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S. Zamir^a; D. Singer^a; N. Spielberg^b; E. J. Wachtel^a; H. Zimmermann^c; R. Poupko^a; Z. Luz^a

^a The Weizmann Institute of Science, Rehovot, Israel ^b Department of Physics, Kent State University, Kent, Ohio, USA ^c Max-Planck-Institut für Medizinische Forschung, AG Molekülkristalle, Heidelberg, Germany

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Columnar mesophases of octa-alkyloxydibenzopyrenes and their charge transfer complexes: Synthesis, X-ray and NMR

by S. ZAMIR†, D. SINGER†, N. SPIELBERG‡, E. J. WACHTEL†,
H. ZIMMERMANN§, R. POUPKO† and Z. LUZ†*

†The Weizmann Institute of Science, 76100 Rehovot, Israel

‡Department of Physics, Kent State University, Kent, Ohio 44242, USA

§Max-Planck-Institut für Medizinische Forschung, AG Molekulkristalle,
Jahnstrasse 29, 69120 Heidelberg, Germany

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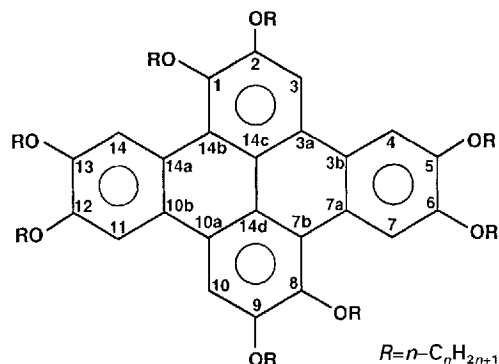
The mesomorphic properties of five homologues of the 1,2,5,6,8,9,12,13-octa-alkyloxydibenzopyrene series (DBP n , where n is the number of carbons in each of the side chains) and their charge transfer complexes with 2,4,7-trinitro-9-fluorenone (TNF) are described. The neat compounds exhibit a single mesophase which has been identified by X-ray diffractometry and optical microscopy as hexagonal columnar (D_{hd}). Two-dimensional unit cell parameters are reported for the various homologues as functions of temperature within the mesophase region. Deuterium NMR of labelled DBP n was used to determine the nature and rate of the molecular reorientation in the mesophase. Addition of the electron acceptor TNF to the donor DBP n mesogens increases the stability range of the mesophases, with a maximum stability for the equimolar donor/acceptor mixtures. X-ray and deuterium NMR measurements on these charge transfer stabilized mesophases are also reported. Besides being thermally more stable, they are more highly ordered and even exhibit well defined intramolecular stacking order, classifying them as D_{ho} . Under certain conditions, a diffraction peak at a position corresponding to twice the normal intracolumnar distance is also observed, indicating that the donor and acceptor molecules are stacked alternately in the columns. When alkanes are added to the 1:1 charge transfer complexes, a lyotropic nematic phase is induced. It is shown that these nematics are of the type N_c , with columnar structures as the mesogenic units.

1. Introduction

Several homologous series derived from the anthracene core have been shown to exhibit discotic columnar mesophases, including derivatives of rufigallol [1(a)] and octa-alkanoyloxyanthraquinone [1(b)]. The symmetry of these compounds, with only a two-fold rotation axis perpendicular to the core plane, is lower than for most discotic mesogens, yet they exhibit well ordered columnar mesophases including some with two-dimensional hexagonal arrangement. In the present work we extend the scope of the study of such discotic mesogens to those with a larger aromatic core, *viz.* dibenzopyrene (dibenzo(fg,op)naphthacene), substituted with eight alkyloxy side chains as indicated in the formula below.

We refer to this homologous series as DBP n , where n is the number of carbons per side chain.

Several members of this family have already been shown to be mesogenic. Bock and Helfrich [2(a),(b)]



determined that DBPs substituted with chiral hexyloxy- and heptyloxy-propyloxy side chains form ferroelectric columnar mesophases and have studied their electric properties and orientational switching under the effect of external electric fields. Henderson *et al.* [2(c)] were the first to show that DBP5 is mesogenic, exhibiting a room temperature hexagonal columnar mesophase (D_h), and addressed the question of its photoconductivity.

*Author for correspondence.

Here we present X-ray diffraction and deuterium NMR results on the $n=4$ to 8 members of this series, all of which exhibit a D_h mesophase of the type reported by Henderson for the $n=5$ homologue. Our results provide information on the structure and on the molecular dynamics of these mesophases.

It has been known for several years that electron rich discotic compounds, when mixed with suitable electron acceptors, form charge transfer complexes, often connected with the stabilization of an existing mesophase or even inducing new mesophases that are not exhibited by the neat compounds [3–8]. Most of this research was done on derivatives of triphenylene with 2,4,7-trinitro-9-fluorenone (TNF) or related acceptors [5]. Other systems with similar properties include complexes of disc-shaped multiynes [6, 7] and of binuclear palladium organyls with TNF [7, 8]. It was argued that the addition of the acceptor to the discotic compounds stabilizes a stacked structure, thus inducing two-dimensional columnar mesophases (D) and/or columnar nematic (N_C) phases. The latter type is usually favoured when steric effects interfere with the formation of a two-dimensional columnar lattice [5(d), 6, 7]. There is even an example of stabilization of a nematic discotic phase (N_D), involving a dinuclear palladodiscogen with TNF [7, 8]. The stabilization of the columnar structures in such binary systems was ascribed to alternate stacking of donor and acceptor molecules [5(a),(b),(d),(e),6(a),(b)]. This view is supported by the observations that (i) the stacking order is higher in the binary systems, compared

with the corresponding neat mesogens, (ii) the maximum stability is usually obtained at or near to equimolar mixtures and (iii) the rate of planar reorientation is similar for the donor and acceptor molecules [5(f)].

