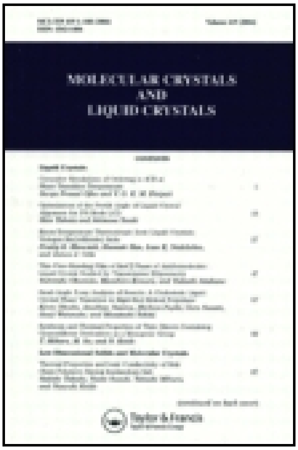

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

A New Series of Thermotropic Liquid Crystals: cis-1,5-Cyclooctyl di-(4-Alkoxybenzoate)s

J. M. G. Cowie [a] & H. H. Wu [a]

[a] Chemistry Department, Stirling University, Stirling, FK9 4LA, Scotland

To cite this article: J. M. G. Cowie & H. H. Wu (1989): A New Series of Thermotropic Liquid Crystals: cis-1,5-Cyclooctyl di-(4-Alkoxybenzoate)s, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 167:1, 141-145

To link to this article: http://dx.doi.org/10.1080/00268948908037170

Mol. Cryst. Liq. Cryst., 1989, Vol. 167, pp. 141–145
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Printed in the United States of America

A New Series of Thermotropic Liquid Crystals: *cis*-1,5-Cyclooctyl di-(4-Alkoxybenzoate)s

J. M. G. COWIE and H. H. WU
Chemistry Department, Stirling University, Stirling FK9 4LA, Scotland

(*Received December 10, 1987; in final form May 12, 1988*)

A series of liquid crystalline *cis*-1,5-cyclooctyl di-(4-alkoxybenzoate)s has been prepared. The effect of the cyclooctyl ring on the phase transitions of these compounds is discussed.

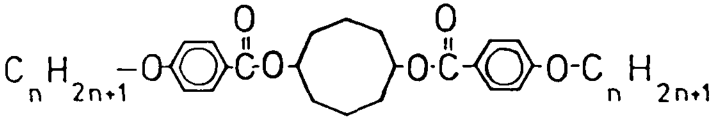
INTRODUCTION

Early studies by Gray[1] recognised that compounds tend to form nematic mesophases if their molecules are rod-shaped and possess polar terminal groups. It was suggested that molecules containing *p*-phenyl groups favour lateral attractions mainly due to the presence of polarisable π-electrons and partly by conjugation of the terminal groups. Using 1,4-bicyclo(2.2.2)octyl and *trans*-1,4-cyclohexyl, Dewar *et al.* later demonstrated that to have a linear rod-shaped molecule of uniform cross section is a more important feature than polarity.[2,3] In general, the mesophase stability of nematic compounds depends upon the balance of four important molecular features, *i.e.*, rigidity, linearity, polarisability and the degree of conjugation.

Here, we report on a new series of thermotropic liquid crystals namely *cis*-1,5-cyclooctyl di-(4-alkoxybenzoate)s (COAB). This work was initiated by our recent studies on thermotropic main-chain liquid crystal polymers containing cyclooctyl units[4–9] and our purpose was to obtain a better understanding of the role of the eight membered ring in mesophase formation.

RESULTS AND DISCUSSION

The general structure of this series of liquid crystals, COAB-*n*, is shown below.



Where *n* varies from 3 to 8 and the sample code is COAB-*n*.

TABLE I

Phase transition temperatures on both heating and cooling cycles for several *n*-COAB

	Heating (°C)	Cooling (°C)			
n	T_{K-I}	T_{I-N}	T_{recryst}	ΔT^{b}	Mesophase
3	138	81	72	9	nematic
4	112	87	75	12	nematic
5	118	84[a]	76	8	nematic
6	116	—	82	0	no LC feature
7	98[c]	65	56	9	nematic
8	80	67	60	7	nematic

[a] Located by hot stage microscope.
[b] $\Delta T = T_{I-N} - T_{\text{recryst}}$.
[c] Polymorphism observed.

The thermal properties of these compounds are listed in Table I.

