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Pressure effects in a plastic columnar discotic triphenylene

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The effect of hydrostatic pressure on the structure of a plastic columnar discotic triphenylene has been investigated. The goal was to determine whether pressure can be used to modify electronic properties via changes in structural properties of columnar discotics to any significant extent. The findings are that (i) the intra- and inter-columnar distances are reduced in a nearly isotropic fashion, (ii) that the crystal sizes are reduced and (iii) that a transition takes place from a more highly ordered plastic columnar to a less ordered hexagonal columnar state with increasing pressure. The induced decrease of the molecular distances, amounting to 6% for pressures up to 17 kbar, are clearly too small to induce an appreciable modification of the electronic structure and thus opto-electronic properties.

1. Introduction

Columnar discotic liquid crystals such as triphenylenes are known to display unusually large mobilities, both for charge carriers and for optical excitations, in particular along the columnar direction [1–4]. The corresponding mobilities are orders of magnitude smaller in the perpendicular direction. The high one-dimensional intracolumnar mobilities are the result of a dense π-stacking of the disc-like molecules within the columns, giving rise to a partial overlap of the electronic orbitals [5, 6]. Structural disorder, in terms of lateral motions of the disc-shaped molecules (twist motions), as well as longitudinal oscillations, disrupt the regular molecular arrangements within the columns with the consequence that discotic systems in general do not display semi-conductor properties characterized by a band–type electronic structure. Cyclovoltammetric investigations have revealed a HOMO-LUMO distance of about 3.5 eV for the triphenylene species considered here, and the absorption spectra are in agreement with these results [7].

The accepted model for the interpretation of the intracolumnar charge carrier mobility is that the rather small intercolumnar interactions — small compared with those displayed by inorganic semiconductors — give rise to an electronic situation characterized by localized electronic sites. Charge carrier transport, which will affect phenomena such as photoconductivity, field effect transistor or light emitting diode characteristics [8–12], takes place via a one-dimensional hopping process between neighbouring sites but possibly also between sites further apart [13–19]. The assumption is that the localized sites are subject to an energy distribution which is controlled by the molecular packing disorder and by the dipolar structure of the discotic molecules. An example which reveals this dependence is the observation that the charge carrier mobility tends to jump typically two orders of magnitude at the isotropic columnar transition within a very narrow temperature interval [1].

To calculate the dependence of the charge carrier mobility, the energy distribution of the localized sites is represented by a Gaussian distribution with a characteristic width σ. Both analytical calculations and Monte Carlo simulations have been used to relate the width of the distribution to the mobility [17–19]. It has been predicted that the mobility increases strongly by decreasing the model parameter σ/kT of the theory and levels off at very small values of this parameter. Furthermore for sufficiently large values of this model parameter, it has been calculated that the mobility depends on the temperature and the electric field. In fact these predictions were proven to be correct by corresponding experimental results: the introduction of dipoles into the molecular structure resulted, for instance, in a transition from a temperature-independent to a strongly temperature-dependent mobility [15]. Furthermore, a strong temperature increase caused the field dependence of the mobility to become smaller.

These results suggest that one should be able to enhance the mobility strongly if one succeeds in increasing the perfection of order, the π-overlap, by

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decreasing the width of the site distribution significantly. Means which have been used in the past to approach this goal were the induction of more highly ordered discotic phases by chemical modification of the discotic systems — the induction of the plastic columnar phase being an example [20, 21] — or the use of more extended cores of the disc-shaped molecules, giving rise to a stronger overlap of the electronic orbitals.

The concept considered in this paper is the use of pressure to increase the molecular order within the columns and to decrease the intracolumnar distance, thus modifying the electronic overlap within the columns. In fact, it has been reported that pressure may be able to induce in 1D stacked systems a transition from an insulator to a semiconductor [22], although the indications given in this paper are at best inconclusive. Detailed quantum chemical calculations involving the density functional approach have been used to make predictions on the effect of structural features such as the intracolumnar distance on the site energies, the spatial overlap and in particular the charge transfer integral, which is directly related to the charge carrier mobilities [23]. The charge transfer integral, for instance, is predicted to increase expontentially with decreasing distance between the stacked molecules. In the following we will report on pressure-induced structural changes, on variations of the intermolecular distances observed for the model triphenylene system AdaPBT (figure 1) as well as on the effect on the electronic, i.e. spectroscopic, properties.