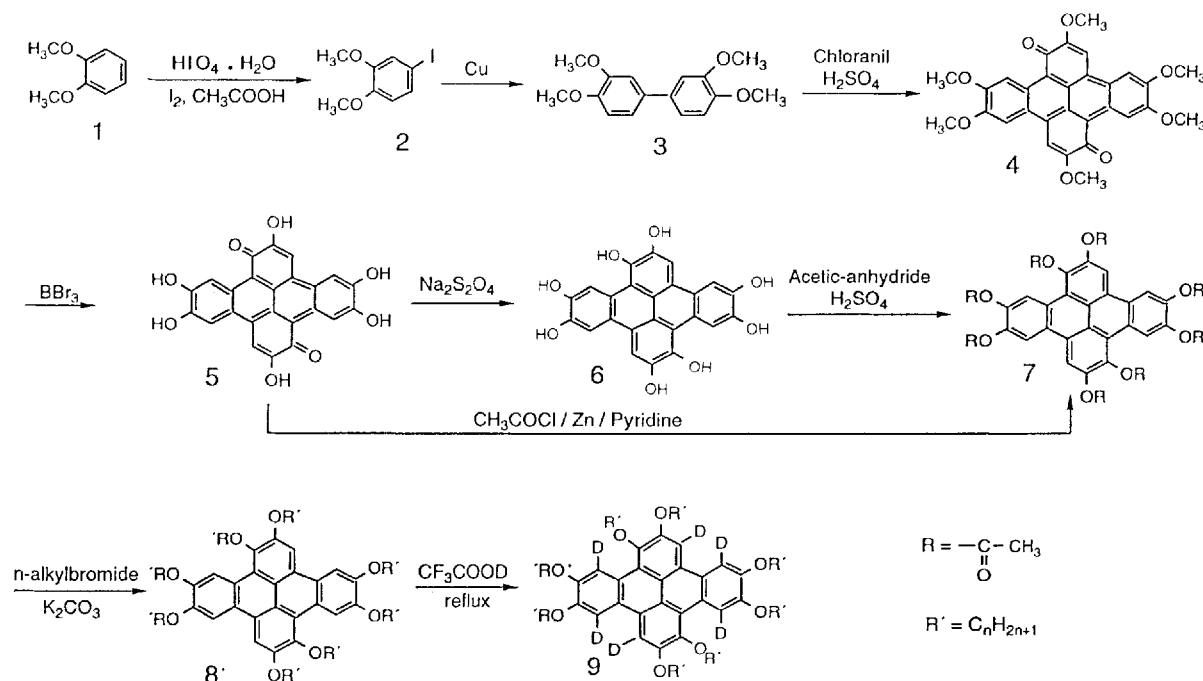
Due to their large polycyclic aromatic core, the DBP n ethers are promising candidates to form charge transfer stabilized columnar phases. Experiments indeed confirmed these expectations and in the second part of the paper we describe the mesomorphic properties of some DBP n /TNF binary mixtures, as well as those of ternary systems which include additional apolar organic solvation. It is shown that the latter induce the formation of a lyotropic nematic columnar mesophase of the type N_C , similar to those recently reported for related systems [7, 9, 10]. However, the present work describes the first case where stabilization of columnar aggregates by charge transfer interactions and induction of nematic phases by apolar solvents are observed in the same system.

2. Experimental

2.1. Synthesis

The synthesis of the DBP n compounds is shown schematically in the diagram below. It is based on the procedure of Musgrave and Webster [11] and is similar to that used by Henderson *et al.* [2(c)].

Veratrole (1) was iodinated [12] with periodic acid to give 1-iodo-3,4-dimethoxybenzene (2). Subsequent Ullman coupling yielded 3,3',4,4'-tetramethoxybiphenyl (3), which was oxidized with chloranil/ H_2SO_4 to



2,5,6,9,12,13-hexamethoxydibenzopyrene-1,8-quinone (**4**) (yield 75%). The methoxy groups were then cleaved with boron tribromide to give the corresponding hexahydroxy compound **5**. Esterification to octaacetyloxydibenzopyrene (**7**) was effected either directly by reductive acetylation of **5** with zinc/pyridine and acetylchloride, or in two steps by first reducing to the octahydroxy derivative **6** with sodium hydrosulphite followed by acetylation with acetic anhydride. The final products, DBP n (**8**), were obtained by alkylation with the desired n -alkyl bromide. Deuteriation of the free aromatic sites (DBP n -d $_6$, **9**) was effected by heating DBP n under reflux with CF $_3$ COOD. The final compounds were purified by extensive column chromatography (silica gel/1. CH $_3$ OH, 2. CH $_2$ Cl $_2$ / n -hexane 65:35). They were found to be of high purity by TLC and 1 H NMR examination.

The perdeuteriated 2,4,7-trinitrofluorenone (TNF-d $_5$) was synthesized in three steps starting with the room temperature perdeuteriation of fluorene with ethylaluminum dichloride in hexadeuteriobenzene. The resulting fluorene-d $_{10}$ was oxidized with sodium dichromate in CH $_3$ COOD yielding fluorenone-d $_8$, which was nitrated by fuming nitric acid/conc. D $_2$ SO $_4$ to give the desired perdeuteriated 2,4,7-trinitrofluorenone (TNF-d $_5$).

The equimolar charge transfer complexes DBP n /TNF were prepared by dissolving appropriate amounts of DBP n and TNF in anhydrous dichloromethane. The resulting dark solutions were allowed to evaporate at ambient temperature and the residues dried in vacuum for 24 h.

2.2. Physical characterization

Differential scanning calorimetry (DSC) was performed with a Mettler DSC 30, heating rate 5 K min $^{-1}$, except for the determination of the clearing temperatures of the charge transfer complexes where a rate of 10 K min $^{-1}$ was used. X-ray diffraction measurements of the neat DBP n compounds were carried out using a Rigaku powder diffractometer (Dmax-B) with rotating anode (12 kW, $\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator crystal ($2d = 6.695 \text{ \AA}$). The temperature dependence measurements were performed as described earlier [13]. The corresponding diffraction patterns of the thermo- and lyo-tropic mesophases of the DBP n /TNF charge transfer complexes were obtained on imaging plates (Fuji) using a Searle camera with Franks optics affixed to an Elliott GX6 rotating anode generator (1.2 kW, CuK $_{\alpha}$ radiation). The imaging plates were scanned with a He-Ne laser (Spectra Physics) in conjunction with a home made reader based on an Optronics (Chelmsford, Mass) densitometer and interfaced to an Apollo DS3500 work station (Hewlett-Packard). Images were also processed on a Power Macintosh PC using the public

domain NIH image program (written by Wayne Rasband at the US National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov).

The deuterium NMR measurements were performed at 46.07 MHz with a high power Bruker CXP 300 spectrometer equipped with a BVT 1000 variable temperature unit. The spectra were recorded using the quadrupole echo sequence, $(\pi/2) \pm x - \tau - (\pi/2) y - \tau - (\pm \text{acquisition})$ followed by Fourier transformation.

3. Results and discussion

3.1. Neat DBP n compounds

3.1.1. The phase sequences

The phase sequences and associated thermodynamic data for the various neat DBP n homologues, as determined by DSC, are summarized in table 1. The data quoted are for the 'first heating' of the crystallized compounds. The phase sequences and the transition temperatures were confirmed by optical polarizing microscopy. All five homologues studied form just one type of mesophase. On cooling from the isotropic liquid, this exhibits fan-shaped textures, characteristic of hexagonal columnar mesophases, as well as homogeneous dark areas, as would be expected from homeotropic domains of a uniaxial phase. The melting process of the hexyloxy to octyloxy homologues is associated with relatively large transition enthalpies (50–60 kJ mol $^{-1}$) while the clearing enthalpies are much smaller (1–4 kJ mol $^{-1}$). For the pentyloxy homologue a very broad transition to the mesophase, ranging from around –50 to 0°C, is observed.

