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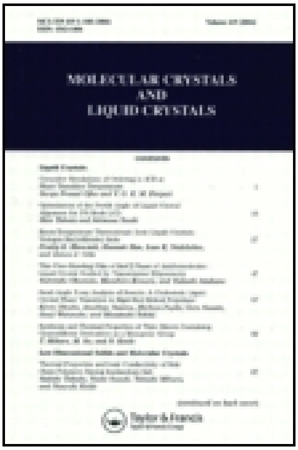

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A COMPARISON OF CPI AND CHARGE-TRANSFER TWO-COMPONENT COLUMNAR PHASES

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The phase diagram for the binary mixture of 2,3,6,7,10,11-hexakis (4′-nonylphenyl) triphenylene and 2,3,6,7,10,11-hexakis(hexyloxytriphenylene) shows formation of a 1:1 compound with a higher clearing temperature and a greater mesophase range than either of the individual components. This and related CPI (Complementary Polytopic Interaction) compounds are compared to 'charge transfer compounds' formed on adding 2,4,7-trinitrofluoen-9-one (or one of its derivatives) to a 2,3,6,7,10,11-hexaalkyloxytriphenylene (or other discogen). There are significant differences between the actual phases formed but in terms of the local molecular packing and in terms of the stabilising interactions involved they are essentially the same. Both can be rationalised using the XED (extended electron distribution) model. In this it is assumed that dispersed coulombic and van der Waals interactions dominate and that other contributions are small.

Keywords: charge transfer; CPI; discotic liquid crystals; TNF

INTRODUCTION

The stability of the columnar mesophase of 2,3,6,7,10,11-hexakis(pentyloxy) triphenylene **1a** (HAT5) or of 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene **1b** (HAT6) can be substantially enhanced by adding either one mole of 2,4,7-trinitrofluoen-9-one **2** (TNF) or one mole of 2,3,6,7,10,11-hexakis(4′-nonylphenyl)triphenylene **3a** (PTP9). There are some similarities between the HAT:TNF and the HAT:PTP systems. For example, both involve intercalation of the additive into the HAT columnar structure (Fig. 2) and both involve similar stabilising intermolecular interactions but there are significant differences between the phases obtained.

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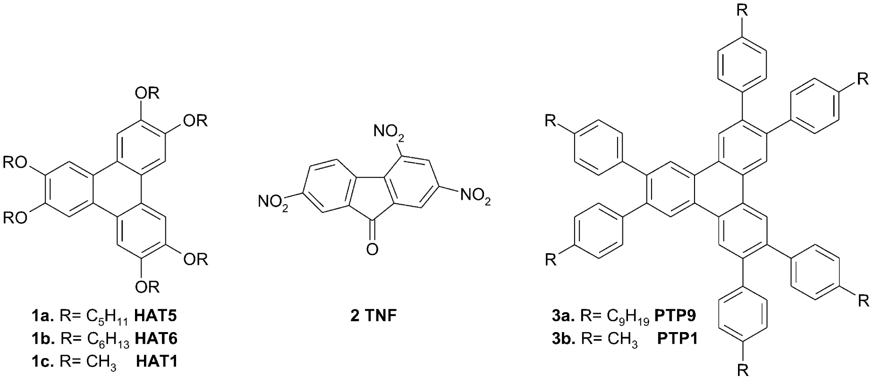

1a. R= C_5H_{11} **HAT5**
1b. R= C_6H_{13} **HAT6**
1c. R= CH_3 **HAT1**

2 TNF

3a. R= C_9H_{19} **PTP9**
3b. R= CH_3 **PTP1**

FIGURE 1 Formulae of compounds forming CPI and charge and transfer two-component columnar phases.

The range of the Col_h mesophase of HAT5 **1a** is 69–122°C [1] and that of a 50:50 mixture of HAT5 **1a** and TNF **2** is 49–232°C [2]. As shown in Figure 3, the phase diagram for HAT6:TNF has a relatively sharp maximum in the clearing temperature/composition curve close to ~40 mol% TNF but at 100°C the two components are fully miscible between 0 and 60 mol% TNF [3]. Equivalent phase diagrams for other TNF derivative/discogen mixtures show that, the maximum in the clearing temperature/composition curve can occur at compositions quite different to 50:50 and they often give a stable homogeneous columnar phase over a wide range of compositions [4]. X-Ray diffraction data for these materials has been interpreted in terms of the columnar structure shown schematically in Figure 2 and it is found that addition of TNF induces increased order in the mesophase. Low-angle X-ray diffraction studies of the Colh phase of HAT5 show a 100 reflection at 19.0 Å, 110 at 11.0 Å and 001 at 3.6 Å [5]. In HAT5:TNF mixtures the 200 reflection is also seen and the intercolumnar correlation length in 75:25

