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Liquid Crystals

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To cite this Article Carfagna, Cosimo , Iannelli, Pio , Roviello, Antonio and Sirigu, Augusto(1987) 'Discotic mesomorphism of rufigallol hexa-*n*-alkoxylates', Liquid Crystals, 2: 5, 611 — 616

To link to this Article: DOI: 10.1080/02678298708086319

URL: http://dx.doi.org/10.1080/02678298708086319

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LIQUID CRYSTALS, 1987, VOL. 2, NO. 5, 611–616

Discotic mesomorphism of rufigallol hexa-*n*-alkoxylates

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(*Received 5 January 1987: accepted 6 June 1987*)

Aliphatic ethers of rufigallol have been prepared and their discotic mesomorphism studied. All the compounds give enantiotropic, columnar mesophases with a regular stacking of the discs along the columns, as revealed by the X-ray diffraction patterns of the mesophases. Calorimetric data indicate a wide range of stability of the mesophase. Solid polymorphism has been demonstrated that involves both solution crystallized and melt crystallized samples.

1. Introduction

In recent years there has been an increasing number of papers reporting the synthesis and characterization of disc-like molecules, a novel class of thermotropic liquid crystals [1–5]. The structural peculiarity of this class of mesogens is the presence in the molecular skeleton of a flat, rigid, disc-like part connected to flexible chains. Most of the discotic compounds known so far contain aromatic groups, although this is not a requisite [6]. The flexible part consists of aliphatic chains that in most cases are bound to the central part by ether or ester linkages. Two different kinds of discotic phases have been described: a columnar mesophase and a nematic phase. Four different columnar mesophases have been identified, the differences being attributed to the regular or irregular stacking of discs along the columns, packed either in hexagonal or rectangular arrangements [2].

In a previous paper [7] we have reported the synthesis and the characterization of a series of aliphatic esters of 1,2,3,5,6,7 hexahydroxyanthraquinone (rufigallol). The range of stability of the discotic mesophase was related to the length of the flexible alkyl chains.

Here we report the results of the characterization of the mesophasic properties of a series of hexa-*n*-alkoxy rufigallols.

2. Experimental

Rufigallol was prepared from 3,4,5 trihydroxybenzoic acid (gallic acid) according to the synthesis previously described [8]. It was purified as the hexa-acetate by standard procedures. In a typical preparation of the ethers 1·8 mmol of rufigallol hexa-acetate were dissolved in 10 ml of N,N′-dimethylformamide with 0·019 mol of sodium carbonate and 0·03 mol of the appropriate alkyl bromide. The solution was heated at 160°C under nitrogen. After 16 hours the mixture was filtered to remove the excess sodium carbonate, and the sodium bromide formed during the reaction. The solution was diluted with ethanol and recrystallized at about −20°C overnight. Further purification was achieved by column chromatography (silica gel + chloroform as eluent). The nature of all the compounds was checked by I.R. and N.M.R. spectroscopy.

The calorimetric behaviour of all the ethers prepared was investigated in the range 253 to 400 K using a Mettler TA 3000 calorimeter, at a scanning rate of 10 K/min under a nitrogen atmosphere. The phase transition enthalpies were obtained using indium as a reference standard sample (Fluka 99·999 per cent, $\Delta H = 28{\cdot}5\,\mathrm{J/g}$). The X-ray diffraction patterns of the liquid crystal phases were recorded using a flat-film camera; CuK_α radiation was used. A Leitz polarizing microscope associated with a Mettler FP-5 micro-furnace was employed for the optical analysis of the phase transitions.

3. Results and discussion

The aliphatic ethers of rufigallol examined (the compounds will be denoted by the short notation *En*, where *n* is the number of carbon atoms contained in each aliphatic chain) melt in the range 300 to 380 K and exhibit enantiotropic mesophases. While the temperatures for the transition to the isotropic phase decrease smoothly with increasing length of the chains, the melting temperature and, as a consequence, the range of stability of the mesophase, follow a more complicated pattern. The thermal data for the compounds investigated are listed in the table. The molar melting enthalpies are not reported, since they are of little significance. In fact in most cases solid state polymorphism was observed. It shows up both as a multiplicity of solid phases stable at different temperatures and as a difference in the crystal structure of solution-crystallized or melt-crystallized samples. Figures 1 and 2 show the D.S.C. traces for two representative cases. As the solid polymorphism is not central to our studies it is not to be discussed any further.

