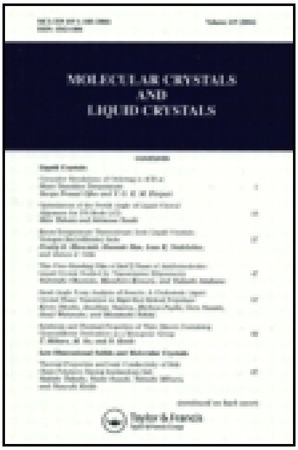

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Solid State Polymorphism of *p*-Azoxyanisole

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Solid state polymorphism of *p*-azoxyanisole has been studied by different experimental methods. A good agreement of differential scanning calorimetry, polarizing microscope, far infrared spectroscopy and neutron diffraction results permitted three solid modifications to be identified.

1 INTRODUCTION

A great number of organic materials which have recently been extensively studied show liquid crystal modifications.[1–3] These materials, e.g. PAA, are often polymorphous in the solid state.[4]

The formation of solid state modifications (C) strongly depends, in most cases, on the experimental conditions, and on the nucleation rate of different modifications,[1] i.e. on the thermal prehistory of the material.

Probably because of the great difficulties involved in the growing and conservation of the sometimes even metastable solid state modifications, no such structures have been reported so far. It seemed that simultaneous investigations by different experimental methods were needed in order to study the creation procedure of solid modifications and to determine the crystal structure at the same time.

The aim of the present work was to get some insight into solid state polymorphism prior to the nematic (N) phase of PAA by the simultaneous use of four different methods, namely, differential scanning calorimetry (DSC) for thermal behaviour study, polarizing microscopy for texture analysis, neutron diffraction technique (ND) for the determination of the crystal

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structure of the observed solid modification,[4] and far infrared spectroscopy (FIS) for investigation of the lattice vibrations.

PAA was chosen because the structure of the stable, so-called yellow form has been already determined from X-ray measurements and the reports describe two contradictory crystallographic structures.[5,6]

A fully deutered sample was synthetized for neutron diffraction studies, i.e. all the hydrogen atoms of the PAA molecules were replaced by deuterium to avoid the high incoherent background due to the large incoherent cross-section of hydrogen. Parallel DSC and polarizing microscope measurements were made on both the normal (*n*-PPA) and the deuterated (*d*-PAA) samples. FIS measurements were made only on normal PAA. No remarkable differences other than somewhat higher transition temperatures of *d*-PAA were observed.

2 CALORIMETRY

A thorough study of the solid state polymorphism of PAA was prompted by Bernal and Crowfoot's[7] observation of two solid phases in this substance. Different solid modifications have been already detected in PAA by calorimetry, however the reported observations are in contradiction with each other.

Robinder and Poirier[8] have shown, in addition to the form which is stable at room temperature, the existence of two monotropic crystalline phases. Recently the existence of a metastable and a stable phase was inferred from the exothermic peaks observed by scanning calorimetry[9] and this inference is now the generally accepted interpretation.

Perkin–Elmer DSC-2 calorimeter was used for recording the phase transitions with high precision. To get rid of the grains of the previous solid modification (C) which would lead to the formation of the same solid modification, cooling was started from the isotropic (I) liquid phase. The upper part of Figure 1 shows the observed exothermic, the lower part the endothermic peaks. On both curves $I \leftrightharpoons N$ transitions were observed at 136°C for *d*-PAA and at 134°C for *n*-PAA. On continued cooling two close lying transitions, the nematic-solid ($N \rightarrow C_1$) at 90°C and a solid-solid ($C_1 \rightarrow C_2$) phase transition above 86°C, were observed. On reheating this sample the $C_2 \rightarrow N$ transition was detected at 121°C (at 119° for *n*-PAA). It was found that the metastable C_1 modification can be stabilized in a wider temperature range by increasing the temperature after the first sign of crystallization when the crystal grains of this modification have already been formed. At this higher temperature the C_1 modification will grow in the whole sample volume without transforming to the C_2 modification. C_1 can be stabilized in

