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Synthesis and Liquid Crystal Properties of Various Dicarboxylic Properties of Various Dicarboxylic Esters[1]

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Synthesis and Liquid Crystal Properties of Various Dicarboxylic Esters[1]

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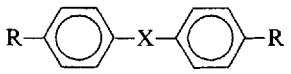
Two series of mesogenic dicarboxylic esters have been prepared and studied, one having an olefinic and the other a *trans*-1,4-cyclohexane central group. The compounds are mainly nematic; however a few also exhibit smectic phases. Twisted-nematic mesophases are observed for the esters having chiral alcohol groups. Comparisons of nematic behavior for compounds with *trans*-, *cis*-, and α-methyl-substituted double bonds indicate the mesophase-destabilizing effects of increases in intermolecular separation and the lesser importance of molecular symmetry. Dicholesteryl *trans*-1,4-cyclohexanedicarboxylate, which contains no aromatic groups, was found to possess the second highest mesophase-isotropic point in either series, surpassed only by the corresponding *p*-methoxyphenyl ester. Several of the nematogenic fumaric acid derivatives exhibited dynamic scattering, indicating that these materials possess a negative dielectric anisotropy. The *trans*-1,4-cyclohexane diesters did not show the dynamic scattering effect.

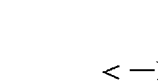
1 INTRODUCTION

For the past few years we[3] and others[4] have been studying the effects on liquid crystal behavior of structurally modifying the central group in mesogens of the general type *A*, where R is alkoxy or *n*-alkyl.



A

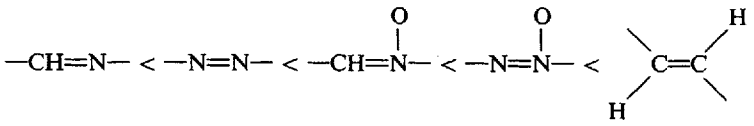
For a given R group, van der Veen and coworkers[4a] found that the nematic clearing point increased in the order —CH=N— and —N=N—



. The permanent dipole of the azoxy group was thought to be

the dominant factor for the higher clearing points in the azoxy series although conformational differences between series were recognized as a contributing factor of unknown importance.

In a paper appearing at almost the same time Young, Haller, and Aviram[4b] reported the synthesis of a series of p,p'-dialkoxy-*trans*-stilbenes. Comparison of the nematic clearing points of the stilbenes with other related series led to the following order of central groups:



The results clearly indicate that a permanent dipole in the central group is not a necessary condition for the occurence of high temperature nematic phases.

In this report we present evidence bearing on the importance of intermolecular separation and stereochemistry on nematic stability. In addition, several examples are given which demonstrate that π-electron density in the central group is not a necessary condition for mesophase formation.

2 RESULTS

Twenty diesters having the following general structure were prepared and characterized. The dicarboxylic acids utilized were fumaric, maleic,

ROOC—X—COOR

mesaconic (α-methylfumaric), and *trans*-1,4-cyclohexanedicarboxylic acid. The data are given in Table I. The compounds are mainly nematogenic but smectic behavior also occurs. For the esters having chiral alcohol moeities, twisted-nematic mesophases are observed.

3 DISCUSSION

The fumarate esters, in which the groups are *trans* about the double bond, are highly symmetrical, belonging to the C_{2h} point group. All exhibited nematic mesomorphism. The only *p*-alkylphenyl fumarate studied, the

p-pentyl derivative **6**, exhibits a monotropic nematic phase just below the crystal melting point. Introduction of a methyl substituent at the double bond of the central group, compounds **7** and **8**, lowers the symmetry to C_s and causes a decrease of more than 40° in the nematic clearing point of the *p*-butoxy ester **7** compared to **4**. Examination of CPK space-filling molecular models indicates that the fumarate esters may adopt an essentially coplanar arrangement and that the introduction of a methyl group at the double bond causes no additional interference to coplanarity. However, the spherically-symmetric α-methyl group does cause an increase in molecular breadth which would be expected to result in an increase in the average intermolecular separation. Since intermolecular attractive forces are approximately proportional to the inverse sixth power of the distance between molecules (Lennard–Jones potential) a small increase in intermolecular separation caused by the presence of an α-methyl group may be responsible for the lower temperature nematic phase of **7** and its absence in **8**, compared to the corresponding fumarate esters.