Transitional properties for the rufigallol hexa-*n*-alkoxylates.

Compound	T_m/K	T_i/K	$\Delta H_\mathrm{i}/\mathrm{kJ\,mol^{-1}}$	$r/\mathrm{\AA}$
E4	378	404	16·2	17·9
E5	356	390	14·7	19·6
E6	326	378	12·7	21·0
E7	322	375	12·3	22·7
E8	310	369	12·0	23·8
E9	305	365	11·4	25·2
E10	321	360	11·2	26·0
E11	299	357	10·9	30·6
E12	310	352	10·6	28·2
E13	335	345	10·5	28·5

T_m = melting temperature; T_i = transition temperature for the formation of the isotropic phase ($\sigma T_\mathrm{i}/T_\mathrm{i} \simeq 0{\cdot}003$); ΔH_i = molar enthalpy for the transition to the isotropic phase ($0{\cdot}05 > \sigma\Delta H_\mathrm{i}/\Delta H_\mathrm{i} > 0{\cdot}01$); r = intercolumnar distance ($\sigma r/r \simeq 0{\cdot}02$).

The X-ray diffraction patterns of the mesophases support their discotic structure with hexagonal packing of the columns. As an example, figure 3 shows the diffraction pattern (recorded at 333 K) of the mesophase of E13. A sharp inner ring, corresponding to a Bragg spacing of 24·7 Å, is clearly evident. This and several diffraction rings at 14·3 Å and 12·4 Å are geometrically related with the ratios 1 : 0·557 : 0·5 as the lattice distance $d(100)$, $d(110)$ and $d(200)$ of a hexagonal lattice. This feature is found

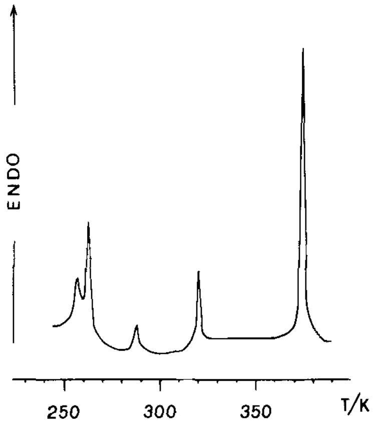

Figure 1. D.S.C. thermogram of E7; heating run of a melt crystallized sample.

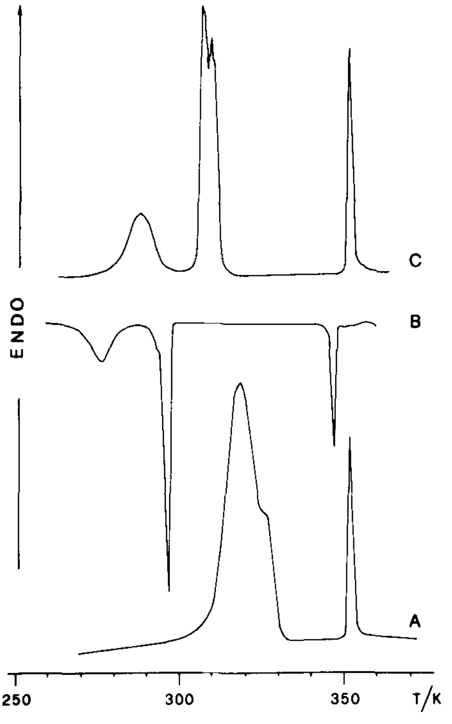

Figure 2. D.S.C. thermogram of E12; (A) solution crystallized sample, first heating run; (B) cooling run; (C) heating run (melt crystallized sample). The D.S.C. traces have been recorded with a different range.

for all the compounds examined. A faint and diffuse halo, characteristic of liquid-like disorder, is present at around $2\theta = 19{\cdot}7°$. A fairly strong diffraction ring is present at higher angles. Its angular position (corresponding to 3·6 Å) is essentially independent of the length of the flexible portion of the molecules, suggesting that the packing of the disc along the columns is little influenced by the length of the aliphatic chains. For the homologous class of ester-linked compounds a very weak diffraction ring is present at $d = 5{\cdot}6$ Å. This feature has been observed by Billard *et al.* [5] for rufigallol