2. Experimental

2.1. *Model compound AdaPBT*

The chosen model compound AdaPBT, 3,6,7,10,11-pentabutyloxytriphenylene-2-yl (1-adamantanoyl-methanoate) is an asymmetrically substituted triphenylene, shown in figure 1. It displays a hexagonal columnar phase at elevated temperatures (transition into the isotropic phase at 187°C) and a plastic columnar phase at lower temperatures (transition into the hexagonal columnar phase at 168°C) which is frozen into the glassy state below 80°C. The synthesis of such asymmetrical triphenylene derivatives has been reported previously [20, 21].

2.2. *X-ray investigations*

The energy dispersive X-ray analysis was performed at the synchrotron set-up F4 (Hasylab laboratory) at the Deutsche Electronen Synchrotron (DESY) in Hamburg, Germany. To perform these investigations under pressure, we used the sapphire pressure cell shown in figure 2. The diameter of the sapphire was 1 mm. The gasket consisted of a thin copper foil carrying a round hole with a diameter of 0.8 mm. Within the sample volume we placed a very small ruby for monitoring the local hydrostatic pressure via its pressure sensitive fluorescence. The whole pressure cell was placed in a stainless steel container with beryllium windows. Pressure was applied to the sapphires via three screws, the planarity being controlled via the observation of Newton's rings. The choice of sapphire rather than diamond for the pressure cell was because we also intended to perform optical absorption studies under pressure. To obtain an estimation of the crystal sizes <*D*> we analysed the width of the X-ray reflections using the Scherrer equation [24] where 2θ is the

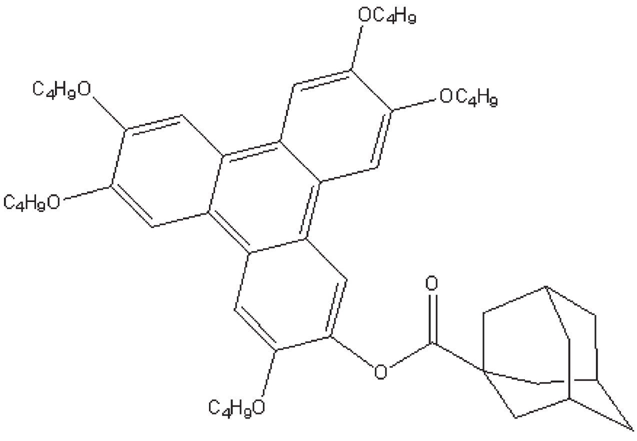

Figure 1. Model compound 3,6,7,10,11-pentabutoxytriphenylene-2-yl (1-adamantenoylmethanoate) (AdaPBT).

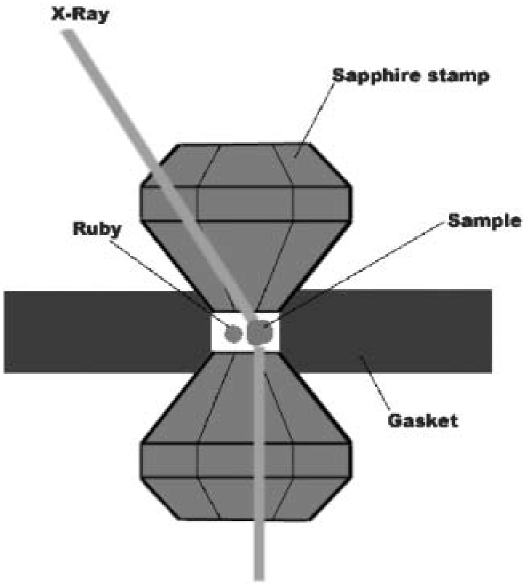

Figure 2. Pressure cell used in this study.