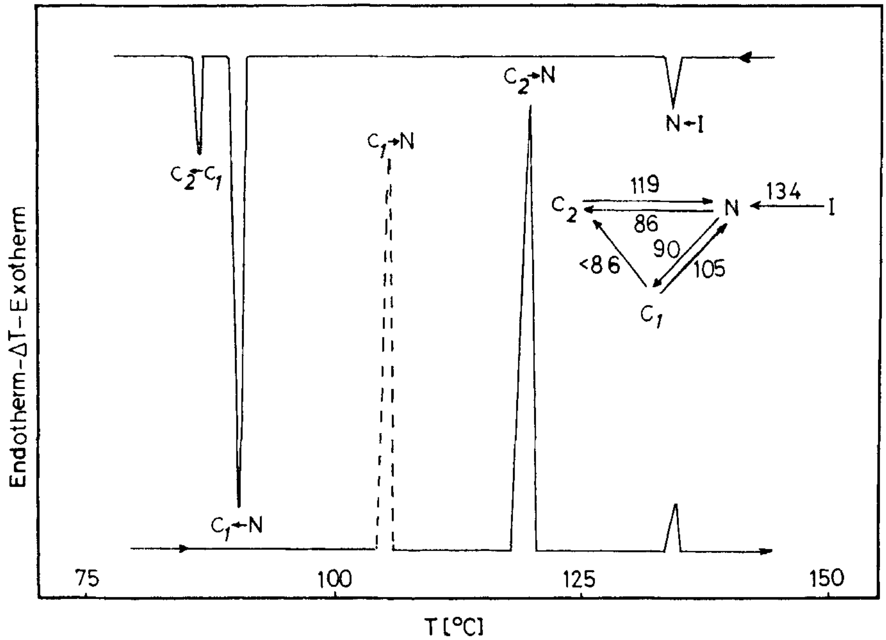

FIGURE 1 DSC exothermic and endothermic curves measured on *n*-PAA and the phase transition scheme.

the temperature range 25° to 108°C for *d*-PAA and from 25° to 105°C for *n*-PAA. (The higher values correspond to the $C_1 \rightarrow N$ transition temperatures, i.e. the dashed line peaks in Figure 1).

The nematic phase can be supercooled to 80°C where a nematic to solid transition can be observed. After this transition no further phase transitions were detected at lower temperatures. The thermal behaviour of this stable modification suggests that it is the same C_2 phase as that formed by the $C_1 \rightarrow C_2$ transition observed in the former experiment. Nothing can be said, however, about the crystal structure of the solid modifications.

The diagram in Figure 1 shows the two possible ways in which the stable phase can be formed: either by cooling first to the C_1 metastable modification which transforms into C_2 at lower temperatures or by supercooling to a lower transition point at which the C_2 stable phase is directly formed. It should be mentioned that no thermal procedure or heat treatment can be given to produce one or the other phase. In most cases, however, on cooling the C_1 metastable phase was formed first. This is reasonable because of the difficulties in supercooling to the transition point of the stable modification.

3 OPTICAL OBSERVATION

In order to verify the results of DSC a series of optical observation experiments was carried out. The different states of liquid crystal substances in given ranges of temperature can be seen under the microscope as patterns with different colours and forms.[2]

A Zeiss polarizing microscope was used which has a hotstage heated or cooled by an ultrathermostat. The sample was a thin (10–50 μm) layer of PAA placed between quartz plates. Figure 2 shows schematically the transitions between the observed different patterns representing different phases. The vertical scale shows the temperature in °C. The dashed and solid lines correspond to cooling and heating, respectively. The *n*-PAA data are given in brackets.

