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The Preparation and Liquid Crystal Behaviour of Pyrimidines and Dioxans Incorporating a Dimethylene Linking Group†

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(*Received October 2, 1984*)

The preparation of 2-(4-cyanophenylethyl)-5-alkylpyrimidines and *trans*-2-(4-(cyanophenylethyl)-5-alkyl-1,3-dioxans, which incorporate a dimethylene linking group into phenylpyrimidine and phenyldioxan structures, is described. The pyrimidinyl compounds exhibit only virtual nematic-isotropic transitions and the dioxan compounds have monotropic nematic-isotropic transitions. Comparisons are made between the liquid crystal behaviour of these compounds and similar materials not incorporating the linking group. Comparisons are also made with related systems incorporating the bicyclo(2.2.2) octane ring and with systems in which the dimethylene group links two phenyl rings.

The materials described have been found to exhibit interesting dielectric properties. The pyrimidine compounds, for example, have higher perpendicular and parallel permittivities than the corresponding materials without the dimethylene linkage.

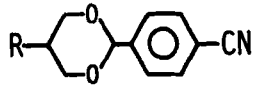
INTRODUCTION

Considerable interest has been shown in compounds such as the 1-(*trans*-4-alkylcyclohexyl)-2-(4-cyanophenyl)ethanes[1] which incorpo-

† Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

TABLE I

Some physical parameters for materials of structure (I)



(I)

R	C—I (°C)	N—I (°C)	ΔH_{fus} (kJ mole^{-1})	η (cP)	Δn	Δε
C_5H_{11}	56	(52)	21	16.8 (41°C)[a]; 46 (20°C)[b]	0.08 (40°C)	—
C_7H_{15}	54	(53)	—		0.09 (42°C)	+11 (42°C)

[a] nematic viscosity
[b] nematic extrapolated viscosity
( ) monotropic transition

rate a dimethylene linking group in the core of a 4-(*trans*-4-alkylcyclohexyl)benzonitrile structure. This presentation is concerned with the preparation and evaluation of the liquid crystal behaviour of the analogous systems where a dimethylene linking group is introduced into the structures of phenylpyrimidines and phenyldioxans.

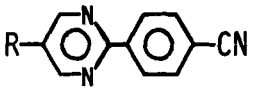
The *trans*-5-alkyl-2-(4-cyanophenyl)-1,3-dioxans (I), reported by Demus and Zaschke,[2] show monotropic nematic phases and have low melting enthalpies which result in the formation of good eutectic mixtures. These materials also exhibit a relatively high positive dielectric anisotropy (Δε), and are of low birefringence (Δ*n*) and moderate viscosity (η).

The 5-alkyl-2-(4-cyanophenyl)pyrimidines (II), reported by Boller *et al.*,[3] often show monotropic nematic phases and exhibit high positive dielectric anisotropy. Low viscosities have also been claimed for these materials, but values usually relate to fairly high temperatures (see Table II).

It has been demonstrated by Carr, Gray, and McDonnell[1] that introduction of a dimethylene linking group into the core of a 4-(*trans*-4-alkylcyclohexyl)benzonitrile (III) (giving a 1-(*trans*-4-alkyl-

TABLE II

Some physical parameters for materials of structure (II)

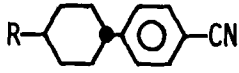


(II)

R	C—N/I (°C)	N—I (°C)	η (cP)	Δε
C_5H_{11}	71	(52)	—	21.3 (51°C)
C_7H_{15}	45	51	25 (38°C); *ca.* 50 (20°C)[a]	—

[a] extrapolated from a graph[3]

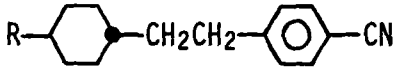
cyclohexyl)-2-(4-cyanophenyl)ethane (IV)) has little effect on the nematic thermal stability.