scattering angle and β (2θ) is the width of the reflection:

$$\langle D\rangle=\lambda/\beta(2\theta)\cos\theta$$

3. Results and discussion

3.1. *Structural properties*

The effect of pressure on structural and opto-electronic properties was investigated for the model triphenylene compound AdaPBT. The important feature of AdaPBT is that it displays a plastic columnar state characterized by a three-dimensional registry of the hexagonal lattice, the packing of the columns and the one-dimensional regular packing along the columns in addition to a hexagonal columnar phase [20, 21]. The hexagonal and the intracolumnar lattice spacings were 18.47 and 3.34 Å, respectively. However, this ordered state is different from a truly crystalline state in that the orientation of the flat disk-like molecules is random, i.e. the molecules rotate about the columnar axis in the fluid plastic columnar state and become frozen within the glassy plastic columnar state. The fluid plastic columnar state exists below a transition temperature from the hexagonal columnar phase at 168°C, and the glass transition occurs at 80°C.

The X-ray diagram of the plastic columnar state differs from that of the conventional hexagonal columnar state. It displays at larger scattering angles a doublet (0 0 2,1 0 2) rather than a single peak (0 0 1), as can be seen from the X-ray diagram of AdaPBT shown in figure 3 (*a*) for ambient pressure. In addition at small scattering angles a strong reflection originating from the two-dimensional packing of the columns is observed (1 0 0) and additional weak reflections.

Figure 3 (*b*) also shows the changes induced by the applied pressure. The general character of the scattering diagram remains but there are a number of variations which will be discussed in more detail. For this purpose we will consider enlarged segments of the scattering diagram, starting with the scattering diagram at smaller values of the scattering vector displaying the (1 0 0) reflection, see figure 4 (*a*). Firstly, figure 4 (*a*) shows that the scattering peak is shifted to larger scattering vectors with increasing pressure. Figure 5 (*a*) displays the results of an analysis on the pressure-induced reduction of the hexagonal lattice constant. It is obvious that the lattice parameter a_{hex} is reduced by about 4.5% for a pressure up to 17 kbar. The absolute value of the lattice parameter is decreased from 18.47 Å at ambient pressure to 17.58 Å at 17.0 kbar. The compressibility deduced for the linear part of this diagram is $6.5\times10^{-11}\,\mathrm{m}^2\,\mathrm{N}^{-1}$. It is clear that the compressibility is strongly reduced with increasing pressure by a factor of about five.