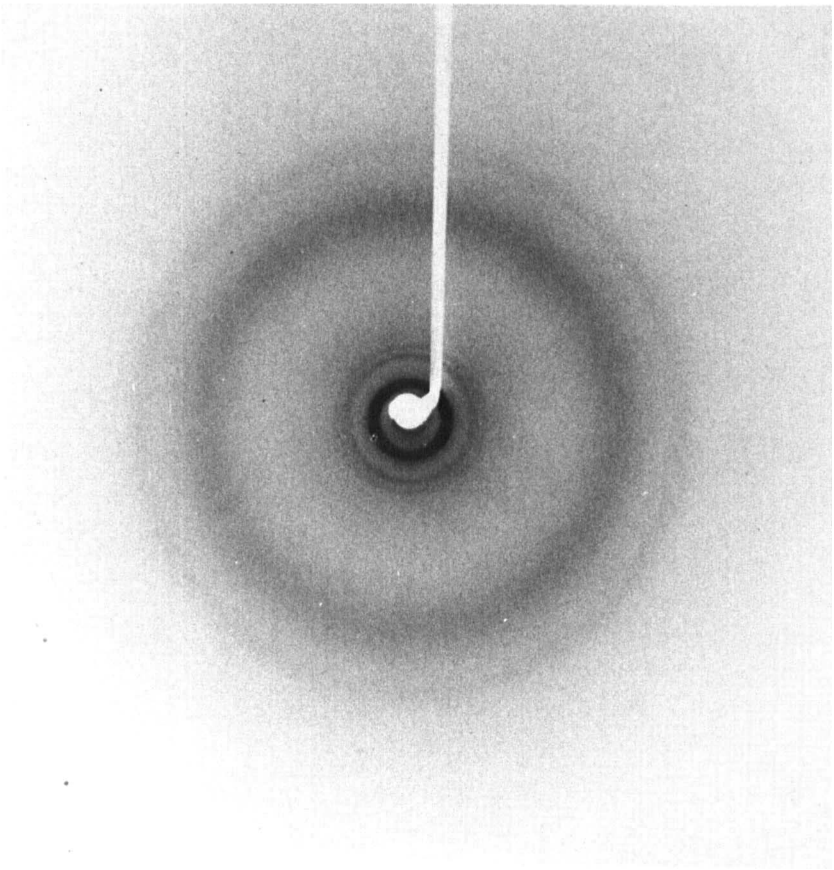

Figure 3. X-ray diffraction pattern of the discotic phase of E13; $T = 333\,\mathrm{K}$.

hexaoctanoate, and by the authors after a more detailed analysis of the diffraction patterns of the homologous series from hexabutanoate to hexatetradecanoate. The increased intermolecular distance along a column for the ester-linked compounds, which is very likely due to the necessary non-coplanarity of the carboxyl groups with respect to the rufigallol moiety, is compensated by a shorter intercolumnar distance. As a consequence, the packing density does not appear to be influenced significantly. As an example, the molecular volume is 1600 Å^3 for E8 and 1630 Å^3 for the ester homologue containing terminal chains of equivalent length; approximate molecular volumes have been calculated as $V \times t\pi r^2/4$, where t is the intermolecular distance along the column and r is the molecular disc diameter. The values of $r = d(100)/\cos 30$ that we have assumed as diameter of the molecular disc, i.e. the intercolumnar distance, are given in the table. In accord with the constant value of the intermolecular distance along the column, r^2 is a linear function of n. A close intracolumnar molecular packing of the alkoxy compounds as compared to the alkanoyloxy-derivatives has also been observed for some triphenylene derivatives [4]. The difference is, however, considerably smaller in this case (3·6 Å for hexaheptyloxytriphenylene; 4 Å for dodecanoyloxytriphenylene) and might be accounted for with a twisted packing of the molecules along the columns. As far as the optical textures are concerned, they are typical of highly ordered mesophases. Figures 4 and 5 show the

