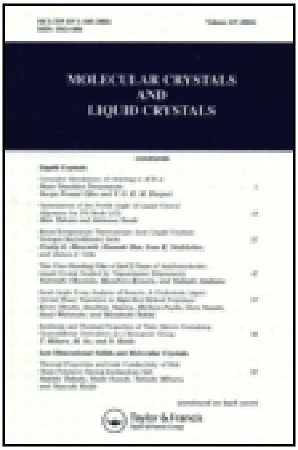

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

On the Short Range Order in a Discotic Liquid Crystal as Reflected by its Fluorescence Properties

O. Braitbart [a] , R. Sasson [a] & A. Weinreb [a]
[a] The Racah Institute of Physics, The Hebrew University of Jerusalem, 91904, Jerusalem, Israel

Version of record first published: 19 Dec 2006.

To cite this article: O. Braitbart , R. Sasson & A. Weinreb (1988): On the Short Range Order in a Discotic Liquid Crystal as Reflected by its Fluorescence Properties, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 159:1, 233-242

To link to this article: http://dx.doi.org/10.1080/00268948808075274

Mol. Cryst. Liq. Cryst., 1988, Vol. 159, pp. 233–242
Photocopying permitted by license only

Printed in the United States of America

On the Short Range Order in a Discotic Liquid Crystal as Reflected by Its Fluorescence Properties

O. BRAITBART, R. SASSON and A. WEINREB

The Racah Institute of Physics, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

(*Received November 4, 1987*)

The emission spectra of hexa-5-alkoxytriphenylene is studied as function of the state of aggregation, namely in low and highly concentrated solutions of the compound in cyclohexane, in the pure liquid, in the mesophase and in the crystal.

Significant changes in the spectra are observed at some of the phase transitions and not in others. These changes are interpreted as a result of the different short range intermolecular interactions in the various phases.

INTRODUCTION

Discotic liquid crystals have recently been the subject of intensive studies.[1–3] The molecules involved and the structures which they form are rather unique in view of the elongated shapes of molecules encountered most frequently in liquid crystals. Among the discotic liquid crystals, those involving molecules with an aromatic core are particularly interesting because of their fluorescence which is highly indicative for their intermolecular interactions. There is hardly a better means to study such short range interactions non-destructively.

As the subject of our present study we chose hexa-5-alkoxytriphenylene (HET $n = 5$) which is representative of a group of discotic mesogenic molecules. The compound was first synthesized in 1978.[4] The structure of the mesophasic state of this system has been studied by x-ray diffraction and light microscopy[5–6] and can thus be related to the spectroscopic features as observed by fluorescence measurements. The structure of the molecule is shown in Figure 1.

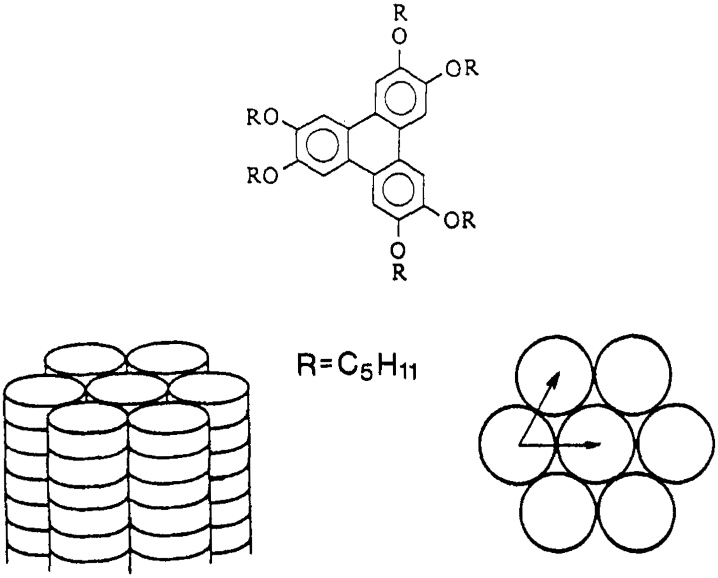

FIGURE 1 Structure of the HET-5 molecule and arrangement of the molecules in the discotic mesophase.