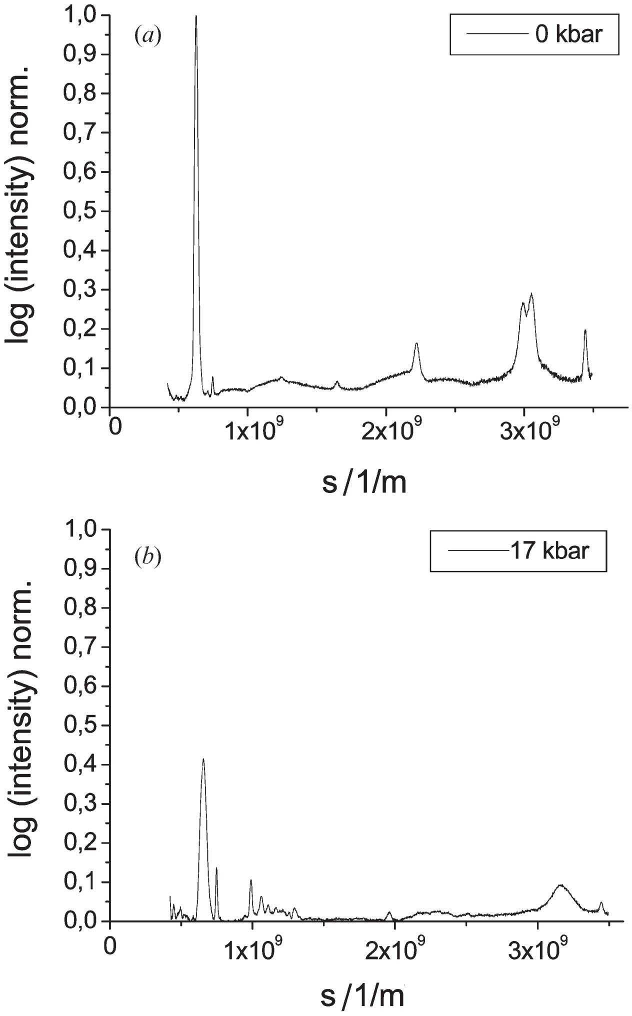

Figure 3. X-ray diagrams of AdaPBT at room temperature for (*a*) ambient pressure and (*b*) a pressure of 17 kbar.

Figure 4 (*a*) yields a further result. The width of the reflection is strongly increased with increasing pressure; it increases by about 50% in this pressure range. The clear reason is that the effective crystal size or the correlation length is reduced by pressure. Using the Scherrer equation [24], which correlates peak width with crystal size, we estimate a reduction from 30 nm at ambient pressures to 18 nm at 17 kbar. This effect will be discussed below in more detail.

Next we consider the scattering range at larger scattering angles displaying the doublet reflection. As pointed out above, the plastic columnar phase displays a doublet (0 0 2,1 0 2) in this scattering range. First, figure 4 (*b*) shows that the positions of the peaks are

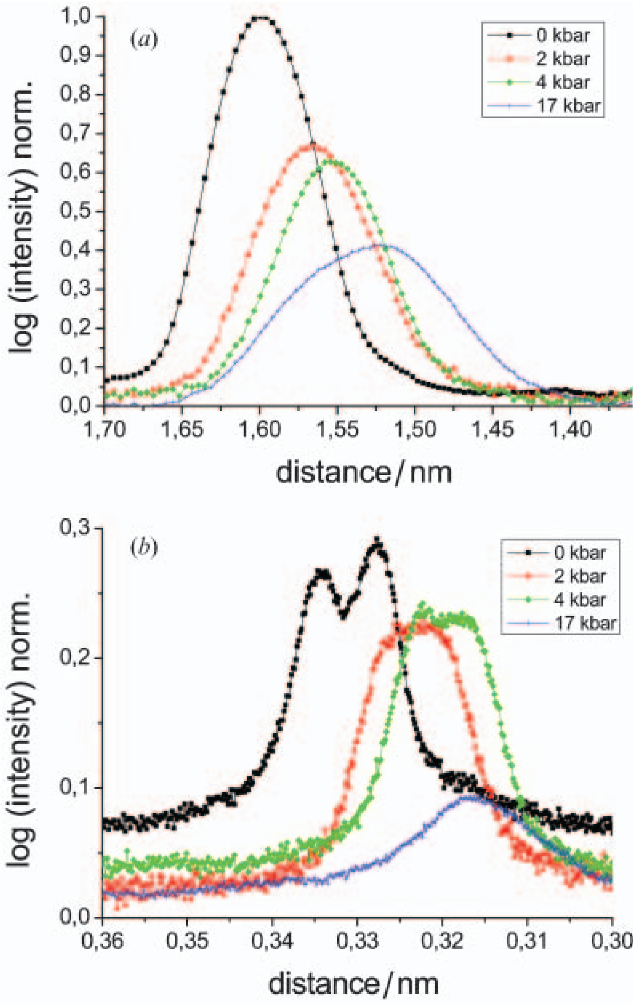

Figure 4. Pressure-induced changes of the X-ray wide angle scattering diagram for AdaPBT.

shifted to larger scattering vectors with increasing pressure. We derived a variation of the packing distance as shown in figure 5 (*b*). The distance corresponding to the intracolumnar packing is reduced by approximately 6% for the largest pressure of 17 kbar, the absolute value of the intracolumnar distance being reduced from 3.34 to 3.15 Å. The linear compressibility derived from the linear part of the diagram is $7.6\times10^{-11}\,\mathrm{m^2\,N^{-1}}$ and also decreases by a factor of approximately five for larger pressures. Again this value will be discussed in more detail later.