No solid–solid transitions were detected for the $n = 5$ to 8 derivatives down to –100°C. However, for the butyloxy homologue, a somewhat unusual sequence was found. On first heating, the crystallized solid (A) melts to the mesophase at 70°C; this transforms to the isotropic liquid at 83.6°C. When the mesophase is kept between 70 and 83°C for some time (of the order of an hour), it gradually solidifies to give another solid polymorph B. This solid melts directly to the isotropic liquid at 86.5°C, while cooling the liquid results in the mesophase. The mesophase readily supercools and on fast cooling it yields solid A, which, if left above 35°C for several hours, is transformed to the B form. No such transformation is observed below 35°C. These results are summarized in the schematic free energy diagram in figure 1. This phase behaviour was confirmed by X-ray measurements. The diffractograms observed for the two crystal polymorphs, A and B, are shown in figure 2. The patterns for the two solids are clearly different, but no attempt was made to interpret the results in terms of crystal structures.

The mesophases of the $n = 6$ to 8 homologues also

Table 1. Phase sequences of the octa-*n*-alkoxydibenzopyrene (DBP*n*) homologues studied in the present work and of their equimolar charge transfer complexes with TNF. The thermodynamic data were obtained by DSC on first heating; the transition temperatures were confirmed by polarizing optical microscopy.^a

<i>n</i>		solid/glass	<i>T</i> /°C	ΔH /kJ mol ⁻¹	<i>D</i> _h	<i>T</i> /°C	ΔH /kJ mol ⁻¹	I
4	Cr (A)	●	70	—	●	83.6	3.7	●
4	Cr (B)	●	86.5	39.8	●	—	—	●
5	—	●	-50-0 ^b	broad	●	93.5	4.2	●
6	Cr	●	55.2	48.8	●	89.6	1.3	●
7	Cr	●	43.3	55.9	●	104.3	3.5	●
8	Cr	●	38.3	61.3	●	103.7	4.2	●
4 + TNF	G	●	-34	—	●	290	—	dec.
5 + TNF	G	●	-41	—	●	283	—	dec.
6 + TNF	G	●	-51	—	●	271	—	● (dec.) ^c
7 + TNF	G	●	-53	—	●	260	—	● (dec.) ^c
8 + TNF ^d	G	●	—	—	●	245	—	● (dec.) ^c

^a Cr = crystalline, G = glass, dec. = decomposition.

^b This compound shows a broad endothermic signal. The nature of the low temperature phase (whether crystalline or amorphous) is not clear.

^c Decomposition starts immediately after clearing.

^d Based only on contact preparation.

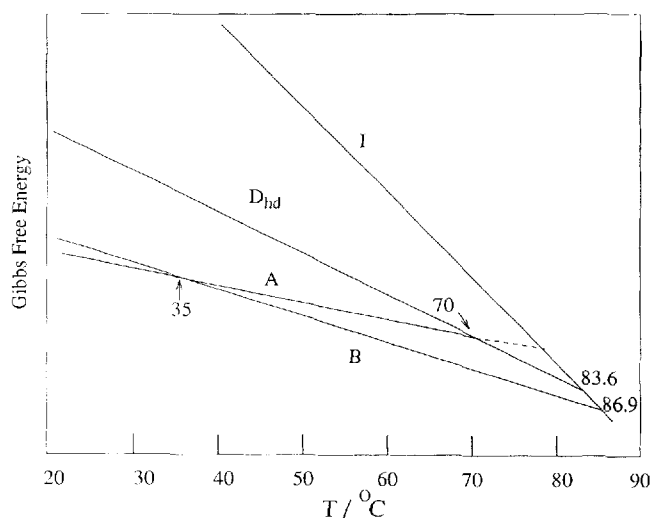


Figure 1. Schematic representation of the Gibbs free energies for the various phases of the DBP4 homologue: A and B, two different solids; *D*_{hd}, hexagonal columnar mesophase; I, isotropic liquid.

supercool easily, but remain stable in that form for long periods (days) before crystallization. The clearing temperatures exhibit a small odd-even effect, while (excluding the pentyloxy derivative) the melting temperatures decrease monotonically with increasing chain length. The abnormal thermodynamic properties of DBP5, in particular the lack of a clear melting transition, may suggest a change in the nature of the packing of the molecules at a chain length of *n* = 5.

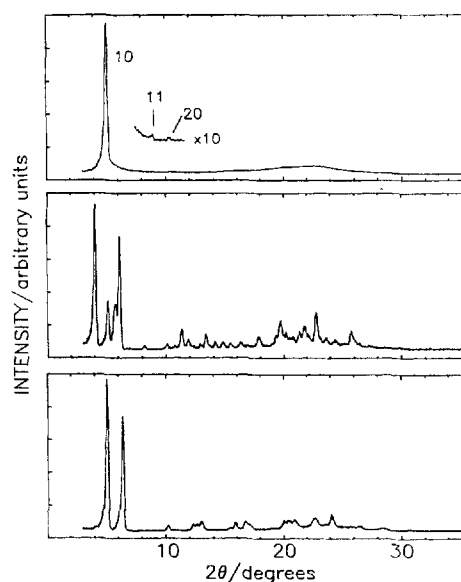


Figure 2. Powder X-ray diffractograms of solid A (bottom), solid B (middle) and the *D*_{hd} mesophase (top) of DBP4. The solid A form was obtained by fast cooling of the mesophase to below 35°C.

3.1.2. X-ray diffractometry

Powder X-ray diffractograms were recorded within the mesophase region for all five homologues as a function of temperature. In all cases three diffraction peaks were detected with *d*-spacings in the ratio 1:1/(3)^½:1/2, which can readily be indexed as the (10), (11) and (20) reflections of a two-dimensional hexagonal lattice. In addition, a broad diffraction at around *d* ≈ 4 Å,

typical of disordered aliphatic chains, is observed, while no peak associated with the stacking periodicity within the columns could be detected. We thus classify the mesophases as of the D_{hd} type. As an example, the X-ray diffractogram of the mesophase of the DBP4 homologue, with assignment of the low angle peaks, is shown in the upper trace of figure 2. The diffraction angles depended slightly on the length of the side chains and had a small temperature dependence. The temperature dependence of the lattice parameters ($a_{hex} = 2d_{10}/(3^{\frac{1}{2}})$) for the various homologues is plotted in figure 3. Their values at a common temperature (75°C) are also summarized in table 2. At a given temperature there is a monotonic increase in a_{hex} as a function of the number of carbons in the side chain. The increase in the unit cell area

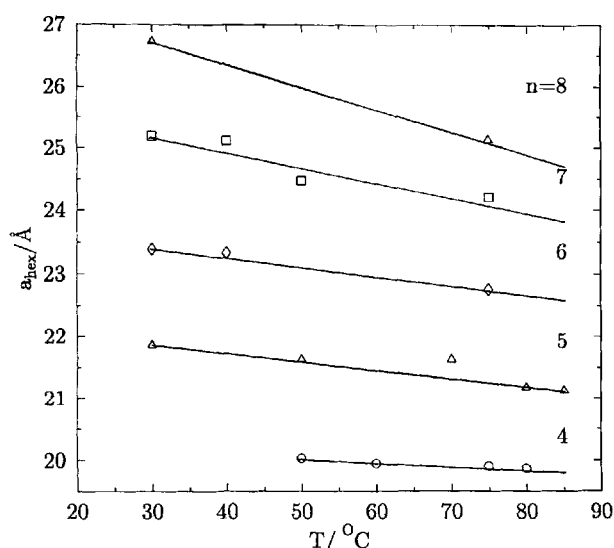


Figure 3. The temperature dependence of the lattice parameter, a_{hex} , in the mesophases of the five DBP n homologues studied. The symbols represent experimental points, while the lines are linear plots which should serve to guide the eye.

