections is smaller in C_2 than in C_1 and the peak positions are also changed (cf. the table).

Neutron diffraction and Raman scattering data are in sufficiently good agreement to enable us to state that the C_2, C_3 and C_4 phases are different, completely ordered crystalline modifications.

In figure 6 intramolecular vibration spectra at low (170–250 cm^{-1}) and high frequencies (1150–1210 cm^{-1}) are presented in order to demonstrate that phase transitions are also accompanied by conformational changes of molecules. The intramolecular spectrum of C_4 resembles that of the non-ordered C_1 phase. We can suppose that the molecular shape does not change during the quenching and it remains nearly the same in the C_1 solid state as in the nematic. It can be assumed that the backbone of a molecule in the nematic phase is very similar to that in the C_4 crystalline modification. It is known from X-ray measurements [7] of an EBBA crystal

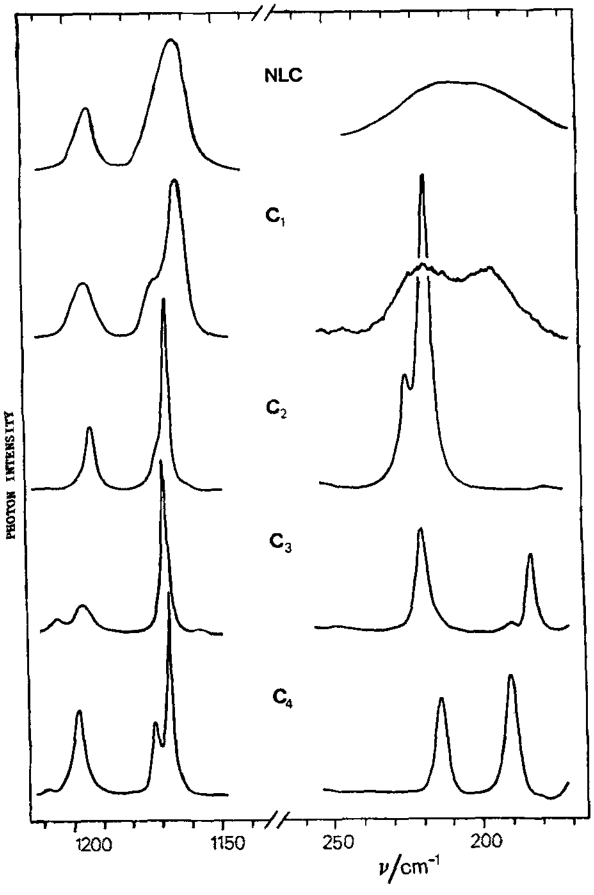

Figure 6. Intramolecular vibrational ranges (170–250 and 1150–1210 cm^{-1}) of the different solid modifications of EBBA at 80 K; from the top: C_1, C_2, C_3, C_4.

(assigned as C_4) that the torsion angle between the planes of the two benzene rings is 57·6°. Although structural methods such as X-ray and neutron diffraction, were not able to determine directly the molecular shape in the nematic phase, the assumption of spectral and structural data leads to the conclusion that the molecules in the liquid crystal state are not planar, i.e. the benzene rings are twisted in relation to each other forming an angle of about 57°.

5. Summary

As a result of D.S.C., neutron diffraction and Raman scattering measurements the solid state polymorphism of EBBA has been clarified. Four different solid modifications have been identified, among them an incompletely ordered metastable, C_1, two other metastable, C_2 and C_3, and one stable, C_4, crystalline phase. In contrast to the results published in [5], we did not find a glassy transition and we did observe a difference between the rapidly-cooled states of MBBA (non-ordered) and EBBA (C_1-partially ordered). The molecular shape in the nematic phase is concluded to be very similar to that in the stable C_4 phase with an angle between the benzene rings of about 57°.

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