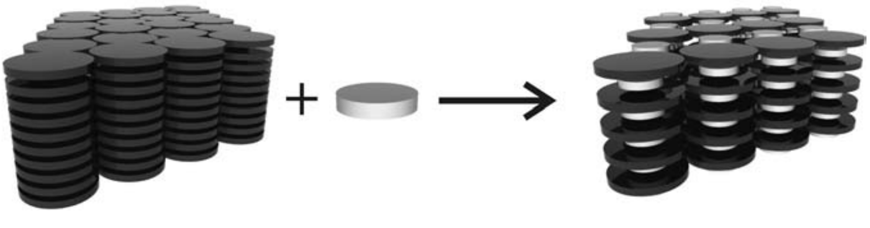

FIGURE 2 Schematic representation of the columnar phase formed by intercalating TNF or PTP into the Col_h phase of HAT.

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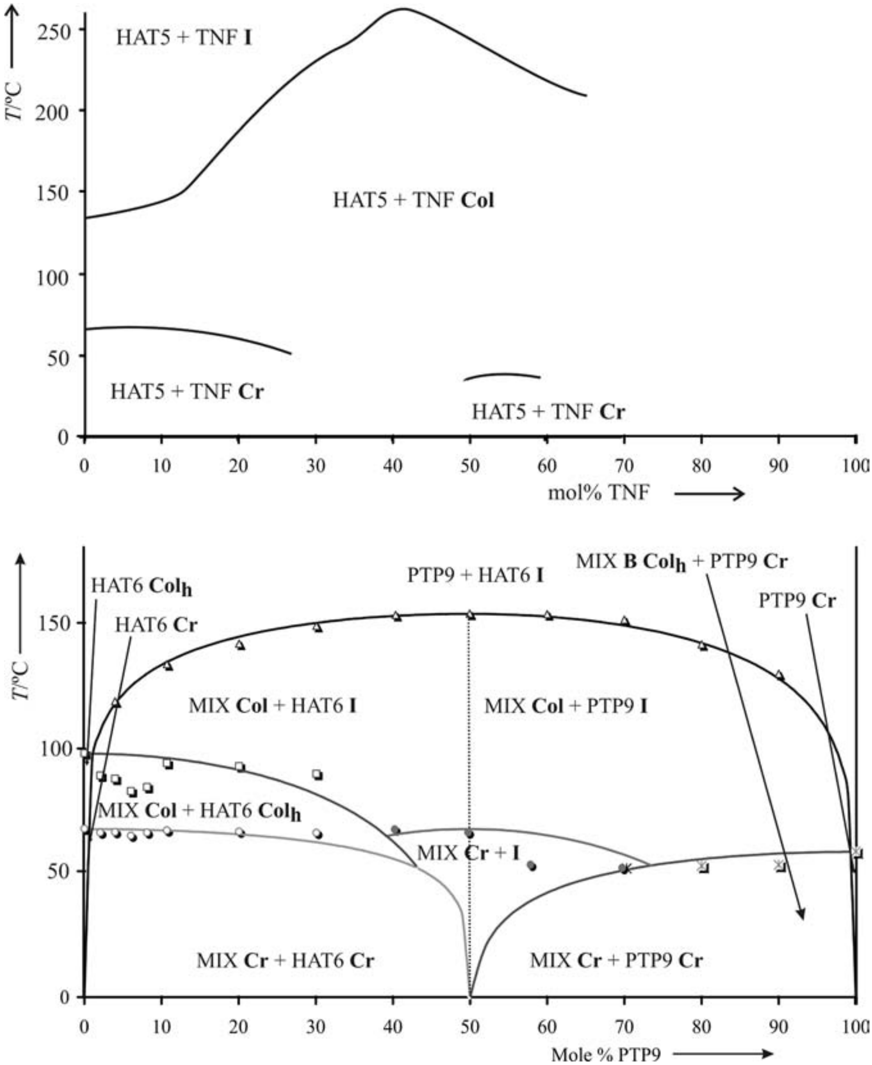

FIGURE 3 Phase diagrams of (top) HAT5 **1a** : TNF **2** (adapted from reference 3) and (bottom) HAT6 **1b** : PTP9 **3a**$^{(12)}$. The term MIX refers to the 1:1 compounds formed between HAT6 **1b** and PTP9 **3a**. Details of how the phase diagram was constructed are given in the experimental section.