Table 2. The lattice parameter a_{hex} for the D_h mesophases of the neat DBP n homologues (at 75°C) and for their corresponding equimolar charge transfer (CT) complexes with TNF (at 72°C).

n	$a_{hex}/\text{\AA}$ neat	$a_{hex}/\text{\AA}$ CT	$d^b/\text{\AA}$ CT
4	19.97	— ^a	— ^a
5	21.36	19.14	3.39
6	22.76	20.01	3.37
7	24.22	21.3	3.40
8	25.80	— ^a	— ^a

^a Not measured.

^b d is the stacking distance in the D_{ho} mesophases of the equimolar charge transfer DBP n /TNF complexes.

corresponds to approximately 8.5\AA^2 per single added CH_2 group.

The results in figure 3 indicate a small but conspicuous decrease in the lattice parameter with increasing temperature for all homologues. The decrease, expressed in terms of transverse linear expansion coefficients, depends on the chain length and ranges from $-0.25 \times 10^{-3} \text{K}^{-1}$ for $n=4$ to $-1.3 \times 10^{-3} \text{K}^{-1}$ for $n=8$. Similar negative transverse thermal expansion coefficients were observed for the D_{hd} phase of oriented strands of hexahexylthiotriphenylene [14(a)] and the smectic A phase of hexa-substituted tribenzocyclonone [14(b)]; from data given in these references values of $-1.7 \times 10^{-3} \text{K}^{-1}$ and $-1.5 \times 10^{-3} \text{K}^{-1}$, respectively, can be calculated. This effect most likely reflects the increase in the chain disorder with increasing temperature. At low temperatures, the fraction of chains which are in the all-*trans*-conformation is larger, resulting in a larger excluded volume, while the chain disorder, introduced on heating, results in better space filling. Whether concomitant changes also occur in the longitudinal dimensions of the columns is not known, because no diffraction peaks corresponding to intracolumnar order are observed. It is noticeable, however, that the negative expansion is small for the lower homologue and becomes larger with increasing length of the side chain, where the degree of disorder becomes more significant.

3.1.3. Deuterium NMR spectroscopy

Two of the DBP n homologues ($n=5,6$) were deuterated in the unsubstituted aromatic sites for deuterium NMR measurements. Examples of spectra for the DBP6 homologue in the solid and (supercooled) mesophase regions are shown in figure 4. A central peak, apparently due to impurities, has been truncated in some of the traces. In the solid phase, the spectrum exhibits a rigid Pake doublet with a quadrupolar splitting of $\nu_Q = \frac{3}{4}(e^2qQ/h) = 137 \text{kHz}$ and a small asymmetry parameter ($\eta=0.07$). In the mesophase region, the line shape changes with temperature and exhibits characteristic features due to molecular reorientation. The motionally averaged spectrum at high temperatures corresponds to a uniaxial Pake doublet with an average quadrupolar splitting of $\langle \nu_Q \rangle \approx 48 \text{kHz}$. Thus, while in the solid state the molecular cores are rigid, in the mesophase they are reorienting at rates comparable to the quadrupole interaction frequency. We were able to simulate the temperature dependent spectra reasonably well using a diffusion model similar to that discussed earlier in connection with some pyramidal liquid crystals [15]. In this model, the molecules are assumed to undergo planar diffusional reorientation around the columnar axis. On the other hand attempts to simulate the spectra with discrete (three- or four-fold) jumps were inconsistent with the

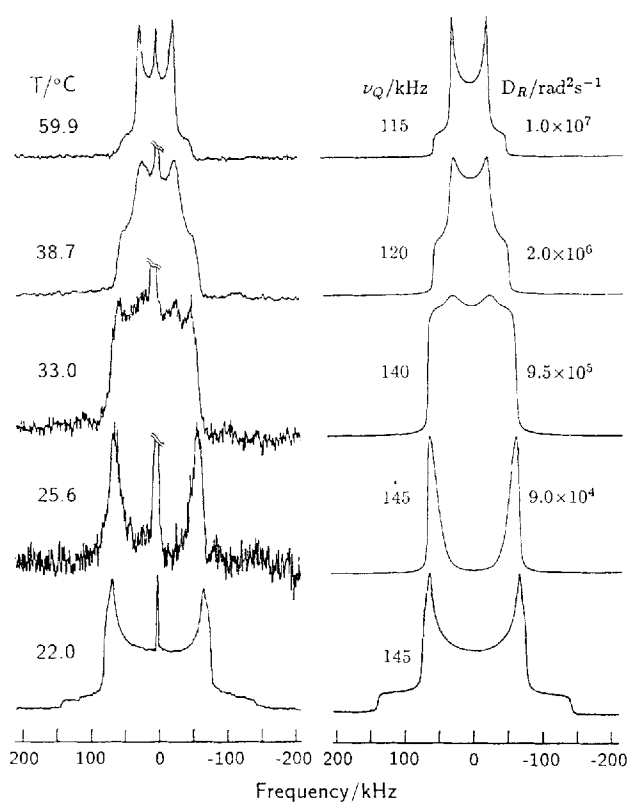


Figure 4. Left: deuterium NMR spectra of a powder sample of deuterated DBP6 at the indicated temperatures; the spectra were recorded by the quadrupole echo sequence with a delay between the two $\pi/2$ pulses of $\tau = 15 \mu\text{s}$; a centre peak due to an isotropic impurity has been truncated in some of the spectra. Right: simulated spectra for the indicated diffusion rates D_R and ν_Q values ($1/T_2 = 5 \times 10^3 \text{ s}^{-1}$).

experiments. Examples of simulated spectra using the planar diffusion model are shown in the right hand column of figure 4. For the final simulation, it was necessary to fit not only the diffusion rate constants D_R , but also the 'static' quadrupolar coupling constant, ν_Q , at each temperature. The fitted values are indicated in the figure. Similar results were also obtained for the $n=5$ homologue. The diffusion rate constants so obtained for DBP5 and DBP6 are plotted versus the reciprocal absolute temperature in figure 5. They correspond to an activation energy of about $75 \pm 10 \text{ kJ mol}^{-1}$.

