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Control of single crystal structure and liquid crystal phase behaviour *via* arene–perfluoroarene interactions†

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In contrast to the solid-state structures of the individual compounds, arene-perfluoroarene face-to-face stacking and C–H···F–C in-plane interactions dominate the solid-state structure of 1 : 1 co-crystals of 1,4-bis(phenylethynyl)-tetrafluorobenzene 1b and 1,4-bis(pentafluorophenylethynyl)-benzene 1c, with this supramolecular aggregation leading to the stabilisation of a nematic liquid crystalline phase.

Non-covalent interactions between aromatic units play a significant role in determining the structures and properties of molecular assemblies in biology, chemistry and materials science.[1] In the past ten years, arene–arene interactions have been employed widely in supramolecular chemistry[2] and are critical to the packing of organic molecules in crystals and in crystal engineering for the design of functional materials.[3] The stability and phase behaviour of many liquid crystals have also been reported to arise from such interactions.[4] Arene–perfluoroarene interactions are a special case which have been studied extensively since 1960 when Patrick and Prosser reported[5] that benzene (mp 5.5 °C) and hexafluorobenzene (mp 4 °C) form a 1 : 1 complex with a melting point of 24 °C. Although the exact nature of these face-to-face interactions is still a subject of study, they may be dominated by electrostatic forces and the large but opposite in sign quadrupole moments of C_6H_6 and C_6F_6.[6] While our work was in progress, Coates and Grubbs *et al.* reported the use of arene–perfluoroarene interactions in buta-1,3-diynes and stilbene derivatives to induce crystal packing suitable for topochemical polymerisation or dimerisation in the solid-state.[7] Herein, we present our results on the liquid crystal (LC) phase behaviour of a series of 1,4-bis(phenylethynyl)benzenes containing 0, 4, 10 or 14 fluorine atoms, namely 1,4-bis(phenylethynyl)benzene **1a**, 1,4-bis(phenylethynyl)tetrafluorobenzene **1b**, 1,4-bis(pentafluorophenylethynyl)benzene **1c** and 1,4-bis(pentafluorophenylethynyl)tetrafluorobenzene **1d**, and the single crystal structure and LC properties of 1:1 co-crystals‡ of **1b·1c**. These compounds were prepared by Pd/Cu catalysed cross-coupling reactions of appropriate terminal alkynes and iodoarenes as part of a larger study in our laboratories on the structure, linear and non-linear optical properties, and LC phase behaviour of conjugated rigid-rod systems.[8]

In contrast to the single crystal structures of **1a**–**d**, in which there is no evidence of any type of arene–arene interaction, 1 : 1 co-crystals‡ of **1b·1c** show two such interactions (Fig. 1). Thus, there is clear π-stacking of *all* arene and perfluoroarene moieties along the *b* axis [Fig. 1(*c*)] with the lateral slippage typical of such systems being about one C–C bond length [Fig. 1(*a*)]. As all molecules lie on inversion centres, the stacking is regular rather than alternating (*i.e.* the spacing between all molecules along *b* is equal). The perpendicular separation between mean planes in a stack is 3.337 Å. The intermolecular C–H···F–C interactions[7] shown dashed in Fig. 1(*b*) are 2.500–2.574 Å§ (sum of van der Waals radii = 2.67 Å) with C–F···H and C–H···F angles of 120–160°, the molecules thereby forming sheets which are very close to planar. We have not yet been able to grow single co-crystals of **1a·1d** suitable for X-ray diffraction; the sample discussed below was prepared by dissolving equimolar quantities of the two components in $CHCl_3$ and removing the solvent *in vacuo*.