A second feature which is apparent from figure 4 (*b*) is that the doublet tends to be transformed into a single reflection with increasing pressure. We tentatively take this result as an indication that the plastic columnar phase is transformed into a hexagonal columnar phase with increasing pressure. This is a rather unexpected result which is discussed later in more detail.

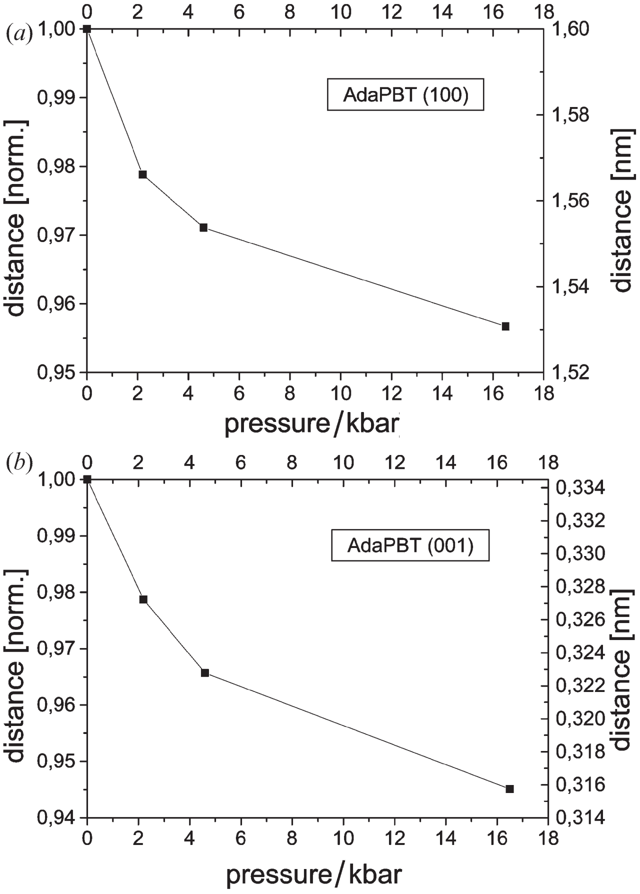

Figure 5. Pressure-induced modification of molecular distances: (*a*) intercolumnar, (*b*) intracolumnar.

A third feature clear from figure 3 is that additional reflections occur with increasing pressure. These can be assigned neither to the plastic columnar nor to the

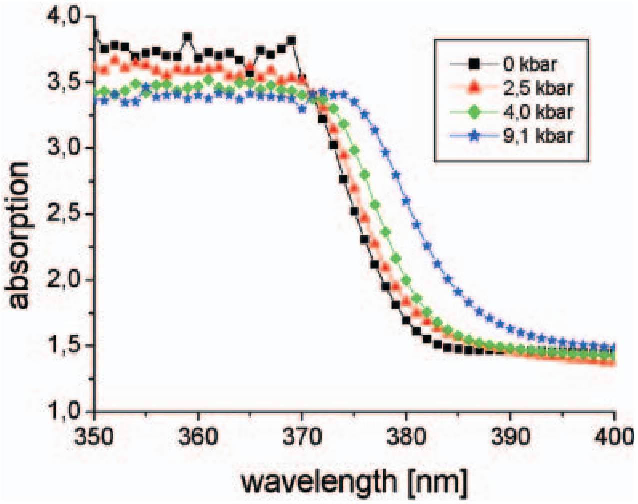

Figure 6. Shift of absorption edge with pressure.