Using the same notation as in calorimetry, it was found that on cooling from the isotropic through the nematic phase the C_1 metastable modification

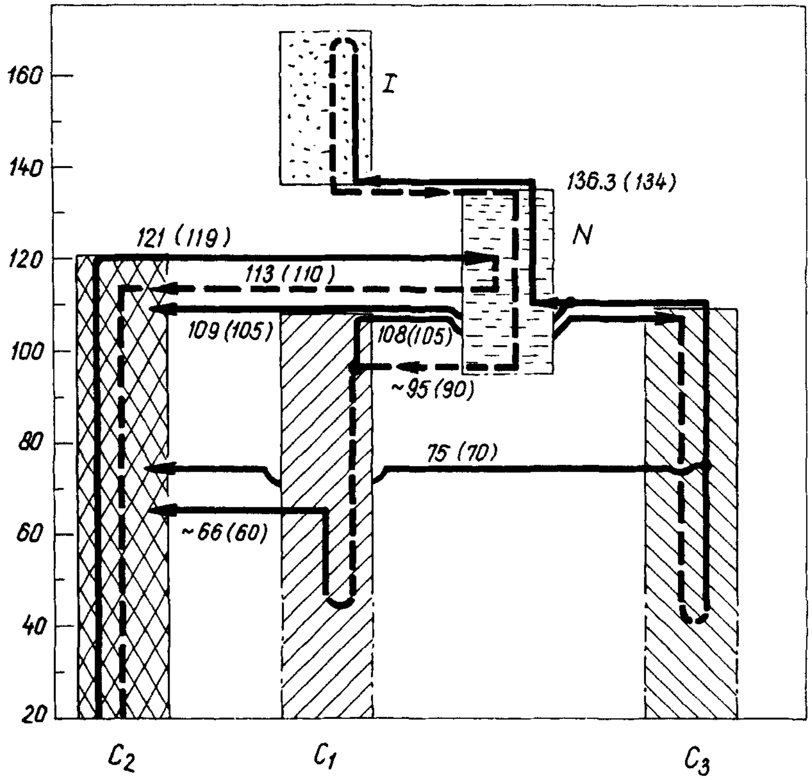

FIGURE 2 Phase diagram from polarizing microscope studies showing the different patterns and their transitions from one to another.

is observed in the same temperature range as in the case of DSC. The transition N → C, takes place usually after supercooling of the nematic phase. Sometimes C_1 could be supercooled to 40°C by a very fast cooling process. The $C_1 \rightarrow C_2$ transition was observed in this case on reheating to 66°C (to 60°C for *n*-PAA).

In contrast to DSC measurements the C_2 phase, stable at room temperature, could not be obtained directly by fast supercooling from a thin layer of the nematic phase (below 110°C). In this case, it formed only after a $C_1 \rightarrow C_2$ transition. A $C_2 \rightarrow N \rightarrow C_2$ transition circle was observed to yield directly the stable phase. This means that after reheating from the C_2 to the nematic temperatures and then immediately cooling to 113°C an $N \rightarrow C_2$ transition takes place. When two phases are present the equilibrium transition $N \leftrightharpoons C_2$ takes place at 121°C (119°C for *n*-PAA).

Optical observation permitted a third, C_3 pattern to be identified although it is difficult to distinguish this mosaic-like pattern from the very similar one of the stable C_2 modification.

Slow and careful heating transforms C_1 into C_3 at 108°C. The following properties of this C_3 modification were observed:

a) It can be supercooled to room temperature where it slowly transforms into the C_2 stable phase. The $C_3 \rightarrow C_2$ transition is connected with recrystallization. The C_2 phase can be identified on reheating when the nematic phase is formed at 121°C.

b) On supercooling C_3 to room temperature and then immediately reheating it the $C_3 \rightarrow C_2$ transition can be observed at 75°C if the temperature is slowly increased; the transition appears at 109°C if the temperature is increased rapidly. The latter transition competes with the $C_3 \rightarrow N$ transition which has its equilibrium temperature at 109°C (105°C for *n*-PAA).

