Unsymmetrical Liquid Crystalline Esters

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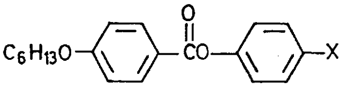
Summary Unsymmetrical (4-substituted phenyl) 4-n-hexyloxybenzoates were found to have low crystal-to-nematic phase transition temperatures and relatively low nematic thermal stability.

RECENTLY several investigations[1–3] have been carried out in order to understand the effects of symmetry and molecular structure in liquid crystals containing ester linkages. The majority of these investigations have included relatively large molecules with any dissymmetry being introduced by various terminal or lateral substituents. Completely unsymmetrical esters, 4-alkoxyphenyl 4-(alkyoxycarbonyloxy)benzoates, have also been prepared[4] and found to have very low crystal-to-nematic transition temperatures, but contained the chemically reactive carbonyldioxy-group. These studies indicated that esters with similar unsymmetrical structures would also be mesomorphic and have low crystal-to-nematic transition temperatures. This communication reports various 4-n-hexyloxybenzoates that have an overall unsymmetrical structure, in relation to the linkage functional groups, and low crystal-to-nematic transition temperatures.



(1) $X = C_6H_{13}O$
(2) $X = Pr^nCO_2$
(3) $X = MeCO$
(4) $X = PhCO_2$

The unsymmetrical 4-n-hexyloxyphenyl (1) (nematic phase 64—89°) and 4-n-butyryloxyphenyl (2) (nematic phase 63—98°) esters of 4-n-hexyloxybenzoic acid displayed low crystal-to-nematic transition temperatures of 64 and 63° with nematic ranges of 25 and 35°, respectively. The analogous ketone, the acetophenone ester (3) (nematic phase 87—89°), however, did not melt until 87° and had a nematic range of only two degrees. Thus, for the general structure of 4-n-alkoxybenzoates that can form the liquid crystalline phase, the ester group can include not only the carbonates, but esters, ethers, and ketones. The unsymmetrical structure probably decreases the packing efficiency in the crystal lattice, resulting in low crystal-to-nematic transition temperatures, but also lowers the thermal stability in the nematic phase as reflected in the low (<100°) liquid crystal-to-liquid transition temperatures.

Benzoates with three phenylene rings generally have higher crystal-to-nematic transition temperatures. For the 4-benzoyloxyphenyl ester (4) (nematic phase 115—141°), which contains a three phenylene system in contrast to the foregoing esters, the nematic transition temperature was not very different from those of the analogous symmetrical *p*-phenylene ester of hydroquinone[1,2] (nematic phase 124—213°) and the unsymmetrical 4-phenylazophenyl 4-n-hexyloxybenzoate (nematic phase 127—149°).[2] The thermal stability of the nematic phase as indicated by the length of the mesomorphic range is higher for the symmetrical compound (89°) than for the unsymmetrical benzoates [26 and 22° for (4) and the azo benzoate, respectively].

All the esters were prepared by reactions of the appropriate acid chlorides with hydroxy-compounds. The ethers were synthesized from n-hexyl bromide and the appropriate hydroxy-compound in refluxing methanol containing potassium hydroxide.[5] The final products were recrystallized from methanol and sublimed under reduced pressure. Combustion, i.r., and n.m.r. analyses were consistent with the structures reported. The transition temperatures given were observed with a Reichert hot-stage microscopic m.p. apparatus with crossed polarizers. The temperatures were verified by use of standards and are accurate to ±1·5°. The nematic-to-isotropic transition temperatures were completely reversible, but the crystal-to-nematic transition temperatures were observed to be lower and variable during a cooling cycle owing to supercooling of the liquid crystalline phase. Those reported are for the heating cycle. All of the mesomorphic phases were determined to be of the nematic 'threaded texture'.[6]

The examples reported here make it clear that for liquid crystals containing ester linkages, the crystal-to-nematic phase transition temperature will be lower for compounds with an overall unsymmetrical structure. An unsymmetrical structure will also lower the thermal stability of the nematic phase and will result in shorter mesomorphic ranges.

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