HAT5:TNF is about twice that in HAT5 at the same temperature [3]. The experimental difference between the first oxidation potential of HAT and the first reduction potential of TNF is 1.17 V and when HAT5 is mixed with

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TNF in heptane a brown solution is formed [6]. A broad charge transfer band is observed in the uv/vis. spectrum at 496 nm (shoulder 600 nm) [2]. The original literature on discogen/TNF mixtures ascribed the stability of the discogen/TNF pair to this charge-transfer interaction stressing that the discogens are good electron donors whereas TNF is an electron acceptor [4,7]. However, more recently this view has been revised in line with a reinterpretation of bonding in charge transfer complexes in particular and pi-stacked systems in general. It is now recognised that the energetic contribution of the charge transfer interaction is relatively small in the ground state and that van der Waals and coulombic terms dominate [8]. Hence Bates and Luckhurst have developed a model for the benzenemultiyne: TNF pair based on the fact that the discogen molecules and TNF molecules have opposite (attractive) net quadrupole moments [9]. We have suggested a similar model for the same system in which a dispersed rather than net quadrupole moment is invoked [10].

RESULTS AND DISCUSSION

The $\mathrm{Col_h}$ mesophase range of HAT6 **1b** is 70–100°C [1] and that of a 50:50 mixture of HAT6 **1b** and PTP9 **3a** from below room temperature to 154°C [11]. The phase diagram is shown in Figure 3. It exhibits a broad maximum in the clearing temperature/composition curve centred on the 50:50 composition. The two-phase regions are very broad and compositions only a little different to 50:50 result in phase separation. Unlike HAT and TNF, excess HAT or PTP have very limited solubility in the corresponding 50:50 mixture.

Low-angle X-ray diffraction studies of the $\mathrm{Col_h}$ phase of HAT6 show a 100 reflection at 19.5 Å, 110 at 11.2 Å and 001 at 3.6 Å. The columnar phase for the HAT6:PTP9 mixture at 110°C shows many reflections:- 23.3 Å (100), 13.7 Å (110), 11.9 Å (200), 7.6(300), 7.1 Å, 6.6 Å (220), 6.1 Å (310), 5.8 Å (400), 5.3 Å (320), 5.0 Å (500), 4.5 Å (330), 4.2 Å (510), 4.0 Å (600) 3.6 Å(001), 3.5 Å [12]. This is also interpreted in terms of a hexagonal columnar phase in which the HAT6 and PTP9 molecules alternate within the stack (Fig. 2). It is clearly a phase which is much more ordered than the $\mathrm{Col_h}$ phase of HAT6 but whether some of these reflections correspond three dimensional ordering and hence a plastic phase [13] is not yet wholly clear. In a practical sense it behaves like a $\mathrm{Col_h}$ phase. It is readily sheared, aligns in a homeotropic manner between glass slides when annealed, and giving TOF photoconduction transit indicative of an absence of deep trap grain boundaries [14]. When HAT6 is mixed with PTP9 in heptane there is no change in colour and no charge transfer band is observed in the UV/visible spectrum [11]. The measured energy difference between first

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oxidation potential of HAT and the first reduction potential of PTP shows this to be at least 1.69 V [6]. The stability of the discogen/PTP pair cannot be ascribed to a charge-transfer interaction. Neither can it be ascribed to matching attractive net quadrupole moments since the signs of the net quadrupole of HAT and PTP are the same (Table 1).

We have studied a wide range of HAT derivatives and PTP derivatives and shown that in some cases stable 50:50 mixtures are formed but not in others. The formation/non-formation of a stable 'compound' can be rationalised using the CPIXED (extended electron distribution) model and so far this has proved to be the only reliable 'predictive' tool [15]. In this model the pi stacking interaction is expressed as a sum of atom-centred van der Waals and coulombic (pole + dipole + quadrupole) terms. It is a CPI (*c*omplementary *p*olytopic) interaction involving matching interactions between many sites within the two components. By comparison of the energies U_{AA} of the homo-dimers of HAT1 (**1c** + **1c**), TNF (**2** + **2**), and PTP1 (**3b** + **3b**) with the energies U_{AB} of the hetero-dimers **1c** + **2**, and **1c** + **3b** it is clear that mixed stacks rather than segregated stacks are favoured in both cases (Table 3) i.e., ΔE_{total} is negative where;

$$\Delta E = U_{AB} - (U_{AA} + U_{BB})/2$$

Not only can the CPI model be used to explain the formation/non-formation of these systems but also the stability and structure, of other so-called 'charge-transfer' complexes as well of aromatic hydrocarbon/aromatic fluorocarbon mixed stacks [10]. The predicted structures of the dimers of HAT with TNF or PTP are shown in Figures 4 and 5 and the interaction energies are given in Table 2.