The d.s.c. thermograms are depicted in Figure 1 where both heating and cooling cycles are shown, and it was observed that monotropism is a common feature of this series of liquid crystals except when $n = 6$, for which no mesophase was observed. All the other compounds exhibit a typical nematic mesophase. As seen in Table I, the sample with butoxy terminal groups gives the widest monotropic mesophase range (12°C). This can be compared with the enantiotropic mesophase ranges of analogous butoxybenzoates containing *p*-phenyl, 1,4-bicyclo(2.2.2)octyl, and *trans*-1,4-cyclohexyl central groupings, which are 88°C, 69°C and 28°C respectively. Similarly, the monotropic mesophase thermal stability for sample $n = 4$ ($T_{I-N} = 87$°C) is much less than the values $T_{N-I} = 241$°C, 221°C and 157°C, quoted for the analogous compounds, respectively.[11] It is obvious that the depression of the thermal stability can be attributed to the non-rod-shaped and non-conjugated nature of the cyclooctyl ring. The rigidity and the polarisability usually required for nematic liquid crystals is impeded by the incorporation of the eight member ring; however, the mesophase is still present although in a much less stable form. At low temperatures the *cis*-conformers of the cyclo-octyl ring are more stable[12] and as this does not encourage linearity in the molecules, orientation is more difficult. The population of the *trans*-conformers, which will lead to greater linearity in the structures, increases at higher temperatures and so the nematic mesophase which is induced by long range orientation of the molecules is more likely to occur when the molecules are cooled from the isotropic phase.

The thermal transitions plotted against the length of the alkoxy terminal groups are illustrated in Figure 2. These compounds do not show the well defined odd-even effect which is commonly observed for liquid crystal materials containing alkyl end groups[3] and many liquid crystal polymers containing flexible linear spacers.[7]

No liquid crystal feature could be detected by either d.s.c. or polarising microscopy when $n = 6$, and the sudden disappearance of a mesophase is difficult to comprehend, as there is no evidence from our nmr and elemental analyses of impurities which might influence the behavior of this compound. As is shown in Figure 1, the other samples all appear to be monotropic although a double en-

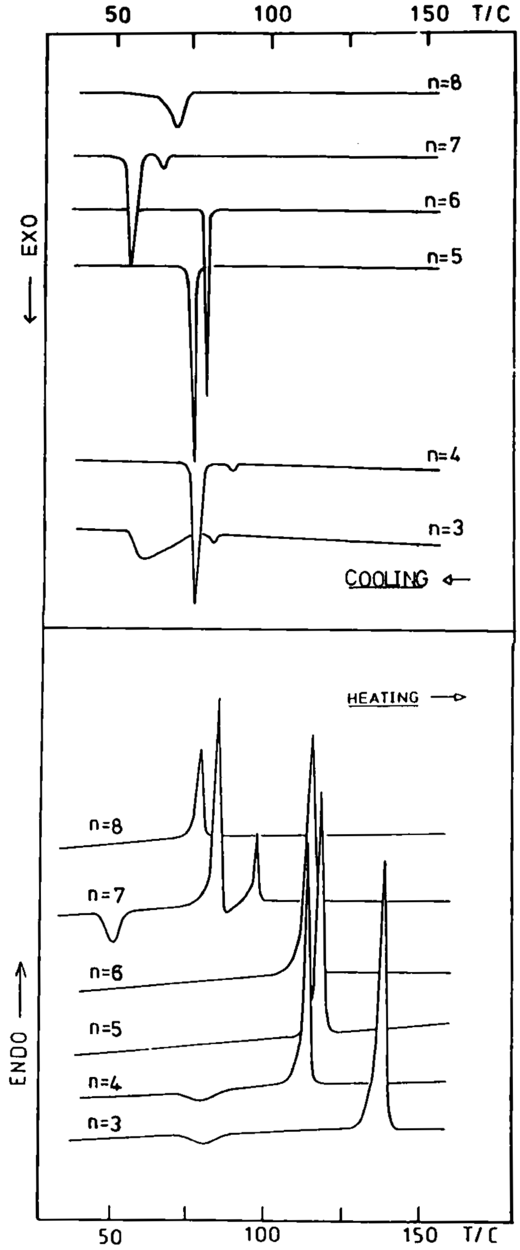


FIGURE 1 The dsc thermograms of COAB compounds.