(III)

R = C_5H_{11} has C-N 30°C and N-I 55°C

R = C_7H_{15} has C-N 30°C and N-I 57°C



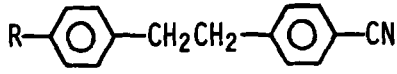
(IV)

R = C_5H_{11} has C-N 30°C and N-I 51°C

R = C_7H_{15} has C-N 45°C and N-I 54.5°C

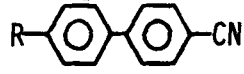
Indeed, the physical and electro-optical properties of materials (III) and (IV) are closely similar, except that the dye order parameters for the materials (IV) are generally higher[4] than those for the materials (III). This makes the materials (IV) useful for dyed cholesteric-nematic phase change displays.

However, incorporation of a dimethylene linking group into an alkylcyanobiphenyl (VI), to give a 1-(4-alkylphenyl)-2-(4-cyanophenyl)ethane (V),[1] results in a dramatic fall in nematic thermal stability.



(V)

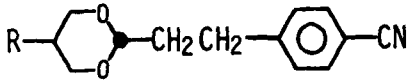
R = C_5H_{11} has C-I 62°C and N-I [-24°C]



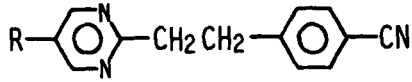
(VI)

R = C_5H_{11} has C-N 22.5°C and N-I 35°C

In view of the information given above, and to investigate further the effect of the dimethylene linking group, we have prepared examples of compounds (VII) and (VIII), which involve the incorporation of a dimethylene linking group into structures (I) and (II) respectively.



(VII)

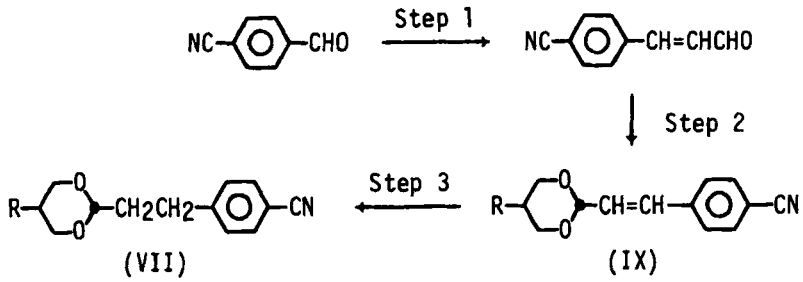


(VIII)

RESULTS AND DISCUSSION

The *trans*-5-alkyl-2-(2-(4-cyanophenyl)ethyl)-1,3-dioxans (VII) were prepared by Synthetic Route I.

SYNTHETIC ROUTE I



(VII) (IX)

Step 1 $CH_3CHO/NaOH$ (aq)

Step 2 $RCH(CH_2OH)_2/CH_3C_6H_4SO_3H$/Azeotropic removal of water

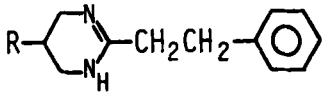
Step 3 $NaBH_4/Te$[5]

Compounds prepared had R = C_3, C_5 and C_7

This route represents the most successful of the several routes which were tried to prepare compound (VII). The carbonyl group of 4-cyanobenzaldehyde is activated for the aldol condensation and the reaction gives 68% of pure *trans*-alkene after recrystallisation. The *cis*- and *trans*-isomers of the dioxan ring were readily separated by recrystallisation of the compounds (IX) (which are higher melting and less soluble than the compounds (VII)), and reduction of the *trans*-isomer occurred in good yield (55% of 99.7% pure material after recrystallisation) without isomerisation.

The 5-alkyl-2-(2-(4-cyanophenyl)ethyl)pyrimidines (VIII) were prepared by Synthetic Route II.

