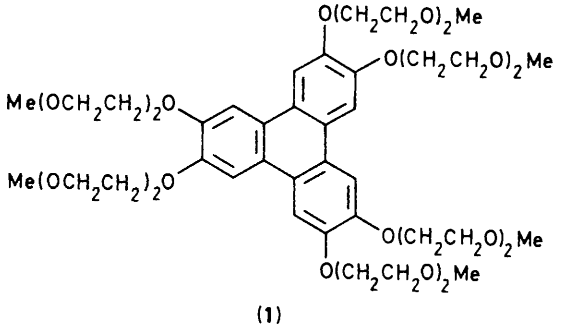
The *X*-Ray Crystal Structure of the Discoid Amphiphile 2,3,6,7,10,11-Hexa-(1,4,7,-trioxaoctyl)triphenylene (TP6E02M)

Neville Boden,[a] Richard J. Bushby,[a] Malini V. Jesudason,[a] and Bernard Sheldrick[b]

[a]School of Chemistry and [b]Astbury Department of Biophysics, The University, Leeds LS2 9JT, U.K.

In the anhydrous crystal the discoid amphiphile TP6E02M (**1**) packs in tilted columns whereas in the more hydrated liquid crystal phases these columns are vertical.

To exploit the supramolecular organisation inherent in liquid crystals (for example by building in chemical functionality) it is necessary to engineer systems where the nature of this organisation is wholly predictable. One approach to this problem is to make a disc-shaped amphiphile[1—5] such as 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)triphenylene (**1**) (TP6EO2M)[1—4] in which a rigid hydrophobic core is surrounded by a ring of hydrophilic groups. In water such a discoid amphiphile must give *columnar* aggregates. We have shown that TP6EO2M forms such aggregates in an extended sequence of phases [at 3 °C with increasing hydration: crystal → modified monoclinic structure (C_{mo}) → tetragonal phase



(**1**)

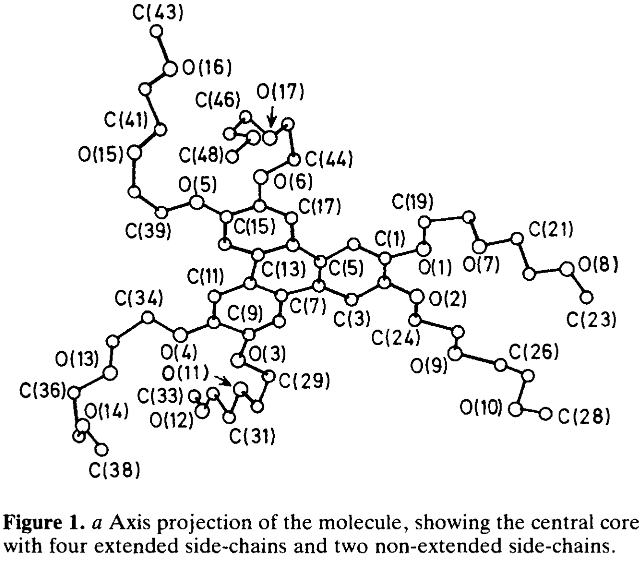


Figure 1. *a* Axis projection of the molecule, showing the central core with four extended side-chains and two non-extended side-chains.