The ν_Q values used in the simulations of the DBP5 and DBP6 spectra decrease gradually with increasing temperature (cf. figure 4), reflecting a decrease in the orientational order parameter in the mesophase. For perfect ordering, fast molecular reorientation would result in an average $\langle \nu_Q \rangle$ value of exactly $-1/2$ the static one. Hence, from the experimental spectrum, an order parameter of $S = 2 \times 48/140 \approx 0.7$ is calculated for 60°C . This value is rather low for discotic mesophases

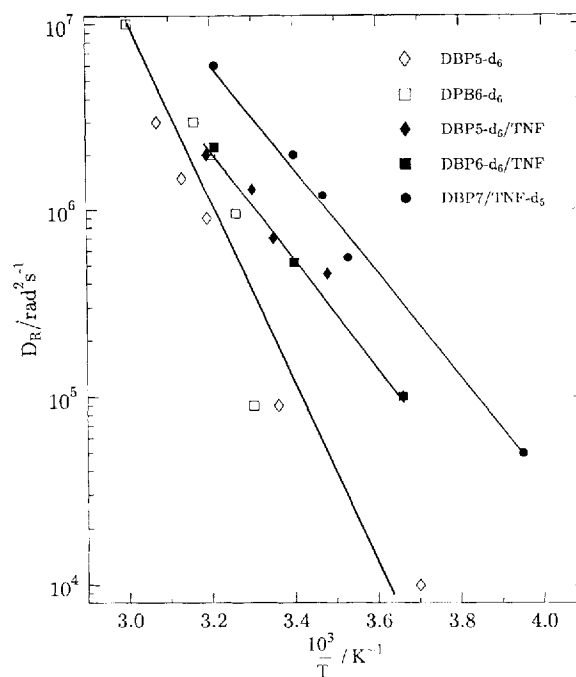


Figure 5. Arrhenius plots for the planar diffusion rate constants, D_R , in the mesophases of neat DBP5- d_6 and DBP6- d_6 , and for the deuterated species in the mesophases of the 1:1 charge transfer complexes DBP5- d_6 /TNF, DBP6- d_6 /TNF and DBP7/TNF- d_5 . The three lines refer, respectively, to the neat DBP n compounds, the DBP n donor molecules in the charge transfer stabilized mesophases, and the electron acceptor TNF in the latter.

of the D_h type. For example in triphenylene discogens, order parameters around 0.9 are more common [16]. The lower values found in the DBP n homologues could result from packing disorder of the molecules within the columns, misalignment of the columns with respect to the mesophase director, or a combination of both. From the NMR results we cannot distinguish between these possibilities.

3.2. The charge transfer complexes

In this section we describe the mesomorphic properties of binary charge transfer mixtures involving the DBP n homologues and the electron acceptor 2,4,7-trinitro-9-fluorenone (TNF). Because of shortage of some of the DBP n compounds, not all mixtures were studied. In the next section, lyotropic ternary mixtures involving these charge transfer complexes and apolar solvents will be discussed.

3.2.1. The phase behaviour of binary DBP n /TNF mixtures

Contact preparations of the DBP n homologues with the electron acceptor TNF (m.p. 176°C) exhibit, on

heating, dark interface zones of highly viscous mesophases. The dark colour of the binary mixture is ascribed to the formation of charge transfer complexes. These charge transfer based mesophases are thermally much more stable than those of the neat discogens. For $n=4$ and 5, the mesophases in the contact zones persist up to 295 and 285°C, respectively, where they decompose, while for the $n=6, 7$ and 8 homologues the maximum clearing temperatures are 270, 260 and 245°C, respectively. These mixtures start to decompose immediately after clearing. For several related discotic systems with charge transfer based mesophases, maximum stability was found for equimolar donor-acceptor mixtures [6(a),(b), 7, 8]. To check whether this is also the case here, we have determined the phase sequences of 1:1 mixtures of the DBP n homologues with TNF. In all cases, the clearing (or decomposition) temperatures indeed matched those observed in the contact preparations (cf. table 1) indicating that there, too, the equimolar mixtures are most stable. On cooling the isotropic liquid of such 1:1 mixtures, one usually observes star shaped homeotropic domains with hexagonal symmetry and fan-shaped textures characteristic of D_h mesophases. On further cooling, they evolve into mosaic textures with high birefringence. These binary mixtures do not show any endothermic melting peak in the DSC, but rather glass transitions at around -30 to -50°C . A schematic representation of the DBP n /TNF binary phase diagram is shown for the $n=7$ homologue in figure 6.

3.2.2. X-ray diffraction of the mesophases of the equimolar DBP n /TNF complexes

The powder X-ray diffraction of the mesophases formed by equimolar DBP n /TNF mixtures for the $n=5, 6$ and 7 homologues was measured at 20°C and 72°C. All mixtures exhibited similar patterns, which in view of the above discussion, we interpret on the basis of a two-

dimensional hexagonal symmetry. In the low angle regime, all mixtures with the exception of the $n=7$ homologue, exhibit only one sharp peak which we identify as the (10) diffraction. For DBP7, a weak diffraction peak associated with the (11) reflection could also be detected. The lack of higher order diffraction peaks is not unusual for charge transfer based D_h mesophases. The lattice parameters, a_{hex} , derived from these low angle peaks (at 72°C) are included in table 2. It is noteworthy that these lattice parameters are somewhat smaller than those for the corresponding neat mesophases, and contrary to the latter, their dependence on the chain length and on the temperature is quite small. This difference may reflect the lower density in the aliphatic periphery of the columns in the charge transfer stabilized mesophases due to the intercalation of the TNF molecules, resulting in smaller excluded volume effects at the beginning of the side chains and easier interlacing of the remaining parts of the chains.

In the wide angle regime on the imaging plate, two additional diffraction rings were observed: a very broad one at 4.4 Å, characteristic of scattering from disordered liquid-like alkyl chains, and a less broad peak corresponding to a d -spacing of about 3.4 Å. We identify the latter as the stacking distance between the aromatic moieties within the columns. The measured values for these stacking distances are also shown in table 2. The fact that such diffraction peaks are observed at all indicates high ordering within the columns and classifies the mesophases formed by the DBP n /TNF charge transfer mixtures as D_{ho} . It should be realized that this additional classification as an ordered columnar phase is only qualitative, meaning that the columns are more ordered than in similar D_h mesophases, where such diffraction peaks are not detected, as in those of the neat DBP n compounds, which are therefore labelled D_{hd} (for disordered). From the width of the 3.4 Å reflections ($\Delta 2\theta \approx 0.025$ radians) a minimum correlation length for the columns in the D_{ho} mesophases of about 63 Å (~ 19 molecules) can be calculated, which is similar to values determined for other charge transfer stabilized mesophases [17].