These optical observations fit the earlier optical and calorimetric data published by Robinder and Poirier[8] except that the monotropic crystalline C_1 and C_3 phases could not be supercooled in their experiment. However, this can be attributed to the different experimental conditions, e.g. the wall-effects in our thin-film and their bulk samples. In agreement with the results of,[8] the C_1 and C_3 modifications can be equilibrated with the nematic phase at 108–109°C, that is, much lower that the $C_2 \rightarrow N$ equilibrium transition at 121°C. Furthermore, it was found that C_1 and C_3 are usually formed when small crystallines are grown since the stable C_2 phase grows with large single crystal blocks by a very sudden transition from the nematic phase on cooling, whereas the $C_3 \rightarrow C_2$ and $C_1 \rightarrow C_2$ transitions are slow, continuous processes observed on heating.

It can be inferred from both the earlier reported and now observed optical data that PAA has a solid stable C_2 phase, a distinct metastable C_1 phase and a less distinquishable, also metastable solid C_3 phase which has a very low nucleation energy and which does not appreciably differ in thermal behaviour and microscope pattern from the stable phase. The macroscopic information about the polymorphism of PAA obtained from calorimetry and optical observation had to be completed by microscopic data on the crystal structure of the observed three solid modifications. For this purpose FIS and ND investigations were used.

4 FAR INFRARED SPECTROSCOPY

Taking into account the results on the determination of temperature ranges in which different solid modifications of PAA were identified the far infrared range of their optical spectra, corresponding to the optical excitations of lattice vibrations, could be analyzed.

The distinct phases were produced in a special glass vessel with windows made of crystalline quartz, which is transparent in the proper range of frequencies. A Beckman IR-II spectrophotometer with an optical condenser similar to that described in,[10] restricting the cross-section of the light-beam to 6 × 4 mm^2 was used for recording the FI spectra. The glass vessel was placed into the focus of the condenser. To reduce the absorption by water vapour, dry air was circulated in the spectrometer. In addition, dry nitrogen has been blown through the condenser with the sample chamber. The measured data for the stable modification C_2 coincide with the earlier reported IR results in the 40–120 cm^{-1} frequency range.[11,12]

Figure 3 shows the measured transmission spectra. They were corrected by the calibration curves of the empty glass vessel and the radiation spectrum of the sample as well as the glass vessel at the given temperature. Since the condenser and the glass vessel contain traces of water vapour which cannot be compensated even in a double beam measurement, values of the absolute transmission contain an error of about 5%. The relative error of the transmission spectral distribution is not higher than 2–3%.

It can be inferred from these curves that the spectra of the stable modification (C_2) and the metastable one (C_1) are very similar to each other in spite of the significant difference in measurement temperatures.

In contrast, the spectrum of C_3 differs considerably and contains a much more ample structure. As far as the liquid phase N is concerned, as has already been stated, its spectrum significantly depends on the prehistory of the sample. The spectrum, measured directly after the $C_3 \rightarrow N$ transition is reminiscent of that of the C_3 modification. Keeping the nematic phase at 130°C for 30–60 minutes, the spectrum becomes smooth, having almost the form characterizing the isotropic liquid phase I. It is noteworthy that the well

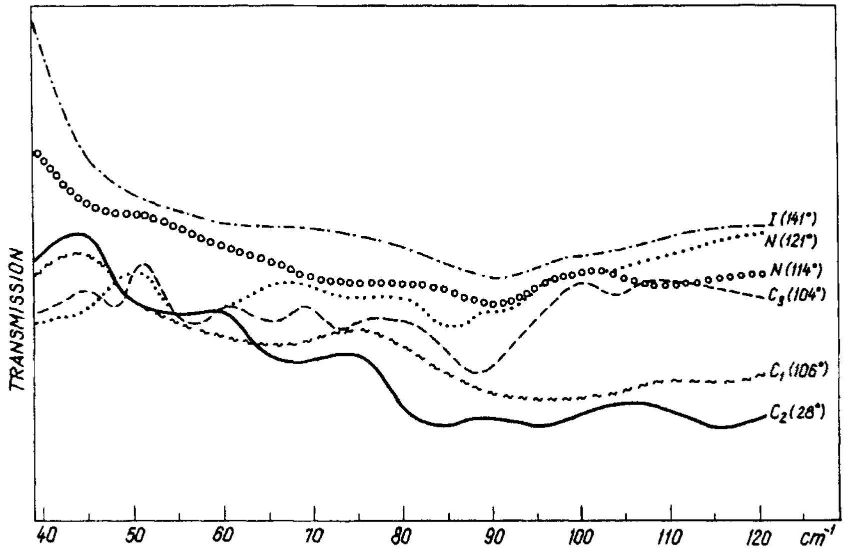

FIGURE 3 Far infrared transmission spectra for different phases of PAA (spectrum I (141°) and N (121°) are scaled down by 50 and 40% respectively for better comparison).