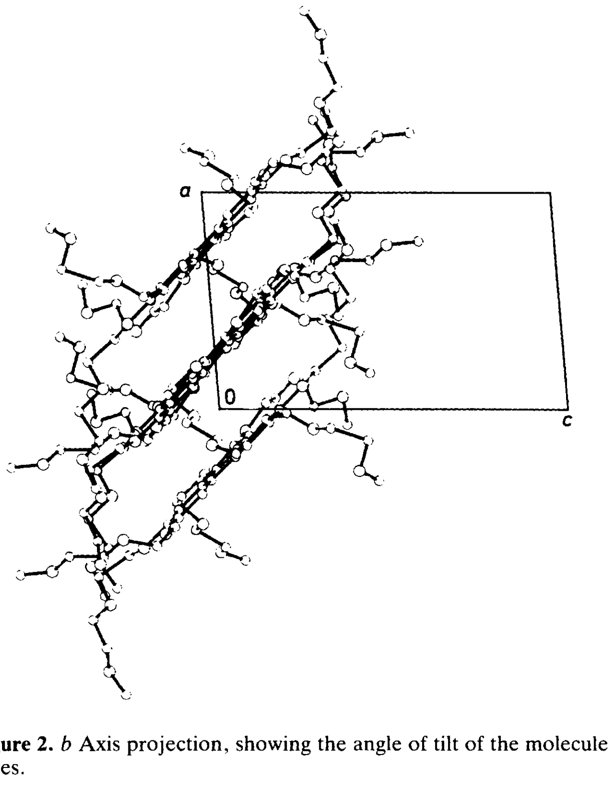


Figure 2. *b* Axis projection, showing the angle of tilt of the molecule cores.

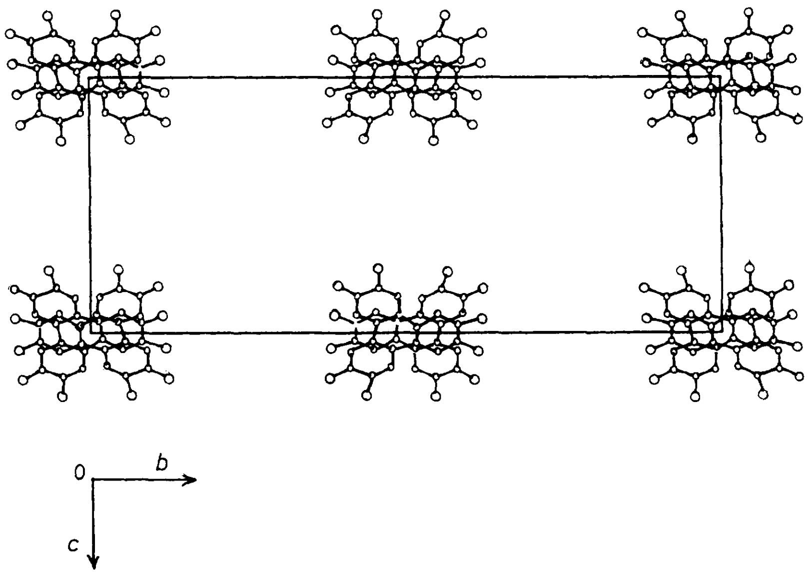


Figure 3. *a* Axis projection of the unit cell with only the central cores of the 12 molecules drawn in for clarity. This show the alternation of the orientation of the molecules up the *a* axis. Direction of *b* and *c* axes as indicated.

(C_{td}) → hexagonal phase (C_{hd}) → nematic phase (N_D^-)→ isotropic micellar solution].[1—4] Whereas the structures of the liquid crystal phases of TP6EO2M are now clear a complete understanding of the phase behaviour requires a crystal structure for the unhydrated compound.

