

A Discotic Mesophase with Binary or Tetragonal Symmetry

By ROSE FUGNITTO and HELENA STRZELECKA

(Groupe de Recherche no. 12, C.N.R.S., F 94320 Thiais, France)

ANNIE ZANN and JEAN-CLAUDE DUBOIS

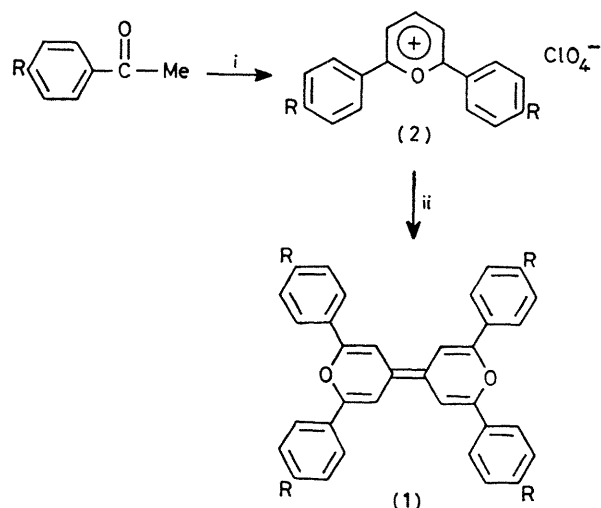
(Compagnie Thomson-CSF, Domaine de Corbeville, F 91401 Orsay, France)

and JEAN BILLARD

(College de France, F 75231 Paris, France)

Summary The 2,2',6,6'-tetra-arylbiopyran-4-ylidenes (**1b**) and (**1c**), disc-like molecules with a novel core and four n-alkyl side chains, exhibit a discotic mesophase which allows either four- or two-fold symmetry.

THE degrees of symmetry known so far for discotic† mesophases are three or six,¹⁻³ or infinite, as recently discovered.⁴ Compounds exhibiting these mesophases have an aromatic central core with six side chains (n-alkanoyloxy,¹ n-alkoxy,² or 4-n-alkoxy or 4-n-alkylbenzoyloxy⁴). We describe here a series of disc-like molecules (**1**) with a novel heterocyclic core and four n-alkyl side chains which exhibits a discotic mesophase with four- or two-fold symmetry.

R = C_nH_{2n+1}

a; n = 5

b; n = 9

c; n = 12

SCHEME. i, CH(OEt)₃, HClO₄; ii, Zn, MeCN.

The 2,2',6,6'-tetra-arylbiopyran-4-ylidenes (**1a—c**) may be synthesised in two steps (Scheme).^{5,6} The intermediate perchlorates (**2a—c**) were obtained in 90, 65, and 72% yields, respectively. Compounds (**1a—c**) were isolated by extraction with toluene, purified by crystallisation from ethanol-hexane (1:1), and obtained in 62, 27, and 55% yields, respectively. Contrary to (**1**; R = H), which does not have side chains, (**1a—c**) are insoluble in polar solvents but are soluble in hydrocarbons.

TABLE. Phase transitions for (**1a—c**)^a

n	Crystal 1	Crystal 2	Mesophase	Liquid
5	×	135	×	228
9		53.5 (2.0)	×	171.5 (5.0)
12	×	40 (6.8)	×	147 (6.7)

^a The temperatures (°C) and molar enthalpy changes (in parentheses, kcal/mol) correspond to the transitions between the phases indicated by ×.

Calorimetry, X-ray powder diffraction, and optical microscopy gave the phase sequences reported in the Table. For (**1a**), which does not form an enantiotropic mesophase, a virtual discotic mesophase-liquid transition at 157 °C can be obtained from the phase diagram of a mixture of (**1a**) and (**1c**) (Figure) by a method previously described.⁷ For (**1b**)

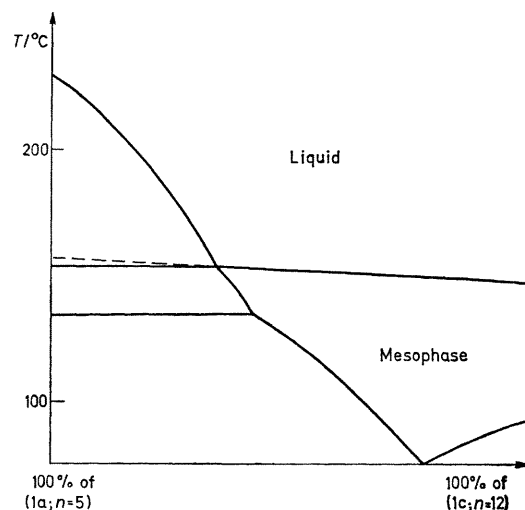


FIGURE. Isobaric phase diagram of the binary mixture of compounds (**1a**) (left) and (**1c**) (right). The extrapolation of the discotic liquid spindle (dashed lines) gives a virtual discotic phase-liquid transition at 157 °C.

and (**1c**) the molar enthalpies are larger for fluid-fluid transitions than for melting. This exceptional situation, first observed for a smectogen with a thread-like ordering of the molecules in its smectic phase,⁸ is observed here for the first time with discogens. Compounds (**1b**) and (**1c**) are totally co-miscible in the mesomorphic and liquid states and therefore have mesophases of the same type.

† The term discotic refers to saucer-shaped molecules arranged with a partial ordering.

On cooling the isotropic liquids of these materials a highly viscous and birefringent phase appeared in domains with finger-like contours allowing a four-fold symmetry. Pressing over a domain produces defects with a rectilinear axis² in only two perpendicular directions. On further cooling of (1b) and (1c) the crystalline needles formed in a mesomorphic single domain are parallel to two rectangular directions.

These two disc-like heterocyclic compounds, having a bipyran core and four n-alkyl side chains, hence form, at atmospheric pressure, a mesophase allowing either two- or four-fold symmetry.

(Received, 28th November 1979, Com 1241)

¹ S Chandrasekhar, B K Sadashiva, and K A Suresh, *Pramana*, 1977, **9**, 471

² J Billard, J C Dubois, Nguyen Huu Tinh, and A Zann, *Nouv J Chim*, 1978, **2**, 535

³ A Queguiner, A Zann, J C Dubois, and J Billard, Bangalore Conference, 1979

⁴ Nguyen Huu Tinh, C Destrade, and H Gasparoux, *Phys Letters*, 1979, **72 A**, 251

⁵ G N Dorofeenko, U V Majeritskii, E P Olekhovitch, and A L Wasserman, *Zhur org Khim*, 1973, **9**, 395

⁶ C Fabre, R Fugnitto and H Strzelecka, *Compt rend*, 1976, **282 C**, 175

⁷ M Domon and J Billard, *Pramana*, 1973, suppl **1**, 131

⁸ A de Vries and D L Fishel, *Mol Cryst and Liq Cryst*, 1972, **16**, 311