dotherm was detected in the dsc heating thermogram for sample $n = 7$. However, it is more likely that this represents a crystal–crystal transition rather than a T_{N-I}, as no firm evidence of a nematic structure could be detected by optical microscopy and the endotherms obtained by dsc were much larger than one would expect for a T_{N-I} transition.

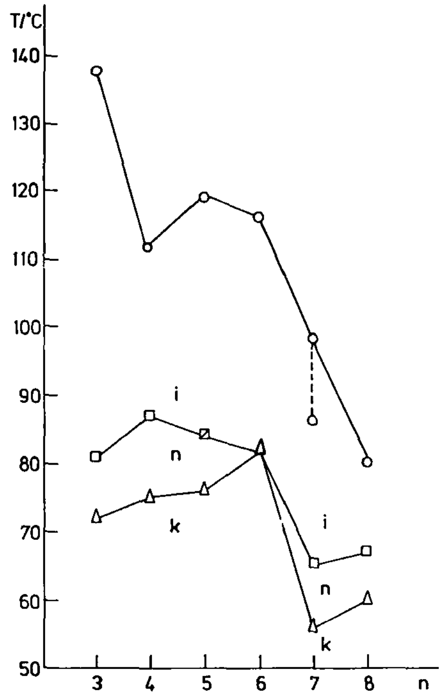


FIGURE 2 The phase diagram for the COAB compounds. (○) melting transition, T_{K-I}; (□) isotropic to nematic transition, T_{I-N}; (△) recrystallization transition, $T_{recryst}$ obtained by dsc. (□) is based on microscopic observation.

CONCLUSIONS

A new series of liquid crystal materials has been synthesized which demonstrates the effect of the cyclooctyl ring upon mesophase formation. Nematic mesophases were observed for all compounds except when *n* = 6, and monotropic behavior was common to all the others. The mesophases occurred within the range 87°C to 56°C, which is much lower than for analogous systems containing saturated rings, but the main conclusion appears to be that the inclusion of the more flexible cyclooctyl unit weakens the tendency for liquid crystal phases to form.

EXPERIMENTAL

The designated model compounds were prepared by condensing the appropriate alkoxybenzoyl chloride with *cis*-1,5-cyclooctanediol (Aldrich) and the preparation of the alkoxybenzoic acids was as described by Gray.[10] The synthesis of the COAB compounds is exemplified by that for *cis*-1,5-cyclooctyl di-(4-pentoxybenzoate) as follows:

A solution of *cis*-1,5-cyclooctanediol (6.5 mmol) and 4-pentoxybenzoyl chloride (14.4 mmol) in dry pyridine (5 cm^3) and chloroform (15 cm^3) was stirred for 24 h at room temperature. Excess of solvent was removed by distillation at reduced pressure. The reaction mixture was then poured onto ice and acidified with concentrated hydrochloric acid, and filtered. The crude product was washed first with water, then with dilute HCl, and finally with water. Without drying, the product was stirred in 10% sodium carbonate solution for 10 hours, then filtered and washed again with water. The designated product was crystallized from ethyl acetate three times.

Results of combustion analyses were in agreement with the expected theoretical values for the compounds. The thermal transitions, T_{K-I}, T_{I-N} and recrystallization $T_{recryst}$, were recorded from differential scanning calorimeter measurements made using a Perkin Elmer DSC-2. Cold crystallization exotherms were located in samples $n = 3$, 4, and 7 at 80°C, 80°C and 50°C respectively. The rates of both heating and cooling cycles were 10°C per min. Mesophase identification was assisted by observing the phase changes using a Reichert Thermovar hot stage polarizing microscope. In all cases typical *schlieren* textures, characteristic of the nematic phase were detected.

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