In the mesophasic state which prevails between 69°C and 122°C, the molecules are stacked in columns of regularly spaced molecular discs at a distance of 3.59 Å between neighboring molecules in the column. The columns are arranged in a hexagonal lattice (Figure 1). The distance between the axes of neighboring columns in the mesophase is 18.94 Å. The molecules in a column are arranged in a helical array; the pitch length of the helix is 13 Å. This helical arrangement is maintained within about 30 Å (less than 3 pitch lengths) while the correlation length for the distances in the column is about 300 Å.[7]

The spectroscopic properties of the material are determined by the triphenylene core of the molecules; these are, however strongly modified by the oxygen bridges which connect the aliphatic side chains to the core. The fluorescence of triphenylene in solution has been studied previously[8]; however, no information on the absorption and emission of HET-5 could be found in the literature for any state of aggregation of the molecules.

EXPERIMENTAL

Hexa-5-alkoxytriphenylene was synthesized and then purified twice by chromatography and recrystallisation. Its absorption spectrum was determined for a solution of 0.01 g/l in spectroscopic grade cyclohexane. For the fluorescence measurements the samples were deposited on the sapphire bottom window of a cylindrical, open cell. Sapphire was used for its relatively high heat conductivity in order to assure uniform heating of the sample. The thickness of the sample was of the order of 200 μ. The sample cell was held in a thermostated cell holder, the temperature of which could be kept constant within 0.3°C. The fluorescence was excited at 277 nm by illumination of the free surface of the sample, since excitation through a window may lead to fluorescence quenching at the window. Such effects may occur in layers of the sample which are adjacent to the window when the absorption coefficient for the exciting radiation is very high.[9]

The (free) front surface fluorescence, was measured via a quartz optic fiber which was connected to a monochromator. This way, distortion of the spectrum by self-absorption, and in particular, by scattering was eliminated. All fluorescence measurements were carried out at thermal equilibrium. For comparison with the state of isolated molecules the fluorescence spectra of low and high concentration solutions of HET-5 in cyclohexane were also measured.

All emission measurements were accompanied by polarizing microscope inspections of the sample texture.

RESULTS

Figure 2a shows the absorption and emission spectra of a solution of 0.01 g/l HET-5 in cyclohexane. For comparison, the absorption and emission spectra of 0.1 g/l triphenylene in cyclohexane are shown in Figure 2b. In the first absorption band the two absorption spectra differ significantly in intensity.

Figure 3 shows the emission spectra of HET-5 at various phases. The spectrum of the liquid (molten) state (curve a) was taken at 130°C, that of the liquid crystalline state (curve b) at 82°C, and that of the crystal (curve c) at 30°C. The transition temperatures are indicated in the Introduction. It is seen that the emission spectrum of the liquid resembles closely that of the liquid crystal except for the red shift of about 376 cm^{-1} of the latter relative to the former. The red shift proceeds gradually from the onset of the liquid crystalline state (at 123°C) down to temperatures which are very close to the temperature of the transition to the solid phase (at 53°C. This temperature differs from the temperature of the transition from the solid to the liquid crystal; see below). The red shift of the emission spectrum