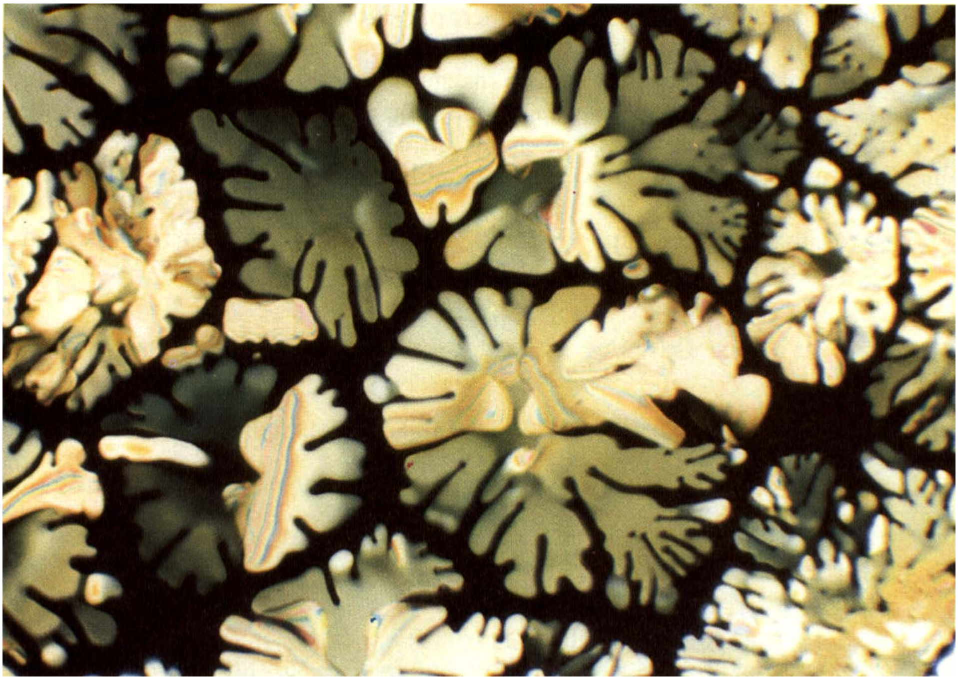

Figure 4. Discotic phase of E5, crossed polarizers; T = 389 K.

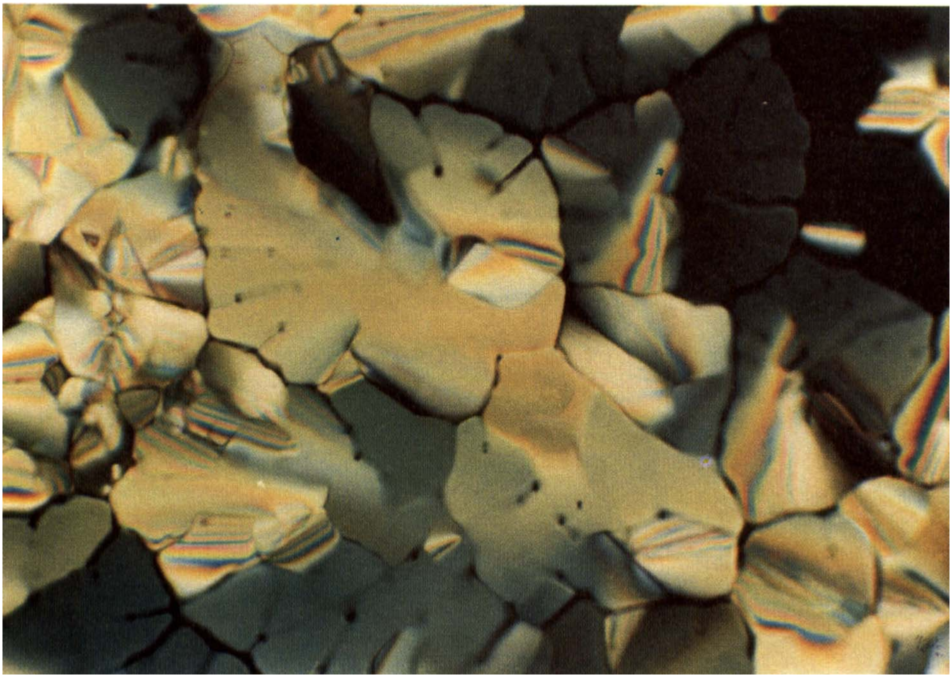

Figure 5. Discotic phase of E8, crossed polarizers; T = 368 K.

textures observed under the polarizing microscope for the discotic phases of E5 and E8, respectively. The thermodynamic data concerning the transitions to the isotropic phase are listed in the table. Both transition temperatures and molar enthalpy changes decrease smoothly with increasing length of the aliphatic chains. No odd–even effects that might imply ordering of these chains in the discotic phase are detectable. A similar feature has been observed for the ester analogues.

This research has been supported by Ministero della Pubblica Istruzione, Italy.

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