This increase in the positional stacking order relative to those of the neat DBP n discogens and the stability maximum at the 1:1 electron donor to acceptor ratio suggest an alternating stacking of the DBP n and TNF molecules within the mesophase columns. A stronger support for this model comes, however, from the observation of a weak and broad diffraction maximum which corresponds to a d -spacing of ~ 6.7 Å in the mesophase of a 1:1 DBP5/TNF mixture. This sample was partially aligned, resulting in broad diffraction arcs with the maxima of the 3.4 Å diffraction at a 90° offset from that due to the (10) reflection. The identification of the 6.7 Å arc as due to intracolumnar scattering is confirmed by

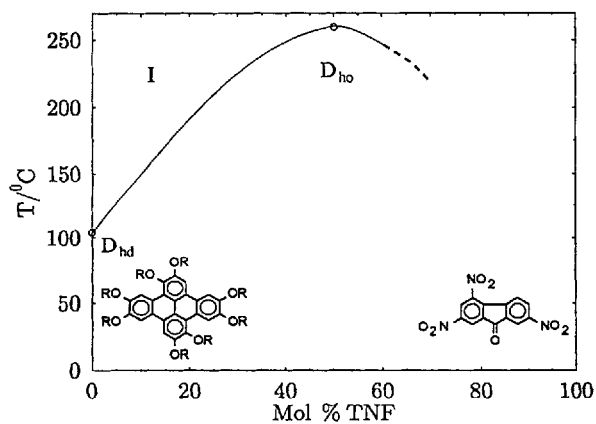


Figure 6. Schematic representation of the binary DBP7/TNF phase diagram.

the fact that its orientation profile corresponds to that of the 3.4 Å ring. We attribute the 6.7 Å peak to the periodic DBP5/TNF stacking. The very fact that this diffraction is observed emphasizes the dissimilarity in the electron density of the donor and acceptor molecules. A careful examination of the diffractogram of the 1:1 DBP7/TNF mesophase also revealed hints of the presence of a 6.7 Å ring. X-ray diffraction peaks corresponding to such alternating stacking were also observed in some complexes of alkyloxytriphenylene derivatives with TNF [5(b),(e)].

3.2.3. Deuterium NMR of equimolar charge transfer mixtures DBP n /TNF

Deuterium NMR spectra were recorded of equimolar DBP n -d $_6$ /TNF mixtures for $n=5, 6$ and for DBP7/TNF-d $_5$. In the mesophase region, the spectra exhibit dynamic features typical of planar reorientational diffusion, as found for the mesophases of the neat DBP n compounds. Examples of spectra for both types of deuteriated molecules, together with corresponding simulations, are shown in figure 7. The small splitting in the high temperature (140°C) spectrum in figure 7 is ascribed to an inequivalence of the deuterons in sites 3, 4 and 7 of the dibenzopyrene core. This inequivalence was incorporated in the simulation by superposing two subspectra with similar dynamic parameters, but different quadrupole couplings, $\nu_Q^1 = 141$ kHz, $\nu_Q^2 = 122$ kHz with relative intensities of 2:1, respectively. The fit between the experimental and simulated spectra is quite satisfactory, providing strong proof for the planar diffusion model. Particularly

sensitive to this mechanism is the ratio of the ‘horns’ to the central ‘trough’ in the spectra, which is well reproduced by the simulations. The diffusion rate constants D_R derived from the simulation are included in figure 5. In general they are somewhat higher in the mesophases of the charge transfer complexes than in those of the neat compounds. The D_R values for the (chainless) TNF acceptor are only slightly higher than for the heavier (DBP n) donor molecules. This suggests that the motion of the acceptor and donor molecules in the charge transfer based mesophases is correlated.

From the high temperature (140°C) spectrum, an orientational order parameter of $S=0.93$ can be calculated for the DBP6-d $_6$ molecule in the mesophase of the DBP6/TNF mixture. A similar value ($S \approx 1$) was found for TNF-d $_5$ in the corresponding DBP7/TNF mixture. These values may be compared with $S \approx 0.7$ determined for the neat DBP n mesophases and show that in these systems, at least, increase in ordering goes hand in hand with increased stability.

3.3. Lyomesophases of the equimolar charge transfer mixtures with alkanes

Recently an interesting observation was made, concerning the mesomorphic self association of disc-shaped compounds and especially their charge transfer complexes with strong electron acceptors such as TNF. It was found that the addition of an apolar organic solvent to mesogens aggregating into columnar structures of suitable stability leads to the formation of nematic

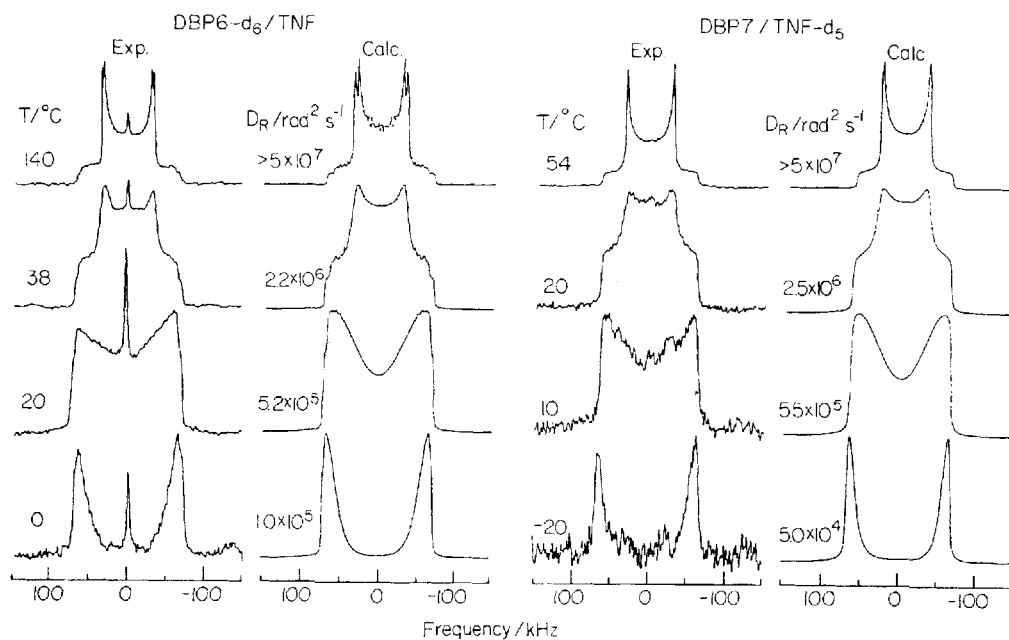


Figure 7. Experimental and simulated quadrupole echo ($\tau=20\mu\text{s}$) deuterium NMR spectra as function of temperature in the mesophases of the 1:1 DBP n /TNF binary systems indicated. Other details as in figure 4.

columnar (N_C) mesophases. This type of lyomesomorphism with alkane solvents has been observed in some discotic systems, including metallo-discogens and charge transfer complexes [7, 9, 10]. Following these observations we have also studied the effect of adding alkane solvents to the equimolar DBP n /TNF charge transfer mixtures. Because of shortage of material, only homologues with $n=5, 6$ and 7 were used. Contact preparations for the $n=6, 7$ homologues with tridecane ($C_{13}H_{28}$) showed the formation of nematic phases with typical schlieren textures, thermal fluctuations and high fluidity. The equimolar DBP5/TNF mixture exhibited a nematic mesophase only with lower alkanes such as heptane and iso-octane, but not with tridecane. All nematic phases were stable down to room temperature. The maximum clearing temperature was found to be 88°C for DBP5/TNF/heptane, 60°C for DBP6/TNF/tridecane and 62°C for DBP7/TNF/tridecane. A schematic representation of a pseudo-binary phase diagram of such a ternary system (not including the bi- or tri-phasic regions) is shown in figure 8.