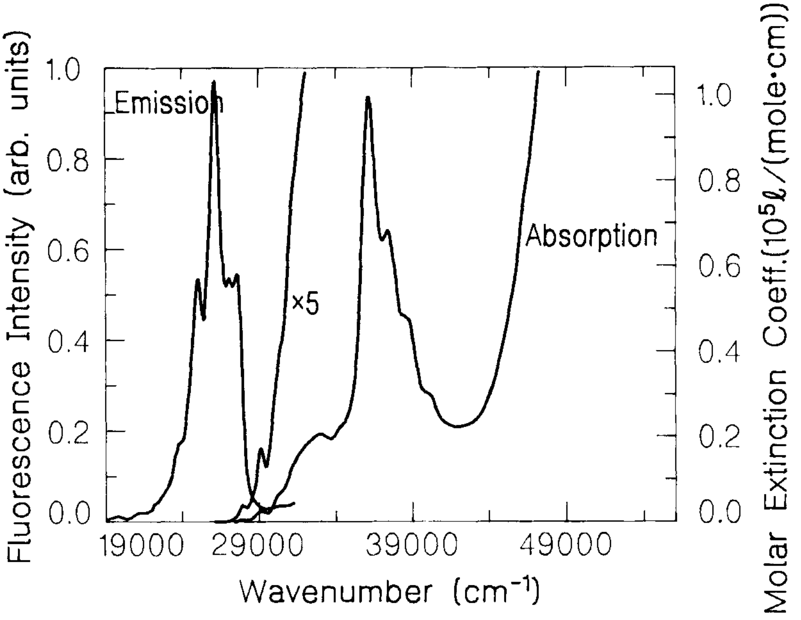

FIGURE 2 a) Absorption and emission spectra of a solution of HET-5 (0.01 g/l) in cyclohexane.

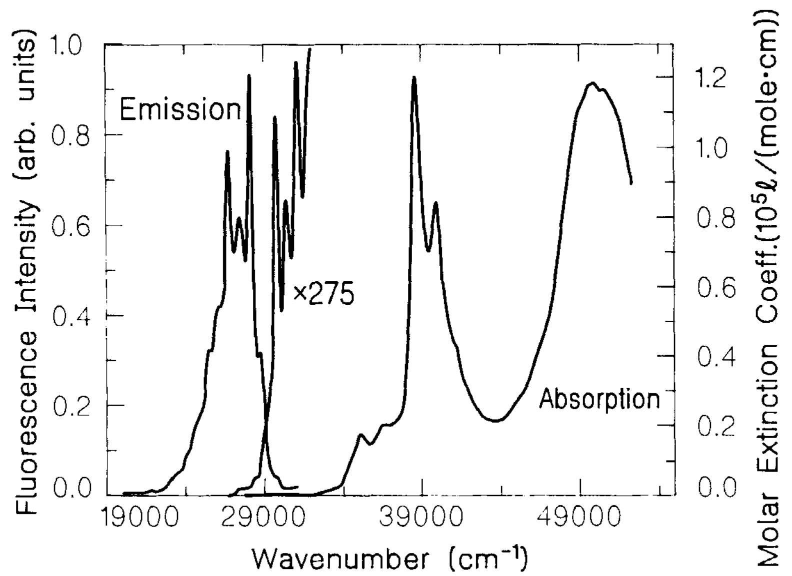

FIGURE 2 b) Absorption and emission spectra of a solution of triphenylene (0.1 g/l) in cyclohexane.