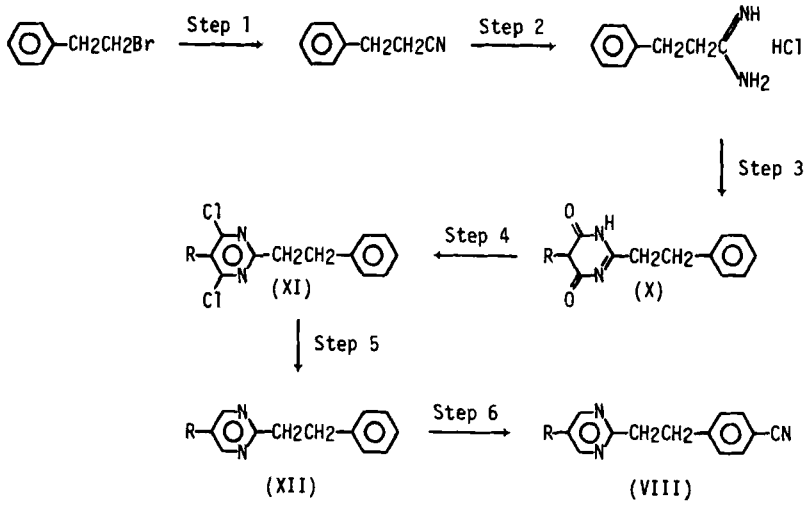
In the dehydrohalogenation of the compounds (XI) to give the compound (XII), we had difficulty in achieving complete removal of the chlorine substituents without formation of significant quantities of the tetrahydro pyrimidine (XIII).



(XIII)

Compound (XIII) is formed by hydrogenation of the pyrimidine ring and the structure has been confirmed by n.m.r. Zaschke[6] reported

SYNTHETIC ROUTE II

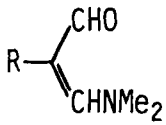


Step 1 NaCN/DMSO
Step 2 (i) HCl (g)/C_2H_5OH; (ii) NH_3/CH_3OH
Step 3 $RCH(CO_2C_2H_5)_2/NaOC_2H_5/C_2H_5OH$
Step 4 $POCl_3/PhNMe_2$
Step 5 $H_2/Pd/KO_2CCH_3$
Step 6 (i) $(COCl)_2/AlCl_3$; (ii) NH_3 (aq); (iii) $SOCl_2$/DMF

Compounds prepared had R = C_3 and C_5

similar results and overcame the problem by adding water to the reaction mixture.

The synthesis of the compounds (VIII) has subsequently been improved by employing 3-(4-bromophenyl)propionitrile as starting material; this facilitates the introduction of the cyano group at the end of the synthesis. The diethyl alkylmalonate employed to prepare the compound (X) can be replaced by compound (XIV) (prepared by Vilsmeier Haak formylation of the diethyl acetal of an aldehyde[7]); this gives compounds (XII) directly and removes the need for the chlorination and dechlorination steps.



(XIV)

The transition temperatures for the mesogenic intermediates (IX), and for compounds (VII) and (VIII) are given in Tables III, IV and V.

The enthalpies of fusion for the C_5H_{11} homologues of compounds (VII) and (VIII) are also given in these tables. That for the C_5 dioxan incorporating the dimethylene linking group is higher than that for the material (I) without the linkage (Table I). Mixtures of the materials (VII) would not therefore be expected to give such large depressions of melting point as those obtained with the materials (I).

The transition temperatures for several well known terminally cyano substituted nematogens and their analogues incorporating a dimethylene link are given in Table VI arranged in order of decreasing T_{N-I}. The data are also represented graphically in Figure 1.

We observe that there is no significant change in the *order* of nematic thermal stability on introduction of the linking group. However, introduction of the linking group does significantly change the *differences* in T_{N-I} values, increasing particularly those between the materials with cyclohexane, dioxan and pyrimidine rings.