distinguishable band at 40 cm^{-1} in the C_2 spectrum disappears in the case of the I phase, furthermore all bands become blurred. Undoubtedly the bands in the 40–95 cm^{-1} region correspond to intermolecular modes of lattice vibrations, while bands at about 100 cm^{-1} are considered by certain authors as intramolecular modes of vibrations.[13]

5 NEUTRON DIFFRACTION

The neutron scattering experiments were carried out on the triple axis spectrometer, used in diffraction geometry, at a 5 Mwatt reactor. Using wavelengths of 1.5 and 2.9 Å from a Zn monochromator, a wide range of reflecting interplanar distances from 2 to 20 Å were covered by the measurements.

The aluminium sample-holder containing about 5 g of *d*-PAA was electrically heated. The temperature was controlled by a Cr-Al thermocouple. All the transition temperatures were somewhat higher than in Figure 1 because of the large volume of the sample. A large number of diffraction patterns were recorded in the solid phases formed on cooling from the isotropic through the nematic phase. Typical diffraction patterns are shown in Figure 4, as taken from the central part of the most characteristic set of

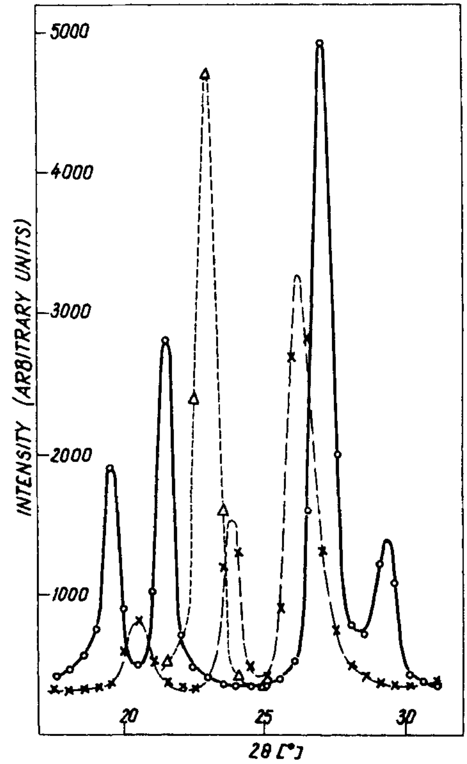

FIGURE 4 Neutron intensities as a function of the scattering angle for different crystalline states of *d*-PAA.

diagrams measured in different conditions, i.e. for different phases. The peaks, drawn with different lines, correspond to different solid structures.

In Figure 5, the observed neutron diagrams (*a*, *b*) are compared with a calculated line diagram based on X-ray data (*c*) shown in the lower part of the figure. The X-ray results obtained on the stable phase of PAA were reported by Krigbaum, *et al.*[5] A monoclinic lattice with four molecules in the unit cell was assigned to the diffraction patterns with parameters $a = 15.776$, $b = 8.112$, $c = 11.018$ Å and $\beta = 114.57$ Å. These parameters were used for calculating the line diagram showing the main reflection positions and intensities. The neutron diffraction diagrams represent the sum of many measured patterns from which the background and the second order contaminations have already been subtracted. Peak intensities are normalized to the calculated $(22\bar{2})$ reflection intensity at $\mathscr{H} = 1.946$ Å^{-1}.