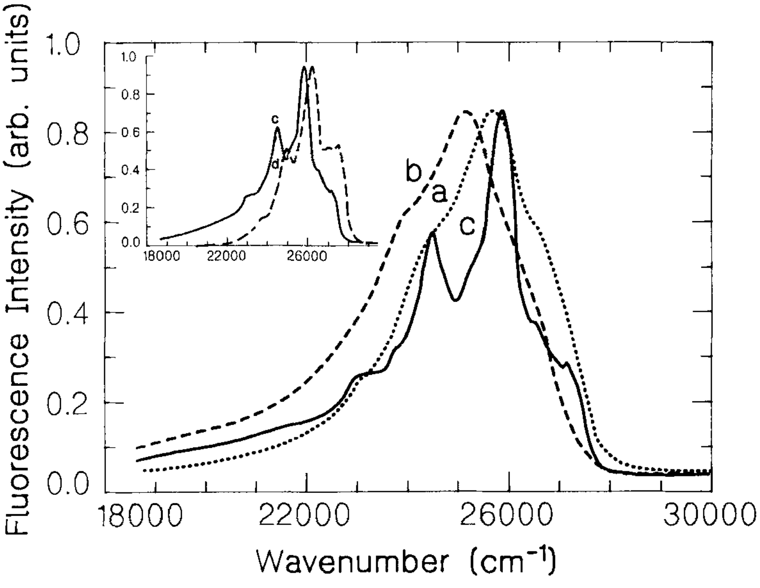

FIGURE 3 Fluorescence spectra of HET-5 in the condensed phase. (a) melt, 130°C; (b) liquid crystal, 82°C; (c) solid, 30°C, for comparison, this spectrum is reproduced with that of a dilute solution (curve d) in the inlet. The spectra have been normalized at their highest intensity.

is accompanied by a gradual decrease in quantum yield up to a factor of two, approximately, from the liquid to the liquid crystal–solid transition. At 53°C the rather structureless emission of the liquid crystal turns abruptly into the clearly structured spectrum of the crystal shown in curve c, and the intensity increases by at least a factor of three. Upon further cooling (down to room temperature) the spectrum does not change.

The phase transitions are clearly discerned by observation through the polarizing microscope. The transition from the liquid to the mesophase is characterized by the evolution, at different sites, of hexagonal flower-shaped domains, as has been reported previously.[6] Upon further cooling these domains increase in size. They appear to be uniaxial with the optical axis perpendicular to the sapphire substrate. At the transition to the solid phase the visual field brightens, indicating the destruction of the uniaxial structure. The appearance of the structure is now that of single needles; these intersect each other at angles which are multiples of 30°.

The behavior of the system upon heating differs rather markedly from that observed for cooling. The transition from the solid to the liquid crystal starting at 69°C (as against 53°C for decreasing temperatures) develops gradually as observed by both the change in the emission spectrum and the texture of the sample. In fact at no stage is the uniaxial arrangement, so clearly observed in the cooling part of the cycle, attained. The transition from the mesophase to the liquid state occurs at the same temperature as the inverse transition upon cooling. In spite of the difference in the texture of the liquid crystalline phase at 82°C when the phase has been reached by cooling as compared to the heating of the sample, the emission spectra are the same for both directions of temperature change.

Figure 4, curve a, shows the emission spectrum of a dilute solution (1.3×10^{-4} mole/liter) and curve b of a concentrated solution (0.17 mole/liter) of HET-5 in cyclohexane. Except for a blue shift of 255 cm^{-1} the spectrum of the concentrated solution is similar to that of the molten HET-5 at 130°C (Figure 3). When the cyclohexane is left to evaporate the spectrum of the solid formed is identical with that of the crystalline phase reached from the melt via the liquid crystal.

DISCUSSION

Since the chromophoric group of HET-5 is the triphenylene core of the molecule it seems natural to tie the changes in the emission