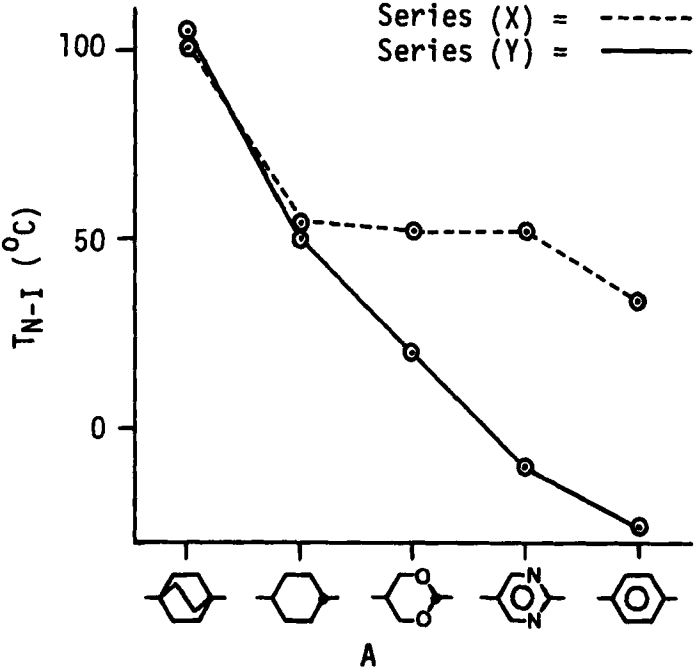
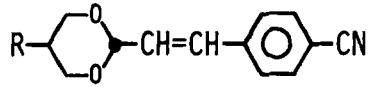


FIGURE 1 Graphical representation of the data in Table VI.

TABLE III

Transition temperatures for the compounds (IX)



(IX)

R	C—N/S_A (°C)	S_A—N (°C)	N—I (°C)
C_3H_7	89	—	98.5
C_5H_{11}	64	—	102
C_7H_{15}	62	74	100

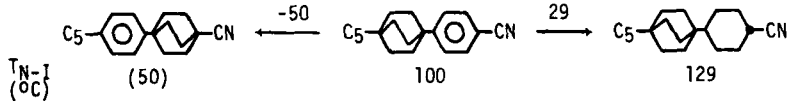
On the basis of the foregoing results, we may draw attention to the following points.

(1) It has already been shown[1] that the isolation of two aromatic (benzene) rings by —CH_2CH_2— has an adverse effect on nematic thermal stability.

(2) The above point is reinforced by the adverse effect on $T_{N—I}$ observed on isolation of the heteroaromatic pyrimidine ring from the aromatic benzene ring by the —CH_2CH_2— group.

(3) Similar isolation of the dipolar dioxan ring from the benzene ring also has quite a serious effect on $T_{N—I}$, but the effect is not as drastic as that noted in points (1) and (2) above.

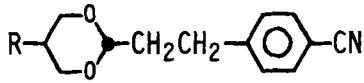
These conclusions are also consistent with some earlier observations by Carr, Gray and McDonnell[1] concerning the following interesting set of materials.



The higher $T_{N—I}$ values are found for the two systems where only one polar/polarisable centre (—CN or —C_6H_4CN) exists in the mol-

TABLE IV

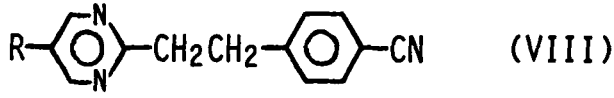
Transition temperatures and enthalpies of fusion for the compounds (VII)



(VII)

R	C—I (°C)	N—I (°C)	ΔH_{fus} (kJ mole^{-1})
C_3H_7	55	(4)	—
C_5H_{11}	66	(19)	28.9
C_7H_{15}	55	(24.5)	—

TABLE V



(VIII)

Transition temperatures and enthalpies of fusion for the compounds (VIII)

R	C—I (°C)	N—I (°C)	ΔH_{fus} (kJ mole^{-1})
C_3H_7	71	[−32][a]	—
C_5H_{11}	51	[−11][a]	18.4
C_7H_{15}[8]	60	(−1)	—

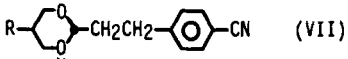
[a] virtual transition temperatures extrapolated from mixtures with E7

ecule. Isolation of the cyano and phenyl groups gives a low $T_{N—I}$ value. Similar effects have been discussed by Eidenschink,[9] who regards the molecules as consisting of coupling emitters and receivers of energy, and treats them as antennae.