To determine the nature of these nematic phases, in particular whether their mesogenic units consist of isolated molecules or charge transfer pairs, forming the nematic discotic (N_D) type, or of columnar aggregates in a nematic columnar (N_C) type, X-ray diffractograms were taken of suitable mixtures. To ensure that the mixtures contain minimal amounts of the D_{ho} mesophase, samples with relatively high alkane contents were prepared. Indeed, in ternary mixtures of the $n=6$ and 7 homologues, containing ~ 38 wt % tridecane, no (10) peaks due to the D_{ho} phase were detected. Instead, broad low angle diffraction maxima were observed, corresponding to $d=22.7 \text{ \AA}$ and 27.2 \AA for the $n=6$ and 7 homologues, respectively. Also observed were broad haloes at 4.5 \AA , related to scattering from alkyl chains, and relatively narrower reflections at 3.39 \AA ($n=6$) and

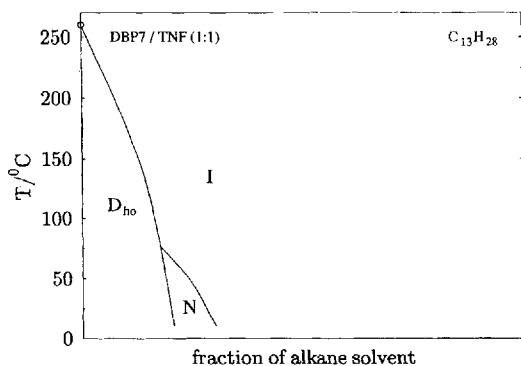


Figure 8. Schematic representation of the pseudo-binary phase diagram of the system consisting of the equimolar DBP7/TNF charge transfer complex (left) and tridecane (right).

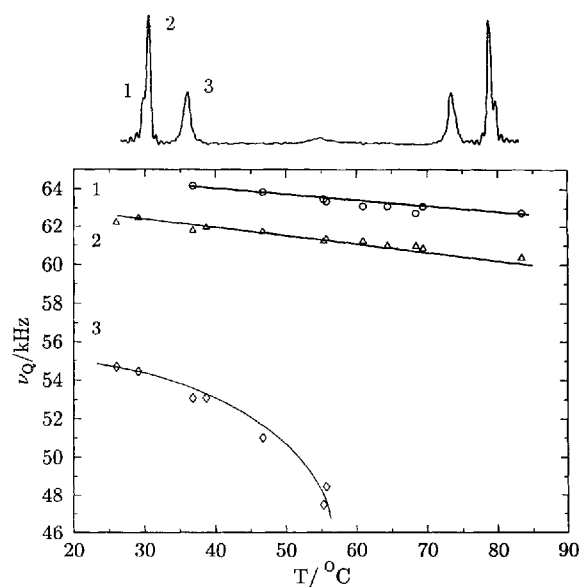


Figure 9. Top: the deuterium NMR spectrum for a ternary mixture containing about 65 wt % of the equimolar charge transfer complex DBP7/TNF- d_5 and 35% tridecane at 55°C ; peaks 1 and 2 are due to the D_{ho} phase, while peak 3 corresponds to the N_C phase in the biphasic mixture. Bottom: plots of the quadrupolar splitting in the above mixture as function of temperature.

3.31 \AA ($n=7$). We attribute the latter to the intracolumnar stacking periodicity, and thus identify the nematic mesophases in these mixtures as N_C . From the width of these peaks a minimum correlation length of $\sim 50 \text{ \AA}$ for the intracolumnar stacking can be estimated.

Deuterium NMR spectra were recorded of a ternary mixture containing a 1:1 DBP7/TNF- d_5 mixture and about 35 wt % tridecane. This mixture is biphasic (D_{ho} and N_C) as confirmed by the spectrum shown at the top of figure 9. The spectrum exhibits an outer, weakly split, doublet due to the TNF- d_5 deuterons in the D_{ho} phase and an inner doublet, with somewhat broader peaks due to the N_C phase. This assignment is confirmed by the observation that addition of the alkane solvent results in a decrease in the relative intensity of the outer doublet and a corresponding increase in the inner one. The splitting in the signal of the D_{ho} phase corresponds to two doublets with intensity ratio 1:4 and reflects slight inequivalence of the TNF- d_5 deuterons, with the weaker component probably due to deuteron 3 (which sits between two nitro groups) and the more intense one due to the rest of the deuterons. In the spectrum of the nematic phase, these signals are not resolved, apparently due to the larger width of the peaks in this phase. The fact that well defined doublets are observed in these spectra indicates that the sample aligns in the magnetic field. On the basis of earlier work on similar systems, we can safely assume that the director, i.e. the column,

aligns perpendicular to the magnetic field ($\Delta\chi < 0$) [16]. The temperature dependence of the doublet splittings is shown in Fig. 9. It may be seen that, while the deuterium splittings in the D_{ho} phase are fairly constant, those in the nematic phase decrease appreciably with increasing temperature. This different temperature dependence is typical of discotic columnar and nematic phases, respectively [16]. From the splittings observed in the two phases, the corresponding order parameters for the TNF- d_5 molecules can be determined. In the D_{ho} phase S is nearly constant at ~ 0.9 , while in the N_C phase, the order parameter drops from ~ 0.8 at room temperature to ~ 0.7 at the clearing temperature ($\sim 60^\circ\text{C}$). Deuterium NMR measurements were also made on the system DBP6- d_6 /TNF (1:1) and tridecane (~ 35 wt %). This mixture is predominantly nematic and exhibits just one quadrupolar doublet with a temperature dependent splitting similar to that found for the N_C phase in figure 9.

4. Summary and conclusion

We have shown that neat DBP n homologues with $n = 4$ to 8 are discogenic, exhibiting a hexagonal columnar mesophase. Unlike many other discotic mesogens forming columnar mesophases, where molecular reorientation within the columns is very fast on the NMR time scale, the DBP n mesophases display reorientation rates which are slower and fall within the range amenable to detailed NMR line shape analysis. Such an analysis showed that the reorientation is diffusive, indicating that there is no azimuthal order within the columns. The lack of a diffraction peak at around 3.5 \AA indicates that there is also no stacking order within the columns. Hence we classify these mesophases as D_{hd} .