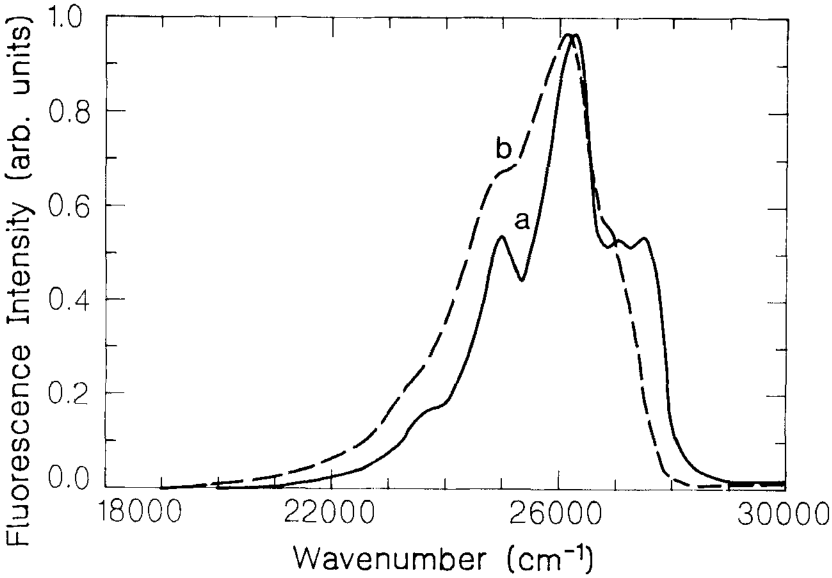

FIGURE 4 Fluorescence spectra of solutions of HET-5 in cyclohexane: (a) dilute solution (1.3×10^{-4} mole/liter); (b) concentrated solution (0.17 mole/liter). The spectra have been normalized at their highest intensity.

spectrum of HET-5 at the different phase transitions with the changing intermolecular interactions which the core undergoes as a result of structural changes of the environment. This simple attitude is, however complicated by the fact that the core emission itself is strongly modified by the 6 oxygen atoms which connect the aliphatic chains to the triphenylene core. The strong influence of oxygen as a substituent on the absorption and emission of aromatic molecules is well known[10]; it causes a remarkable increase in the absorption coefficient of the first electronic band, and a bathochromic shift, as well as a blurring of the vibrational structure. A prominent representative example of this effect is the case of toluene vs. anisole in which the methyl group in the former has been exchanged by the methoxy group in the latter.[8] This effect also causes the remarkable difference between the absorption spectrum of HET-5 and that of triphenylene. Compared to the oxygen effect, the influence of the aliphatic chains on the absorption of HET-5 is negligible. The emission spectra of triphenylene and HET-5 are significantly less different than their absorption spectra, similar to the case of toluene and anisole. In order to understand this fact we have to assume that the repartition of charge in the oxygene–triphenylene system which takes place upon the absorption of the exciting photon is maintained during the $\pi-\pi$ transition to the ground state, with subsequent reorganization of the electronic system.

The vast difference between the emission spectra of the dilute and concentrated solution of HET-5 in cyclohexane is due to the strong interaction between the triphenylene cores of neighboring molecules in the latter. This effect is mediated by the aliphatic chains of the molecules, as can be seen from its absence in highly concentrated solutions of triphenylene.[11] The center to center mean distance in the concentrated HET-5 solution was 21.3 Å, whereas the greatest diameter of a stretched molecule is 24.5 Å. Collisions between neighboring molecules are therefore imminent. Upon the contact between one or more chains of two molecules, the cores continue their motion until they approach each other as closely as the system of chains on both molecules permits. The preferred arrangement is then a roughly parallel overlap between the cores. (In the mesophase, as we have seen, this overlap between neighboring molecules in a stack is complete). This arrangement once established lasts sufficiently long, so that practically every excited core will have at least one unexcited core close to it. Hence the emission process will take place under a considerable electronic interaction between the two cores, which modifies the spectrum appreciably, as born out by the results. However, not only is the vibrational structure of the emission of the concentrated solution largely obliterated, but also the intensity is markedly reduced when compared with that of the dilute solution. This shows that the intermolecular interaction also enhances non-radiative transitions. On the other hand the results also permit to set a lower limit for the distance between the overlapping cores; namely, the absence of an excimer emission indicates that the distance between the cores can hardly be smaller than 3.1 Å. This minimum separation is probably determined by the aliphatic chains of the molecules which hold the cores together but also separate them. It should, however, be noted that triphenylene itself does not exhibit excimer formation for any concentration.[12]

The emission spectrum of pure molten HET-5 is rather similar to that of the concentrated solution in cyclohexane. This indicates that the same interactions between neighboring molecules take place under both circumstances. The roughly parallel arrangement of planar disc-like molecules in the melt has been assumed in order to satisfy the requirement of close packing.[13] The packing depends on the rotational freedom of the side chains (see below). Since the spectrum of the concentrated solution of HET-5 was taken at room temperature while that of the pure liquid was taken at 130°C it follows that the rotational freedom of the chains around their C—C bonds in the concentrated solution is not essentially impaired by the cooling to room temperature.