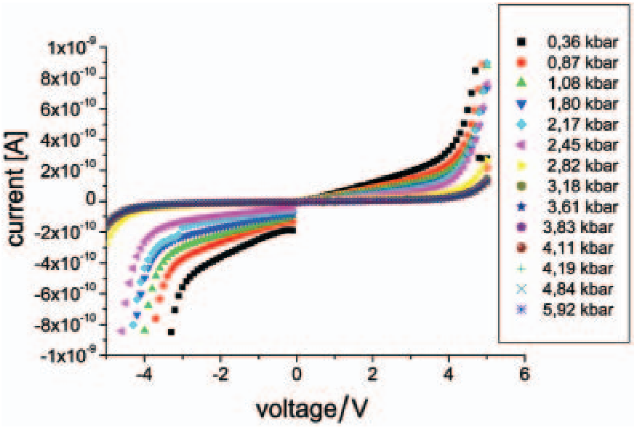

Figure 7. Diode characteristics of an AdaPBT film at various pressures.

columnar hexagonal phase. Thus, it seems that a further phase emerges with increasing pressure, but we are unable to comment on its nature due to the small number of corresponding reflections.

In the following we will discuss the results obtained above in more detail. First, we note that the compressibility of the discotic highly ordered phase is in the range known for disordered glassy organic materials (polystyrene in the glassy state: $\kappa = 3 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$) or crystalline organic materials (benzene in the crystalline state: $\kappa = 3 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$), whereas both polystyrene and benzene in their liquid state have a compressibility of about $9 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$. This agreement becomes clearer if we calculate the isotropic from the linear compressibilities ($\kappa_{\mathrm{long}} + 2\,\kappa_{\mathrm{travers}}$) which results in a value of about $2.1 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$ for smaller pressures.

Therefore, the isothermal compressibility found here is well within the expected range. The more surprising finding is that it is also nearly isotropic to a first approximation. One might have expected large differences between the compressibility along the densely packed columnar axis (π-stacking) and that along the less densely packed directions along the hexagonal lattice. Note that the density of columnar discotics is of the order of $1\,\mathrm{g\,cm^{-3}}$.

Another unexpected finding was that the pressure causes not only a reduction of the molecular distances, but also a structural transition from one phase to another. In fact, previous studies have shown that the plastic columnar phase rather easily becomes unstable with respect to the hexagonal columnar phase, for instance, due either to confinement effects or to doping with electron acceptors [25]. This transition may also be the reason why pressure causes a reduction of the correlation length rather than an increase.

In view of the magnitudes of the linear compressibilities reported above, we are only able to achieve a reduction of the intermolecular distances by 5 to 6%. Quantum mechanical calculations [23], although performed for slightly different triphenylene derivatives such as an alkoxy–substituted triphenylene, can be used to obtain an estimate of the pressure-induced variations of the electronic properties. We will consider just the variation of the intracolumnar distance without changing the twist and lateral motions, which is of course a certain restriction. For the variation of the intracolumnar distance found, we estimate a variation of the site energy of about 0.02–0.05 eV, of the spatial overlap by about 30% and most importantly, of the charge transfer integral of not more than 30%, which would correspond to an increase of the charge carrier mobility by a factor well below two. With regard to these quantum mechanical calculations, we must conclude that the pressure used here probably does not significantly change the opto-electronic properties. This is also apparent from the data reported next.

3.2. *Absorption spectra and diode characteristics*

Absorption spectra were obtained for pressures up to 9.1 kbar, using a sapphire pressure cell. The results are shown for the absorption edge in figure 6. Pressure causes a red-shift of the adsorption edge yet it is restricted to a wavelength shift of 6 nm corresponding to an energy shift of 0.05 eV. These results also show that pressure, at least in the range available, induces only small changes in the electronic structures of the triphenylene model compound. In any case we observed no indications of a transition from an insulator to a semiconductor state with increasing pressure [22]. Pressures well above 100 kbar may induce such changes provided that the compressibility does not decrease strongly with increasing pressure.

Figure 7 represents the diode characteristics obtained for a 8 µm thick AdaPBT layer for various pressures up to about 6 kbar. The results quite clearly demonstrate that there is no significant modification of the current–voltage characteristics with increasing pressure. In fact, for a given voltage the current decreases with increasing pressure. It seems that the pressure-induced enhancement of disorder is responsible for this effect. Again the absorption spectra and the diode characteristics show that pressure is unable to modify the opto-electronic properties of columnar discotics to any appreciable extent.

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