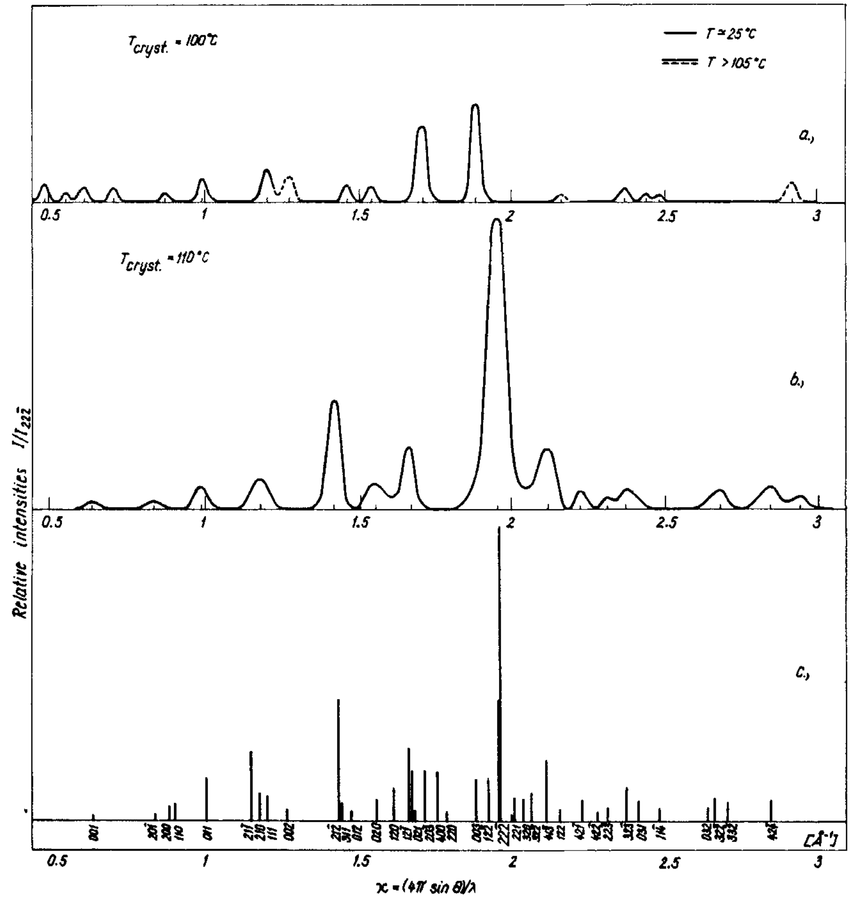

FIGURE 5 Neutron diffraction patterns (a,b) of different solid modifications and a line diagram calculated (c) from X-ray[5] on n-PAA. The temperatures indicated are corrected by thin layer peasurements (see Figure 2).

On comparing the neutron diagrams with the line diagram one can conclude that most of the neutron peaks correspond to several overlapping reflections, as shown in Figure 5. (A high resolution was not chosen because of intensity reasons nevertheless the measured diffraction patterns are good enough for quantitative inferences to be made.)

The upper diagram (Figure 5a) corresponds to a solid phase formed from the nematic on freezing below 100°C. Some peaks, represented by dashed lines, could be observed only when the temperature was increased to 105–108°C immediately after the beginning of crystallization. These peaks could not be detected among the solid line peaks if the sample was kept at room temperature. The intensities were found to be different from crystallization to recrystallization but the intensity ratios of the reflections remained about the same.

The diagram in Figure 5b, was observed for the crystalline state formed from the nematic after slow cooling to 110°C. In this case the high intensity of certain reflections in some measurements and the dependence of peak intensities on the angular position of the sample indicate the growth of large single crystal blocks. (The diagram in Figure 5a, and 5b, shows the average data of many measurements.)

The solid-nematic transition was found at 121°C in all cases. Sometimes a mixture of the two phases could be detected. Unfortunately no data could be obtained on the thermal behaviour of the solid phases and on the transition temperatures because of the technical difficulties presented by the heating and cooling of so large a sample in a closed container.