The TNF molecules in the homodimer (Fig. 4) are predicted to lie with the aromatic cores more-or-less in parallel with the net dipoles opposed. In the TNF + HAT1 heterodimer the TNF molecules are arranged in such a way as to place two nitro groups and the carbonyl group over the triphenylene nucleus.

TABLE 1 Summary of the Net Molecular Quadrupole Moments for HAT1 **1c**, TNF **2** and PTP1 **3b**. The Quadrupole Moments were Calculated at the PM3 Level on the Minimum Energy Conformation Produced by the COSMIC Conformational Search Engine

Molecule	Net quadrupole moment (eÅ^2)	Compound formed with HAT
HAT1	−24.6	
TNF	67.1	Yes
PTP1	−71.2	Yes

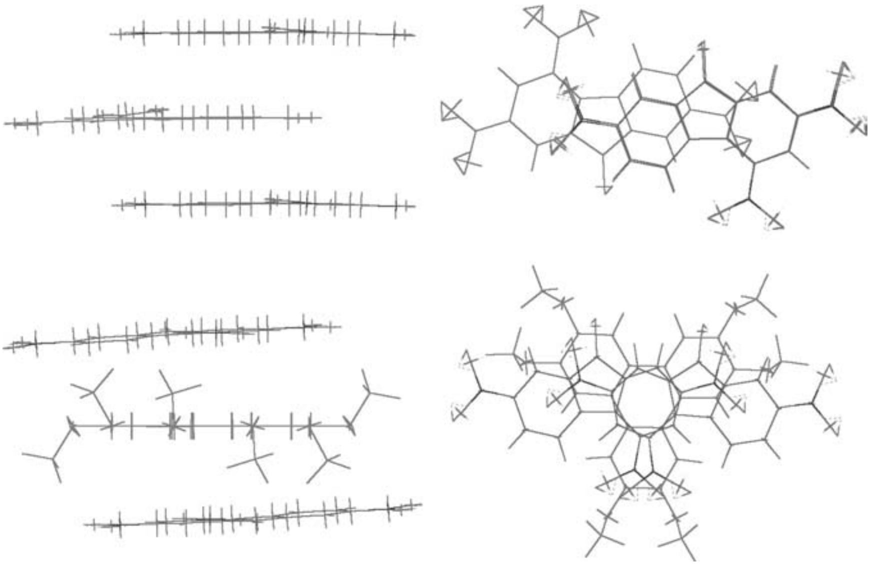

FIGURE 4 Minimum energy geometries for the TNF + TNF homodimer (top) and the TNF + HAT1 heterodimer (bottom). In each case the two lowest energy minimum sites for the mobile TNF are shown: one above and one below the spatially ‘fixed’ TNF or HAT molecules.

In the PTP1 homodimer (Fig. 5), the non-planar nature of the molecule makes it impossible to obtain a stack in which the triphenylene cores lie parallel to each other but in the TNF + HAT1 heterodimer this is possible to achieve and the two molecules fit in such a way that the peripheral phenyl groups on the PTP nucleus fit neatly into the ‘gaps’ in the HAT nucleus.

CONCLUSIONS

Despite significant differences between to phase diagram obtained, there are some similarities between the HAT + TNF and the HAT + PTP systems. Both involve intercalation of the additive into the HAT columnar structure (Fig. 2). Furthermore it is possible to treat bonding within the HAT + TNF, the HAT + PTP and the aromatic hydrocarbon/fluorocarbon systems in the same way [16]. It is becoming clear that, in designing alternating A/B columnar arrays, we are not confined to ‘A = electron rich donor and B = electron poor acceptor’ charge transfer pairs and it seems likely that many non donor/acceptor pairs remain to be discovered.