Table 1 lists the axial ratio and the phase transitions detected on heating for compounds **1a**–**d**, and for the two mixed formulations. Surprisingly, molecules with an axial ratio as low as 4.1 (or 4.0 in the case of one of the co-crystals) are capable of forming liquid crystalline phases. Furthermore, the co-crystallized materials exhibit a greater liquid crystalline range and a higher temperature to obtain a fully isotropic fluid,

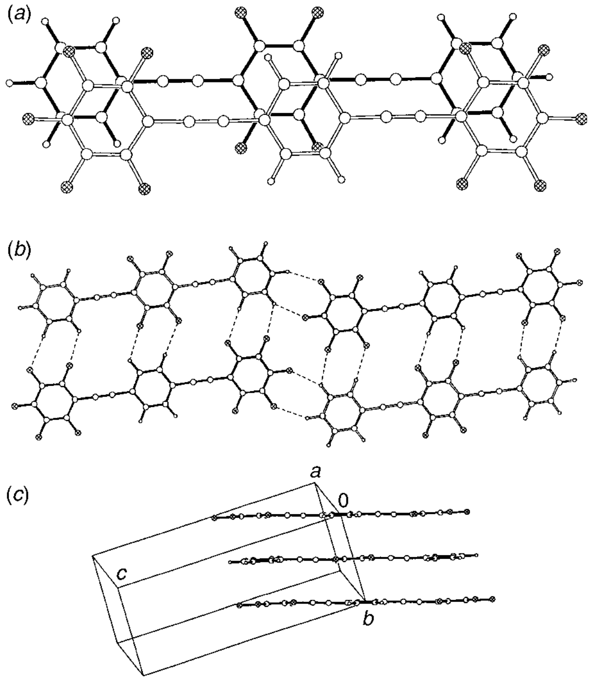

Fig. 1(*a*) Overlap diagram viewed perpendicular to the central C_6 ring of the two molecules in **1b·1c**, drawn in parallel projection without perspective, **1b** with solid bonds and **1c** with hollow bonds. Distances between ring centroids in adjacent molecules are 3.770 Å (central rings) and 3.750 and 3.789 Å (outer rings) with these inter-centroid vectors inclined on average 25.7° to the plane normals. Twists about the C–C≡C–C linkage in **1b·1c** are only 3.9° (**1b**) and 3.0° (**1c**) whereas in crystals of the individual components **1b** and **1c** these angles are 16.7 and 9.7° respectively. (*b*) A view showing the 'in-plane' intermolecular H···F contacts of 2.500–2.574 Å. (*c*) A packing diagram showing the stacking along the *b* axis.

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Table 1 Axial ratio (*L/D*) and phase transitions[a]

Compound	*L/D*	Transitions on heating/°C
PhC≡CC$_6$H$_4$C≡CPh **1a**	4.45	K 181.7 I (I 164.3 N 159.5 K on cooling)
PhC≡CC$_6$F$_4$C≡CPh **1b**	3.98	K 182.5 I
C$_6$F$_5$C≡CC$_6$H$_4$C≡CC$_6$F$_5$ **1c**	4.10	K 196.5 N/I[b]
C$_6$F$_5$C≡CC$_6$F$_4$C≡CC$_6$F$_5$ **1d**	4.10	K 226.1 I
Co-crystal (1 : 1) of **1b·1c**	—	K 189.3 N 199.0 I
Two-component system (*ca.* 1 : 1) of **1a·1d**	—	K 178.5 S$_B$ 196.2 bi N/I[c] 231.5 I

[a] Transition temperatures were determined by DSC and phases were assigned on the basis of the textures observed by transmitted polarised light microscopy. [b] N/I denotes that the nematic phase exists over a very narrow temperature range, and is observed only transiently by microscopy. The crystal-to-nematic and nematic-to-isotropic transition temperatures lie unresolvably close together. A single DSC endotherm is observed, and its onset temperature is quoted. [c] bi N/I denotes that the sample forms a two-phase (biphasic) mixture of both nematic and isotropic material. The subsequent clearing point refers to the nematic regions only.

compared to either of their respective constituents. These results are interesting for three reasons.

First, it is well known[9] that mixing two mesogenic species can lead to a reduction in melting point and so expand the temperature range of liquid crystallinity exhibited by either constituent; often a simple eutectic phase diagram is obtained. Here, however, we have two cases where liquid crystallinity is promoted by mixing compounds that, on their own, show no or only transient tendency to form a LC phase when heated. Also, as noted, it is not just the melting point that is lowered; the clearing points of these mixtures are raised above the temperature needed to render the respective constituents isotropic. Both observations suggest the possibility of intermolecular association in the liquid crystalline phase.