6 DISCUSSION

Starting from the neutron diffraction results, a model of solid state polymorphism can be suggested for *p*-azoxyanisole in agreement with all the available experimental results (calorimetry, optical observation, FIS, X-ray and neutron diffraction).

The good agreement of the diagram of Figure 5b, with the calculated line diagram indicated that the measured neutron diffraction pattern correspond to the structure of the stable solid C_2 phase proposed by Krigbaum, *et al.*[5] The results obtained prove that the $N \rightarrow C_2$ transition can be observed on slow supercooling and in this case no further phase transition can be detected by calorimetry. Evidence of the formation of large single crystal blocks was found after freezing in both optical observation and neutron diffraction measurements.

The diagram of Figure 5a, shows a considerable difference from the C_2 diagram. The characteristic crystallization temperature is also lower in the former case. This suggests that the crystal structure of the C_2 phase differs from that of the other solid modifications. Bernal and Crowfoot[7] have already considered this possibility, stating, however, only that the "white and yellow forms differed remarkably little except in habit." If we compare the diagram Figure 5a, with the line diagram Figure 5c, it can be seen, that a significant change of the structure has occurred.

Supposing that the most intensive ND peaks correspond to the planes with the maximum density of atoms, they can be attributed to the diffraction from the benzene rings of molecules. According to X-ray structure studies[5] there are several planes of this type. Two of them are formed by the two benzene rings inside the molecule. The angle between these planes is about 22°.[5] Because of the presence of translatory-nonequivalent molecules in the unit cell there is at least one more pair of such planes which is nearly perpendicular to the former ones in the given cell. The most intensive four peaks at 1.425 Å^{-1} $(21\bar{2})$; 1.663 Å^{-1} $(12\bar{1})$; 1.946 Å^{-1} $(22\bar{2})$ and 2.117 Å^{-1} $(41\bar{3})$ in Figure 5b, can be correlated with these planes. It can easily be seen that two pairs of planes $(21\bar{2})$ and $(22\bar{2})$ as well as $(12\bar{1})$ and $(41\bar{3})$ form an angle of about 20°. The angle between these pairs of planes $(21\bar{2})$, $(12\bar{1})$ and $(22\bar{2})$, $(41\bar{3})$ is nearly 90°. These results would therefore seem to prove our preliminary qualitative interpretation given above.

The lack or strong decrease of these peaks in the diagram of Figure 5a, shows the significant change of the crystal lattice. The presence of only two intensive peaks (at 1.71 Å^{-1} and 1.88 Å^{-1}) can be explained by the change of the geometric structure of the molecules. Furthermore, the change of the crystal structure is proved by the appearance of new diffraction peaks at and below $\mathscr{H} = 0.627\,\text{Å}^{-1}$ momentum transfer. The peak at $0.627\,\text{Å}^{-1}$ is connected with the interplanes distance of (001) planes and corresponds to the possibly minimal momentum transfer value since reflections from lattice planes of large distances are forbidden.

The existence of these extra peaks can be attributed—in principle—to a larger unit cell of the crystal lattice of a metastable modification. Results on a larger unit cell of the PAA crystal lattice (double volume of the unit cell) were published earlier,[6] however, the experimental conditions of these measurements are not clearly described. Such a doubling of the elementary cell can be connected, e.g. with the simultaneous presence of molecules with different conformation (trans and cis). Since—as is well known—the molecular conformation plays an important role in liquid crystal polymorphism.[9]

It should be mentioned that the hypothesis of lattice doubling in the metastable modification has certain indications in the FIS results, where one can see the increase in the number of absorption peaks for this metastable phase (C_3). In fact the doubling of the unit cell is connected with the increase in the number of branches and therefore with the appearance of new frequencies at zero momentum transfer.

At present the available experimental results are far from being complete which prevents us from drawing any further conclusions on the crystal structure of the polymorphous modifications of PAA.

Detailed ND structure investigations of the observed PAA modifications are being prepared in a wide momentum transfer region; in addition, model computing experiments are being performed. These tasks form the topics of our further investigations.

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