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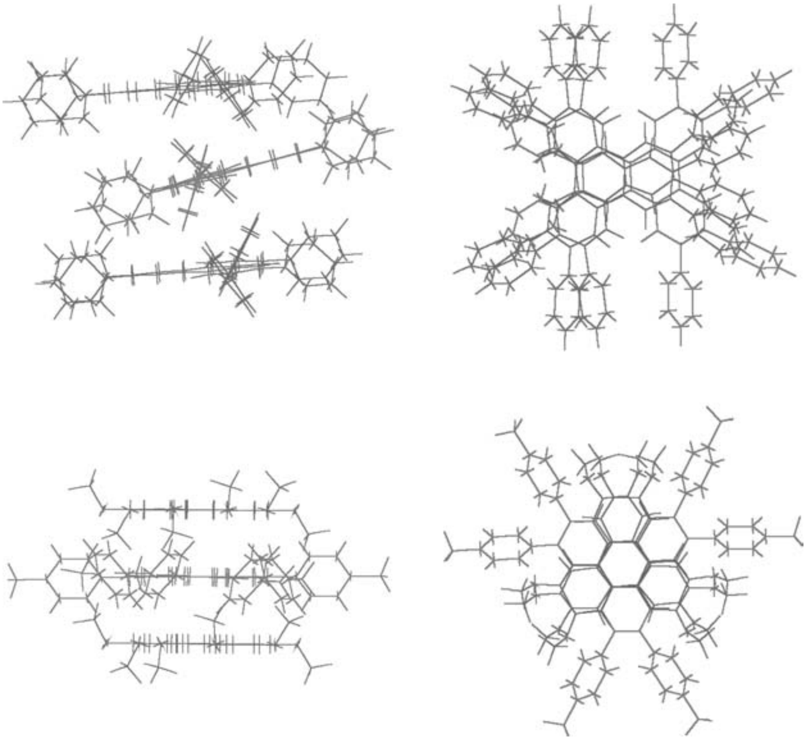

FIGURE 5 Minimum energy geometries PTP1 + PTP1 homodimer (top) and the PTP1 + HAT1 heterodimer (bottom). In each case the two lowest energy minimum sites for the 'mobile' partner are shown: one above and one below the 'fixed' partner.

TABLE 2 XED Calculated Interaction Energies for the Homodimers and Heterodimers (kcal mol^{-1}) of HAT1 **1c**, TNF **2** and PTP1 **3b**

Mixture	E_{VDW}	$E_{Coulomb}$	E_{Total}
HAT1 **1c** + HAT1 **1c**	−37.4	−2.4	−39.8
TNF **2** + TNF **2**	−16.4	−1.8	−18.3
PTP1 **3b** + PTP1 **3b**	−45.9	9.7	−36.2
HAT1 **1c** + TNF **2**	−27.0	−5.2	−32.2
HAT1 **1c** + PTP1 **3b**	−43.8	−6.2	−49.9

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TABLE 3 Energy Changes Upon Mixture Formation (ΔE_{Total}) and the Relative Contributions from Coulombic and van der Waals Terms (kcal mol^{-1})

Mixture	$\Delta E_{Coulomb}$	ΔE_{VDW}	ΔE_{Total}
HAT1 **1c** + TNF **2**	−0.1	−3.1	−3.2
HAT1 **1c** + PTP1 **3b**	−9.5	−2.3	−11.8

EXPERIMENTAL SECTION

Materials

The syntheses of PTP9 **3a**(17) and HAT6 **1c**(18) have previously been described.

Phase Behaviour

The experimental points shown in Figure 3 were determined using a combination of DSC (Perkin-Elmer DSC 7 using 2–3 mg samples in closed A1 pans with heating and cooling at 10°C min^{-1}) and OPM (Olympus BH-2 microscope with a Linkam hot stage). For mixtures containing >10% of the minor component the two components were accurately weighed (±0.001 mg), dissolved in dichloromethane, evaporated under reduced pressure (rotary evaporator-water pump) and dried at 40°C under vacuum (0.01 mmHg) for 5 days to give a colourless power. For mixtures containing <10% of the minor component standard solutions were mixed in the correct proportions using a pipette and the solution evaporated as before. The lines shown on the phase diagram were generated using a thermodynamic model for binary mixtures of an ideal solvent and solute using the method outlined in reference 11.

Calculations

The calculations were performed using the XED software [10,15]. To reduce computation time, the short-chain analogues of the synthesised compounds, HAT1 **1c** and PTP1 **3b**, were used for the modelling. After adding the extended electrons, molecular geometries were optimised and a full conformational search was performed to locate all of the global minima. A series of docking experiments was performed, using the lowest energy (best global energy minimum) structures. In this one molecule is placed in a fixed position while the second one is 'docked' starting from 250 points on a spherical surface around the stationary molecule. This gives the preferred structure of the dimmer, values for the overall energy of the pair as well as the coulombic and the van der Waals contributions.

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