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

By DAVID COATES* and GEORGE W. GRAY

(Department of Chemistry, The University, Hull HU6 7RX)

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 appeared¹⁻³ 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 anisotropy¹ 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.



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 $+60^{\circ}$.

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 (4.6g), 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 together⁹ (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 together¹⁰ (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 = npentyl] 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 photo-

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chemically 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

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- ($\delta = 5.41$, 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 $-C_{6}H_{4}$ -CH=CHCN. Even a much lower photochemical instability than that now reported would make a mesogen most unsuitable for use in electro-optic displays.

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Using material which had been exposed to light for 1

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