The close resemblence of the liquid crystalline emission to that of the melt shows that the intermolecular interactions are similar in the two states. This implies that the distance between the molecules in a molecular pair of the melt is closely similar to that in the liquid crystal. For the liquid crystal the structure and molecular distances are known from X-ray diffraction (see above); still the red shift of 570 cm^{-1} of the liquid crystal emission at 62°C with regard to that of the melt and also the appreciable decrease in quantum yield (by about a factor of 2) indicate that the intermolecular interactions in the liquid crystal are strongly enhanced by the close packed structure of the system. The long range order, however is of no significant influence on these interactions. This is seen from the fact that the emission spectra of the liquid crystal at 82°C for ascending and descending temperatures are identical, although in the heating part of the cycle, the long range order in the liquid crystal does not prevail.

The close resemblance between the emission spectra of the dilute solution of HET-5 and that of the crystal, as well as the drastic increase in quantum yield upon the transition from the mesophase to the crystal show that the close interaction between neighboring molecules which is reflected by the spectrum of the liquid crystal is greatly reduced in the solid. Although the long range order which prevails in the liquid crystal is grossly destructed in the crystal, this, as we have just seen, can not explain the greatly reduced interaction between neighboring molecules. It is therefore necessary to assume that the distance between neighboring molecules in a stack is increased upon solidification of the sample or the angle between the planes of neighboring molecules is increased, or both. We tend to explain this increase in distance by the freezing of the rotational freedom around C—C bonds in the aliphatic chains which occurs upon the transition from the mesophase to the crystalline state. In all phases the shortest distance between the molecular cores is determined by the arrangement of the aliphatic tails. For reasons of close packing these chains arrange themselves in a mode which exploits their internal rotational freedom so that minimum distances are obtained. Upon solidification, however this freedom is reduced so that all carbon atoms in a chain lie now in a plane, which is the preferred arrangement of aliphatic chains in order to minimize their potential energy.[13] This may impose a distance of more than 3.59 Å between neighboring molecular cores and hence explain their reduced electronic interaction. These assumptions are strongly supported by recent X-ray measurements which show a disruption of the liquid-crystalline arrangement of the molecules upon the transition to the crystalline phase.[14]

Acknowledgments

We are indebted to Prof. Z. Luz for providing the sample.

References

1. S. Chandrasekhar, *Phil. Trans. R. Soc. Lond.*, **A309**, 93 (1983).
2. C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
3. L. Y. Chiang, J. P. Stokes, C. R. Safinya and A. N. Bloch, *Mol. Cryst. Liq. Cryst.*, **125**, 279 (1985).
4. J. Billard, J. C. Dubois, N. H. Tinh and A. Zann, *Nouv. J. de Chimie*, **2**, 535 (1978).
5. A. M. Levelut, *J. Phys. Lett.*, **40**, L-81 (1979).
6. Y. Bouligand, *J. Phys.*, **41**, 1307 (1980).
7. A. M. Levelut, *J. de Chim. Phys.*, **80**, 149 (1983).
8. I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules (Academic Press, N.Y. 1971).

9. R. Sasson and A. Weinreb, *J. Luminescence*, **31**, 586 (1984).
10. V. M. Parikh, Absorption Spectroscopy of Organic Molecules (Addison-Wesley, Reading 1974) p. 34.
11. R. Sasson, O. Braitbart and A. Weinreb, *J. Luminescence*, (to appear).
12. J. B. Birks and L. G. Christophorou, *Nature*, **194**, 442 (1962).
13. A. R. Ubbelohde, The Molten State of Matter (Wiley-Interscience, Chichester 1978) p. 148, p. 155.
14. Z. H. Kalman, O. Braitbart, R. Sasson and A. Weinreb, submitted for publication in Mol. Cryst. Liq. Cryst.