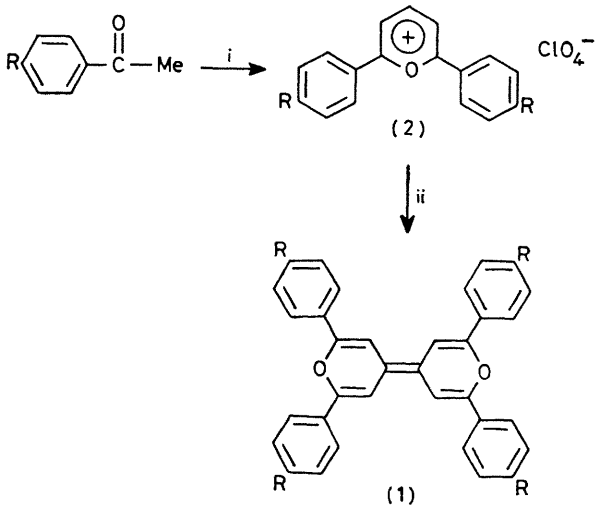
A Discotic Mesophase with Binary or Tetragonal Symmetry

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-arylbipyran-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-alkylbenzoyloxy[4]). 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, $CH(OEt)_3$, $HClO_4$; ii, Zn,MeCN.

The 2,2′,6,6′-tetra-arylbipyran-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)	×	96 (3·8)	×	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**) 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.

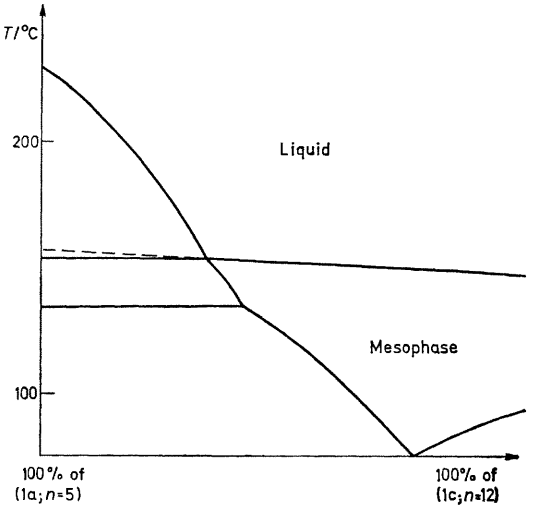


FIGURE. Isobaric phase diagram of the binary mixture of compounds (**1a**) (left) and (**1c**) (right). The extrapolation of the discotic liquid spindle (dashed lines) gives a virtual discotic phase–liquid transition at 157 °C.

† 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 axis[2] 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*, 28*th 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 Olekhnovitch, 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