TP6EO2M was prepared by the method previously reported except that the alkylation step was performed using potassium carbonate/ethanol; a method which gives much better yields than using sodium hydride/dimethyl sulphoxide.[3] The crystal habit (thin hair-like needles) and the low melting point of the solid made it difficult to obtain good *X*-ray diffraction data, but at 0 °C data sufficient to define the interesting features of the system were obtained.† The structure was solved for all non-hydrogen atoms and a large number of hydrogens could be placed at calculated positions. The individual molecules have four extended and two coiled ethyleneoxy chains (Figure 1). The geometry of the triphenylene nucleus and the conformation adopted by the aryl ether bonds[6] are as expected. The conformations of the ethyleneoxy chains for the most part follow the *trans–gauche–trans* pattern seen in other ethyleneoxy derivatives.[7] Packing is rather inefficient leading to a free volume/unit cell[8] of *ca.* 143 Å^3. This may account for the ability of the crystal to take up to 7% by weight of D_2O at 3 °C without change in the lattice dimensions.[4] The interesting feature of the *X*-ray crystal structure, however, is the arrangement of the molecules in tilted stacks. This may be seen from the *a* and *c* axis unit cell projections shown in Figures 2 and 3 which also show the way in which the orientation of the aromatic nucleus alternatives along the column. The tilt of the stack relative to a best plane through the aromatic core and the oxygen atoms is 49°. The sequence: crystal (tilted stacks) →→ C_t phase (possibly tilted stacks) → hexagonal phase (vertical stacks) → nematic phase (vertical stacks) brought about by increasing hydration of TP6EO2M[4] is similar to that induced by increasing the temperature in related *thermotropic* discoid systems.[9,10] For example the sequence of phases for hexadodecanoyloxytriphenylene is: crystal (tilted stacks) → D_1 phase (tilted stacks) → D_2 phase (hexagonal, vertical stacks).[10] The driving force in the lyotropic system may be different but clarification of the exact role of hydrophilic/hydrophobic interactions must await further investigation.

We thank the S.E.R.C. for financial support.

Received, 21st March 1988; Com. 8/01134F

References

1 N. Boden, R. J. Bushby, and C. Hardy, *J. Physique Lett.*, 1985, **46**, L-325.
2 N. Boden, R. J. Bushby, C. Hardy, and F. Sixl, *Chem. Phys. Lett.*, 1986, **123**, 359.
3 N. Boden, R. J. Bushby, L. Ferris, C. Hardy, and F. Sixl, *Liq. Cryst.*, 1986, **1**, 109.
4 N. Boden, R. J. Bushby, K. W. Jolley, M. C. Holmes, and F. Sixl, *Mol. Cryst. Liq. Cryst.*, 1987, **152**, 37.
5 S. Gaspard, A. Hochapfel, and R. Viovy, *C. R. Acad. Sci., Sect. C*, 1979, **289**, 387; J. Piechocki and J. Simon, *Nouv. J. Chim.*, 1985, **9**, 159.
6 G. M. Anderson, P. A. Kollman, L. N. Domelsmith, and K. N. Houk, *J. Am. Chem. Soc.*, 1979, **101**, 2344.
7 J. Dale, *Tetrahedron*, 1974, **30**, 1683.
8 S. S. Rajan, *Acta Crystallogr., Sect. B*, 1975, **31**, 331.
9 C. Destrade, H. Gasparoux, P. Foucher, N. H. Tinh, J. Malthete, and J. Jacques, *J. Chim. Phys.*, 1983, **80**, 137.
10 M. Takabatake and S. Iwayanagi, *Jpn. J. Appl. Phys.*, 1982, **21**, 1682.

---

† *Crystal data* for (**1**): $C_{48}H_{72}O_{18}$, $M = 937.1$, monoclinic, space group $P2_1/a$, $a = 9.28(1)$, $b = 36.59(8)$, $c = 14.88(3)$ Å, $\beta = 94.9(2)°$, $U = 5034.1$ Å^3, $Z = 4$, $F(000) = 2016$; crystal dimensions 0.61 × 0.11 × 0.08 mm; $\mu(\text{Cu-}K_\alpha) = 6.96$ mm^{-1}, $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å, $2\theta_{max.}$ 80°; h,k,l range 0 to 7, −30 to 30, −12 to 12; number of unique reflections 2250; criterion for observed reflections $F_o > 3\sigma(F_o)$; full-matrix least-squares refinement; weighting $w = 1/(\Sigma F^2)$; H atoms calculated; maximum and average Δ/σ 0.317 and 0.028; maximum and minimum $\Delta\rho$ 0.81 and 0.43 e/Å^3; R, R_w 16.52, 11.1%; $T = 274$ K; refinement program SHELX76. Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.