Liquid Crystalline Properties in Some Alkyl and Alkoxycinnamic Acid Esters

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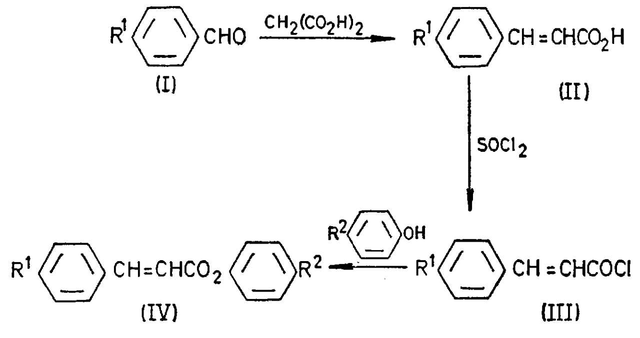
Summary An investigation of several new disubstituted cinnamates reveals the existence of liquid crystalline properties, some exhibiting melting points below 60°.

Research interest in stable as well as broad temperature range liquid crystals has grown in recent years as a result of their increased applications in display devices. Several compounds and mixtures from the Schiff base[1], azo- and azoxy-benzene,[2] chlorostilbene,[3] and benzoyloxybenzoate[4] series have been investigated.

In an extension of these investigations we report our findings on several new liquid crystals, namely derivatives of the *trans*-cinnamic acid ester (IV) (see Scheme). Treatment of (I) with malonic acid in the presence of pyridine–piperidine gave the acid products (II)[5] after several recrystallizations from EtOH. The acids were treated with thionyl chloride in benzene under reflux for two hours to give the cinnamoyl chlorides (III). In each case the acid chlorides were treated *in situ* with the appropriate phenol to give the cinnamates (IV) in 80—95% yield. Satisfactory elemental analyses were obtained and their structures were confirmed by n.m.r. and i.r. spectral analysis. The significant bands of their i.r. spectra are illustrated by the spectrum of the cinnamate (IVb), whose major absorbances are ν_{max} (CCl_4)

1720 (C=O stretching), 1210 (C–O ester stretching), and 976 cm^{-1} (*trans* CH out-of-plane deformation). The n.m.r. analysis for the cinnamate (IVc) taken in $CDCl_3$ shows four major proton absorptions; δ 1·0—2·6 (9H, m), 3·75 (3H, s), 6·52—7·85 (2H, ABq, *J* 78Hz, *trans*-coupled vinyl H), 7·0—7·65 (8H, m, Ph). The nematic temperature ranges for (IV) were determined by d.t.a. and are listed in the Table.



Scheme

A feature shown by the Table is the difference in mesomorphic properties between (IVd) and (IVe) and the alkoxycinnamates. In (IVd) and (IVe), where R^1 and R^2 are alkyl groups, low temperature nematic mesophases exist in both compounds beginning at melting points of 59·7 and 53·6°, respectively, and continuing until the isotropic state is reached at 69·6 and 61·3°. We suggest that the lower polarisability of these compounds relative to the alkyl, alkoxy members of this series is, to a significant degree, responsible for their low melting points.

Table. Nematic temperature ranges for cinnamic acid esters

Compound (IV)	R^1	R^2	Nematic temperature ranges (°)
a	Me	Bu^n	99·7—139·0
b	MeO	Bu^n	81·8—93·0
c	Bu^n	MeO	81·3—88·8
d	Pr^n	C_5H_{11}	59·7—69·6
e	Bu^n	Bu^n	53·6—61·3
f	Bu^n	C_5H_{11}	96·4—103·9
g	$C_5H_{11}O$	Bu^n	96·2—102·0
h	$C_5H_{11}O$	C_5H_{11}	99·1—138·8
i	$C_7H_{15}O$	Bu^n	86·1—110·7

Although the esters have narrow temperature ranges, mixtures have been prepared with nematic mesophases extending over very broad temperatures. For example, the ternary system (A) [wt%, 42 of (IVb), 36 of (IVc), 22 of (IVf)] and the quaternary system, (B) [wt%, 30 of (IVb), 26 of (IVc), 28 of (IVe), 16 of (IVf)] had nematic ranges from 40—90° and 33·5—83·5°, respectively.

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