The maleic acid diesters **9** and **10**, belong to the C_{2v} point group, intermediate in symmetry between the mesaconic and fumarate derivatives. However, the *cis* arrangement of groups about the central double bond in the maleates results in a large deviation from molecular linearity, in effect increasing the intermolecular separation such that no mesomorphic properties are observed. Thus, in agreement with Young, *et al.*[4b] we conclude that symmetry considerations alone are too general to be useful in rationalizing mesomorphic behavior (or lack of it). For our compounds the factor of intermolecular separation appears to dominate.

Compounds **11** to **20** in Table I possess a saturated central group, the *trans*-1,4-cyclohexane ring. The *p*-methoxyphenyl derivative **11**, first prepared by Bacon and Brown,[6] has a high temperature nematic phase of almost 100° range. The nematic clearing points of the *p*-butoxy- and *p*-pentylphenyl esters in this series are higher than those of the corresponding fumarates. Examination of the data for the other cyclohexane derivatives in Table I also leads to the conclusion that the presence of π-electron density in the central group is not a necessary condition for mesophase formation.

Compounds **16** and **20** possess chiral alcohol moieties, active 2-methylbutanol and cholesterol, respectively, and both diesters give rise to twisted-nematic mesophases. The latter compound, dicholesteryl *trans*-1,4-cyclohexanedicarboxylate is the only one investigated which contains no aromatic groups and its clearing point of 232° is surpassed only by the corresponding *p*-methoxyphenyl ester **11**.

Compounds **2**, **3**, **4** and **5** in their nematic phase between transparent glass electrodes were found to exhibit dynamic scattering,[7] a property characteristic of nematogens having a negative dielectric anisotropy.

TABLE I

Transition temperature data for some dicarboxylic esters[a]

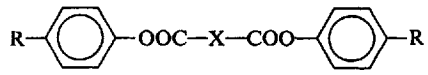
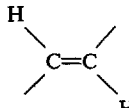
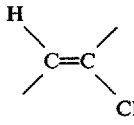
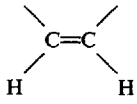
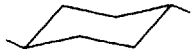
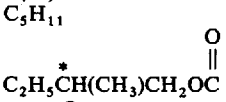
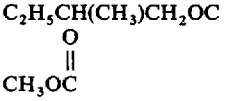
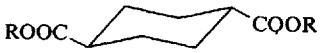
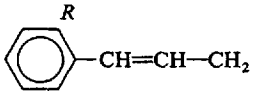
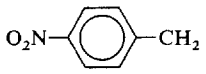
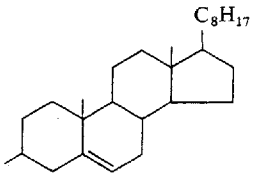
Compound No.	X	R	Phase transitions and temperatures[b]
			
1		CH_3O	K 180 I (142 N)
2		C_2H_5O	K 127 N 147 I
3		C_3H_7O	K 125 N 130 I
4		C_4H_9O	K 104.5 N 137 I
5		$C_7H_{15}O$	K 90 N 119 I
6		C_5H_{11}	K 86 I (85 N)
7		C_4H_9O	K 95 I (94 N)
8		C_5H_{11}	m.p. 68–69
9		C_4H_9O	m.p. 57–58
10		C_5H_{11}	isotropic oil
11		CH_3O	K 143 N 242 I[c]
12		CH_3S	K 107.5 N 138 I
13		C_4H_9O	K 107 N 153 I
14		C_4H_9	K 91 S 105 N 150 I
15		C_5H_{11}	K 101.5 S 135 N 161 I
16			K 124.5 C 130 I
17			K 147 N 162.5 I
			
18			K122 N 130 I

TABLE I (*continued*)

Compound No.	*R*	Phase transitions and temperatures[b]
19		K 103 N 154 I[d]
20	 (cholesterol)	K 125 S 197 C 232 I

[a] All compounds gave correct elemental analyses.
[b] The linear notation is described in ref. 5.
[c] Ref. 6.
[d] The corresponding *p*-nitrophenyl ester (i.e., lacking the CH_2 groups) is not mesogenic, m.p. 185.5–187°.