Addition of the electron acceptor TNF to the electron rich DBP n compounds results in the formation of charge transfer complexes, which also exhibit D_h mesophases. These mesophases have a wider stability range than those of the corresponding neat homologues. Their stability is maximized when the donor/acceptor ratio is unity, with clearing temperatures 150 to 200 K higher than those of the neat donors. The orientational order parameter of the aromatic cores of both the donor and acceptor molecules in these mesophases is high and they also exhibit well defined stacking order within the columns; hence they are classified as D_{ho} . We were also able to show that the intracolumnar stacking of the donors and acceptor molecules in these mesophases is alternating. Despite their high order, molecules in these charge transfer based mesophases undergo fast diffusive reorientation, with similar rates for the donor and acceptor molecules. These rates are somewhat higher than in the corresponding mesophases of the neat DBP n compounds.

An especially interesting property of these charge

transfer complexes is their tendency to form nematic columnar (N_C) mesophases when mixed with apolar organic solvents such as alkanes. The general phase behaviour of these ternary, or more precisely pseudo-binary (if one considers the 1:1 charge transfer complex as a single species), systems resembles that of other lyotropic systems composed of disc-shaped mesogens or their charge transfer complexes with alkane solvents [7, 9, 10]. This type of lyomesomorphism shows strong resemblance to that of the so called chromonic mesogens in aqueous systems [18], especially those based on a central core surrounded by polyethyleneoxy chains [18(a),(b)]. The nematic lyomesophase of the DBP n /TNF complexes with tridecane is the first non-aqueous example for which the columnar structure of the nematogenic units could be proven, due to the fortunate fact that they exhibit a stacking reflection in the X-ray measurements. The intracolumnar minimum correlation length in this N_C phase is only about 10–15% shorter than that in the D_{ho} phase of the equimolar DBP n /TNF complexes, suggesting that the solvent affects predominantly the intercolumnar arrangement.

The octa-alkyloxy dibenzopyrene discogens, and the mesomorphic multicomponent systems derived from them, provide the first case of a detailed examination of the main aspects of mesophase variation/manipulation based on the same series of discotic compounds. Our X-ray diffraction and deuterium NMR results concerning the mesophases of DBP n /TNF charge transfer complexes strongly support the intercalation model proposed earlier [5], in which the donor and the acceptor molecules have a regular alternate stacking order within the columns, see figure 10. Moreover, the similarity in the planar diffusion rates of the electron donor and acceptor molecules in the charge transfer induced mesophases, despite the big difference in their size, suggests that their dynamic behaviour is correlated. This might indicate that, in addition to the regular and alternating stacking, there is also some azimuthal correlation between the donor and acceptor molecules within the plane perpendicular to the column axis. While addition of an electron acceptor to the neat DBP n mesophases predominantly affects the intracolumnar interactions, addition of an alkane solvent to the charge transfer based mesophases mainly changes the intercolumnar aggregation and has only a minor influence on the intracolumnar stacking, as shown schematically by the second step in figure 10.

The results presented here, in combination with other reports on mesophase stabilization/induction in binary or ternary systems [4–10], allow some general conclusions concerning the mesomorphic self-organization of disc-like compounds. The columnar aggregation of disc-like molecules in columnar mesophases can readily be

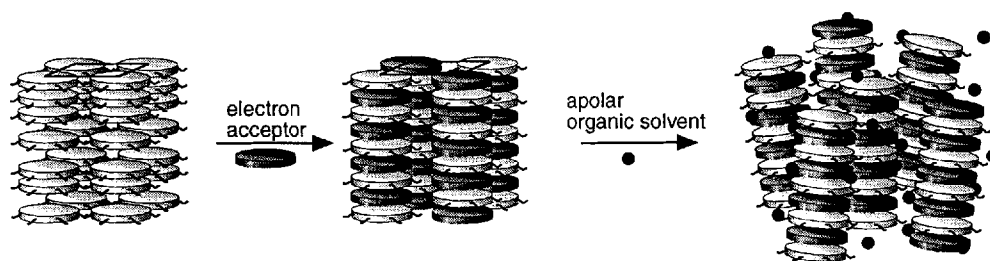


Figure 10. A schematic representation, reading left to right, of the D_{hd} mesophase of the neat DBP_n homologues, the regular alternate D_{ho} mesophase of DBP_n/TNF charge transfer complexes, and the N_c lyomesophase formed in the pseudo-binary system, equimolar DBP_n/TNF with an alkane solvent.

explained in terms of anisotropic attractive and repulsive dispersive forces [19]. For real discogens, the anisotropy of the interaction profile due to the molecular shape is modified by the different parts of the molecules, for example the aromatic core region versus the aliphatic periphery and/or the presence of specific functional groups. However, it seems that for a qualitative discussion of most systems, a separation into an intracolumnar potential and an intercolumnar potential is sufficient. Neat discogens, as for example the DBP_n homologues studied here, show only one type of potential along their column axis. The ordered or disordered nature of a columnar phase depends on the width of the potential minimum in this description, while the thermal stability reflects the depth of the minimum. For most of the known mesogens forming columnar mesophases, the stability of columnar aggregates seems to be insufficient to support the formation of nematic columnar phases. This type of mesophase is usually observed when specific interactions such as enhanced π - π interactions with an electron acceptor [5(d),6(a),(b),7,10], hydrogen bridging of amide groups [9(a),(f),20] or metal-ligand interactions [9(b)-(e),10] are present.

For charge transfer induced or stabilized columnar phases, three types of intermolecular interactions—donor/donor, acceptor/acceptor and donor/acceptor—must be considered. In the case of intercalation of electron acceptors, like TNF, the mixed interaction is the dominant one, with a deeper and narrower potential minimum than for the donor/donor combination of the neat mesogen, leading to alternating stacking and increased stability and intracolumnar positional order. A dominance of the donor/donor and/or acceptor/acceptor interactions might lead to the formation of separate columnar aggregates of the donor and acceptor compounds, a type of self-organization discussed for mesomorphic tetracyanoquinodimethane (TCNQ) complexes of dithiapyranylidene derivatives [4] and well known in crystalline charge transfer complexes. The addition of an alkane solvent to a mesomorphic system built of columns of sufficient stability and surrounded

by aliphatic chains reduces the intercolumnar interaction; the potential minimum normal to the column axis becomes flattened and broadened, resulting in the formation of a nematic columnar mesophase and finally an isotropic solution of columnar aggregates. This behaviour is well known for the so-called chromonic lyomesogens in aqueous systems [18(c)]. A similar manipulation of the intercolumnar aggregation is possible by attaching long chains as a steric restraint to one of the components in discotic donor-acceptor systems [5(d),6(a)].

The picture given above is of course oversimplified; nevertheless, the type of reasoning presented may be helpful for considering other ways of manipulating the mesomorphic self-aggregation of mesogens.

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