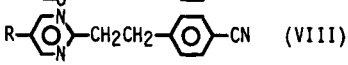
Some other physical properties

1. Viscosity

In both cases the viscosity is raised by introduction of the linking group (see Tables I and II).



(VII)



(VIII)

extrapolated nematic viscosity (ZLI 1132) at 20°C/cP

R = C_5H_{11} 55

R = C_5H_{11} 56

2. Permittivity

Studies of the dielectric properties of the pyrimidines (VIII) show that the materials have higher permittivities than the corresponding materials without the linkage. The results are shown in Table VII wherein we believe that the better comparison is given between the propyl derivatives and the corresponding pentyl derivatives having the same molecular formula. Other experiments on the dioxan analogues (VII) indicate a similar, but smaller effect. These results are interesting and emphasise the desirability of making more detailed studies; these are currently being undertaken and the results will appear in a later publication. Until they are available, it would be

TABLE VI

T_{N-I} values for some related cyano-compounds

R = C_5H_{11}

Series X			Series Y		
	N-I (°C)	Fall in N-I (°C)		N-I (°C)	Fall in N-I (°C)
R-Ph-Ph-CN	100	45	R-Ph-CH_2CH_2-Ph-CN	113	62
R-Cy-Ph-CN	55	3	R-Cy-CH_2CH_2-Ph-CN	51	32
R-Dx-Ph-CN	(52)	0	R-Dx-CH_2CH_2-Ph-CN	(19)	30
R-Py-Ph-CN	(52)	17	R-Py-CH_2CH_2-Ph-CN	[-11]	13
R-Ph-Ph-CN	35		R-Ph-CH_2CH_2-Ph-CN	[-24]	

premature to express any view as to whether the permittivity data may be explained in terms of dipole moments or anti-parallel correlation effects.

EXPERIMENTAL

Materials

All the final products, and where necessary, the intermediates in various steps in the syntheses, were shown to be pure by various techniques (t.l.c., g.l.c., h.p.l.c.) and confirmation of structure was

TABLE VII

Permittivity results for some diemethylene linked materials

	iso (55°C)		iso (55°C)
C_3H_7-Py-CH_2CH_2-Ph-CN	20(±1)	C_5H_{11}-Py-Ph-CN	16.7
C_3H_7-Dx-CH_2CH_2-Ph-CN	17.2	C_5H_{11}-Dx-Ph-CN	15.1
C_3H_7-Cy-CH_2CH_2-Ph-CN	10.1	C_5H_{11}-Cy-Ph-CN	9.8
C_5H_{11}-Py-CH_2CH_2-Ph-CN	17(±1)		
C_5H_{11}-Dx-CH_2CH_2-Ph-CN	15.4		
C_5H_{11}-Cy-CH_2CH_2-Ph-CN	9.2		

obtained, where appropriate, by n.m.r., mass spectrometry, and infra-red spectroscopy.

Preparation of *trans*-5-alkyl-2-(2-(4-cyanophenyl)ethyl)-1,3-dioxans (VII) (see Synthetic Route I)

3-(4-Cyanophenyl)propenal. This was prepared from 4-cyanobenzaldehyde by the method given by Nishimura[10] for the preparation of 3-(4-nitrophenyl)propenal. The yield of 3-(4-cyanophenyl)propenal, m.p. 132–133°C, was 68%. The infra-red spectrum indicated that only the *trans*-isomer was present.

trans-*5-Alkyl-2-(2-(4-cyanophenyl)ethenyl)-1,3-dioxans (IX).* These materials were prepared from 3-(4-cyanophenyl)propenal and a 2-alkylpropan-1,3-diol† by the standard method.[11] Yields were between 45 and 50% of the pure *trans*-dioxan after recrystallisations from methanol. Physical data are given in Table III.

trans-5-Alkyl-2-(2-(4-cyanophenyl)ethyl)-1,3-dioxans (VII). These were prepared from the *trans*-5-alkyl-2-(2-(4-cyanophenyl)ethenyl)-1,3-dioxans (IX) by reduction using sodium hydrogen telluride. The method was that of Ramasamy *et al.*,[5] and the *trans*-5-alkyl-2-(2-(4-cyanophenyl)ethyl)-1,3-dioxans (VII) were obtained in 50 to 55% yield. Physical data are given in Table IV.

