Effect of Light on the Liquid Crystal Transition Temperatures of 4-(4-n-Pentylphenyl)vinyl Cyanide

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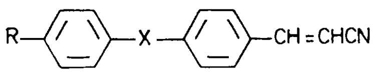
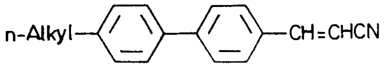
Summary Although 4-(4-n-pentylphenyl)vinyl cyanide gives a nematic mesophase of wide range (48·1°), this material would not be useful for electro-optic displays because of its light sensitivity; similar problems could arise with other mesogens involving the group $-C_6H_4-$CH=CHCN.

Recently, reports have appeared[1–3] about the formation of nematic liquid crystals by derivatives of vinyl cyanide [(I), where R = n-alkyl, n-alkyl–O or n-alkyl–CO·O and X = –CH=N–, –CO·O–, –N=N– or –CH=CH·CO·O–]. The nematic mesophases have a strong positive dielectric anisotropy[1] and mixtures with low m.p.s. and high clearing temperatures are claimed.[2] These properties could attract interest in such materials for use in twisted nematic and other electro-optic displays.



(I)



(II)

The related compounds (II) briefly attracted our interest because of their structural analogy to the 4-n-alkyl-4′-cyanobiphenyls which have provided stable materials giving nematic phases of strong positive dielectric anisotropy in the room temperature range.[4–6] The relatively low nematic–isotropic liquid (N–I) transition temperatures of the 4-n-alkyl-4′-cyanobiphenyls are raised by formulating eutectic mixtures with the 4-n-alkoxy-analogues and with 4-n-alkyl-4″-cyano-*p*-terphenyls.[6–8] This gives stable mixtures with wide nematic ranges, *e.g.*, −10° to +60°.

Compounds of structure (II), in the *trans*-configuration, would be expected to have higher N–I temperatures than those of the 4-n-alkyl- or 4-n-alkoxy-4′-cyanobiphenyls and could provide valuable additional materials for incorporation in eutectic compositions. We therefore prepared 4-(4-n-pentylphenyl)vinyl cyanide, a 'vinylogue' of 4-cyano-4′-n-pentylbiphenyl (5CB), which is the most valuable nematogen in that series and has a m.p. (C–N) of 21° and an N–I transition at 35°.

4-Cyano-4′-n-pentylbiphenyl (4·6 g), Raney nickel (B.D.H. Ltd., 50/50 w/w, 3·2 g), 75% aqueous formic acid (50 ml), and dioxan (40 ml) were heated together[9] (1·5 h). 4′-n-Pentylbiphenyl-4-carboxaldehyde (60%) was isolated as a semi-solid which was characterised by i.r. spectroscopy and mass spectrometry; the 4-nitrophenylhydrazone had m.p. 207—208°. This aldehyde (2·8 g), cyanoacetic acid (0·85 g), ammonium acetate (1·2 g), toluene (6 ml), and pyridine (3 ml) were heated together[10] (30 min). The white precipitate was then redissolved by adding acetic acid and the solution heated overnight under reflux. The crude product was purified by column chromatography (silicic acid; chloroform as eluant) and crystallisation (light petroleum, b.p. 40—60° and ethanol). The colourless 4-(4-n-pentylphenyl)vinyl cyanide (27%) was characterised by i.r. spectroscopy and mass spectrometry. N.m.r. spectroscopy confirmed that the product had the *trans*-configuration. Satisfactory elemental analyses were given by all the above products.

The chromatographically pure product [(II), alkyl = n-pentyl] melted to a smectic A phase at 80° (C–S_A). A S_A–N transition occurred at 99·0° and the nematic phase persisted until 147·1°. However, the product is photochemically very unstable. A sample, mounted as a solidified film between a glass slide and cover slip was exposed to light in the open laboratory for three days; the S_A–N transition temperature was then 90° and the N–I transition temperature 125·5°. Similar exposure for 2 months lowered the S_A–N and N–I transition temperatures to 76° and 91·5°, respectively. In contrast, material stored in the dark for 2 months had unaltered constants, but after exposure to light under the above conditions for only 1 day the transition temperatures were C–S_A, 77–8°; S_A–N, 96·0°; N–I, 136·1°. Similar treatment or much more vigorous irradiation of 5CB has little or no effect on the transition temperatures.[4]

Using material which had been exposed to light for 1 week, n.m.r. spectroscopy showed that the effect on the transition temperatures was caused by formation of the non-linear *cis*-isomer. The ratio of *trans*- (δ 5·86, 1H, d, J 16·3 Hz): *cis*- (δ 5·41, 1H, d, J 12·0 Hz) isomers was 2·6 : 1.

For these reasons, we did not continue studies of the compounds (II) and we report the light sensitivity of the n-pentyl compound to emphasise that related problems could arise with other mesogens involving the structural unit $-C_6H_4-CH=CHCN$. Even a much lower photochemical instability than that now reported would make a mesogen most unsuitable for use in electro-optic displays.

We thank the Ministry of Defence for financial support.

(*Received*, 21*st April* 1975; *Com.* 456.)

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