4 EXPERIMENTAL

The diesters were prepared by two routes. (1) The acid-catalyzed reaction of excess phenol with the diacid in benzene. Azeotroped water was separated in a Dean–Stark trap. (2) Reaction of the diacid chloride of *trans*-1,4-cyclohexanedicarboxylic acid with the alcohol or phenol in the presence of pyridine. Representative procedures are given below.

Mesophases were identified using a 100-power AO Spencer polarizing microscope equipped with a variable temperature stage designed in these laboratories.[8] For mesogenic compounds, the temperatures reported are those at which the solid or mesophase has just disappeared. Temperatures are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

NMR spectra were obtained in $CDCl_3$ using a Varian A-60 spectrometer with TMS as an internal standard.

Di-p-n-butoxyphenyl fumarate (**4**) Fumaric acid is not soluble in benzene but was found to dissolve in an excess of the phenol used in the esterification. Hence, only enough benzene was added to azeotrope off the water formed during the reaction.

A mixture of *p-n*-butoxyphenol (Aldrich, 6.64 g, 0.04 mole), fumaric acid (Eastman, 1.16 g, 0.01 mole), and 5 ml of dry benzene were placed in a 50-ml round bottom flask fitted with a Dean–Stark trap and reflux condenser. Concentrated sulfuric acid (0.5 ml) was added and the reaction mixture refluxed for 48 hours. The reaction mixture was then cooled and 60 ml of ether added. The ether solution was washed twice with 25 ml of cold water, twice with 20 ml of 10% sodium bicarbonate solution, and once more with cold water. The solution was dried (sodium sulfate), filtered, and the ether evaporated to yield a yellow solid. Two recrystallizations from absolute ethanol afforded white crystals of **4**, 1.8 g, 44% yield, K 104.5 N 137 I. NMR: 3.8 ppm, OCH_3(s); 6.7–7.4 ppm, vinyl and aromatic protons.

Anal Calc. for $C_{24}H_{28}O_6$: C, 69.89; H, 6.84; Found, C, 70.01; H, 6.88.

Di-p-n-pentylphenyl trans-1,4-cyclohexanedicarboxylate (**14**) The diacid chloride was prepared by refluxing the diacid (Aldrich) in an excess of thionyl chloride for 6 hours, then distilling under vacuum. The diacid chloride was obtained as a clear, colorless liquid and was used immediately.

The diacid chloride (2.1 g, 0.01 mole) was dissolved in 5 ml of dry pyridine and a solution of *p-n*-pentylphenol (Eastman, 3.3 g, 0.02 mole) in 3 ml of pyridine was added. The solution was stirred at room temperature overnight, then diluted with 30 ml of ether. The ether solution was washed twice with 15 ml portions of cold water, then one with 10% HCl, twice with 10% sodium bicarbonate solution, followed by a cold water wash. The solution was stripped off on a rotary evaporator after being dried (magnesium sulfate). Two recrystallizations from mixed hexanes afforded white crystals of **15**, 2.9 g, 62% yield, K 101.5 S 135 N 161 I. NMR: 0.7–3.0 ppm, aliphatic protons; 7.1 ppm, aromatic protons.

Anal Calc. for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68; Found, C, 77.68; H, 8.74.

Acknowledgement

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1. Presented in part at the Liquid Crystal Symposium, 166th National Meeting, American Chemical Society, Chicago, Aug. 1973; see L. Verbit and R. L. Tuggey, *Liquid Crystals and Ordered Fluids*, Vol. 2, J. F. Johnson and R. S. Porter, Editors, Plenum Press, New York, 1974, p. 307.

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