Second, it has been demonstrated previously for unsubstituted tolan oligomers, which have an approximately uniform charge distribution along the length of each molecule, that an axial ratio of 4.45 is barely sufficient to stabilize liquid crystallinity at ambient pressure.[10] The monotropically nematic compound **1a** illustrates this point. When molecules lack the necessary shape anisotropy, they can nevertheless form a liquid crystalline phase if there are sufficiently strong and anisotropic ‘soft’ interactions between them.[11] In some systems, intermolecular attractions can lead to the assembly of supramolecular aggregates[12] which then promote liquid crystalline order. For example, strong hydrogen bonding between benzoic acids and pyridines can lead to the formation of supramolecular mesogenic structures.[13] Our results suggest that aggregation may play a role in the present case, but that it is probably not due to strong hydrogen bonding.

Third, the fully fluorinated compound **1d** does not exhibit liquid crystallinity, but **1c**, which has the same axial ratio but contains both fluorinated and non-fluorinated phenyl residues, is transiently nematic. We also note that the liquid crystalline two-component systems contain both fluorinated and non-fluorinated phenyls. These observations suggest that arene–perfluoroarene stacking interactions, as observed in the solid-state for **1b·1c**, are the cause of the proposed aggregation in the LC phases.[14] The fact that nematic phases are formed, requiring rod-like or nearly rod-like structures, suggests that it is unlikely that large flat sheets persist at the temperatures of the phase transitions that we observe. Thus, although C–H···F–C interactions in two dimensions may play a role in LC phase behaviour, a one dimensional model based on face-to-face quadrupolar interactions between fluoroarene and arene units is preferred at this time.

Studies examining the phase behaviour of a full range of compositions of these compounds are in progress.

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Notes and references

‡ Co-crystals of ***1b*·1c** suitable for X-ray diffraction were grown by dissolving solid samples of **1b** (70 mg, 0.2 mmol) and **1c** (92 mg, 0.2 mmol) in hot CHCl$_3$ (5 ml). Colourless needles were collected after cooling to ambient temperature. GC/MS analysis showed that these crystals contained **1b** and **1c** in a 1 : 1 ratio (calc. for C$_{44}$H$_{14}$F$_{14}$: C, 65.53; H, 1.41; F, 32.56. Found: C, 65.36; H, 1.75; F, 32.89%). *Crystal data* for **1b·1c**: C$_{22}$H$_{10}$F$_4$·C$_{22}$H$_4$F$_{10}$, M = 808.55, triclinic, space group, $P\bar{1}$ a = 6.0932(7), b = 7.5393(9), c = 19.114(2) Å, α = 96.044(3), β = 99.102(3), γ = 96.538(3)°, U = 854.54(17) Å^3, Z = 1, D_c = 1.571 g cm^{-3}, μ(Mo-Kα) = 0.145mm^{-1}, T = 160(2) K, crystal size = 0.62 × 0.18 × 0.02 mm. Full-matrix least-squares refinement on F^2 (G. M. Sheldrick, SHELXTL manual, Bruker AXS Inc., Madison, WI, USA, 1994, version 5) anisotropic displacements for all non-H atoms and isotropic for H (263 parameters) using 2918 unique data (4436 total collected; R$_{\text{int}}$ = 0.0449) from a Bruker AXS SMART CCD diffractometer (θ < 25.00°) gave $R1$ [$I > 2\sigma(I)$] = 0.0685, $wR2$ (all data) = 0.1661. Residual electron density within ± 0.30 e Å^{-3}. CCDC 182/1475. See http://www.rsc.org/suppdata/cc/1999/2493/ for crystallographic data in .cif format.

§ All C–H bonds have been extended to the expected internuclear separation of 1.08 Å for all geometry calculations in this paper.

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