Preparation of 5-alkyl-2-(2-(4-cyanophenyl)ethyl)pyrimidines (VIII) (see Synthetic Route II)

1-Phenyl-2-cyanoethane. This was prepared by cyanation of phenethyl bromide using the standard procedure given by Vogel.[12] The product had b.p. 76°C at 0.01 mm Hg and was obtained in 80% yield.

3-Phenylpropyl-1-amidine hydrochloride. This was prepared from 1-phenyl-2-cyanoethane, *via* the imino-ether, by the method of Boller *et al.*[3] The material was not purified, but had m.p. 165–167°C and was obtained in 38% yield.

5-Alkyl-2-(2-phenylethyl)-4,6-dihydroxypyrimidines (X). These were prepared from 3-phenylpropyl-1-amidine hydrochloride and the appropriate diethyl alkylmalonate using the method of Dox and Yoder.[13] Yields were above 90% and both the 5-propyl- and 5-pentyl-2-(2-phenylethyl)-4,6-dihydroxypyrimidines had m.p. >300°C.

†Supplied by E. Merck, Darmstadt.

5-Alkyl-2-(2-phenylethyl)-4,6-dichloropyrimidines (XI). These were prepared from the compounds (X) by the action of phosphorus oxychloride using the method of Todd and Bergel.[14] The materials were obtained in 50% yield and had the following constants:

5-propyl-2-(2-phenylethyl)-4,6-dichloropyrimidine, m.p. 56°C;
5-pentyl-2-(2-phenylethyl)-4,6-dichloropyrimidine, b.p. 166°C at 0.1 mm Hg.

5-Alkyl-2-(2-phenylethyl)pyrimidines (XII). The dichloropyrimidine (XI) (0.031 mole) was stirred with 5% palladium-on-carbon (0.5 g) and anhydrous potassium acetate (0.062 mole) in ethanol (150 cm^3). The mixture was maintained under hydrogen at atmospheric pressure and at room temperature until 1½ times the theoretical amount of hydrogen had been absorbed, i.e., 1½ × 0.062 mole, since one mole of hydrogen is required to remove each chlorine. This seems to be the best point at which to stop to optimise the removal of the chlorine with minimum formation of the tetrahydropyrimidine (XIII). The catalyst was then filtered off, washed with ethanol, and the solvent was removed *in vacuo* from the combined filtrate and washings. The residue was taken up in ether (100 cm^3) and washed with water (3 × 80 cm^3). The organic phase was then dried ($MgSO_4$) and filtered; the solvent was then removed. The resulting oil was distilled under reduced pressure. Yields were between 40 and 60% and the materials had the following constants:

5-propyl-2-(2-phenylethyl)pyrimidine, b.p. 110°C at 0.1 mm Hg;
5-pentyl-2-(2-phenylethyl)pyrimidine, b.p. 145°C at 0.01 mm Hg.

5-Alkyl-2-(2-(4-carbamoylphenyl)ethyl)pyrimidines. The 5-alkyl-2-(2-phenylethyl)pyrimidines (XII) were converted into the corresponding 5-alkyl-2-(2-(4-carbamoylphenyl)ethyl)pyrimidines by the method of Neubert and Fishel.[15] Yields were between 15 and 40% of materials with the following constants:

5-propyl-2-(2-(4-carbamoylphenyl)ethyl)pyrimidine, m.p. 166–168°C;
5-pentyl-2-(2-(4-carbamoylphenyl)ethyl)pyrimidine, m.p. 183°C.

5-Alkyl-2-(2-(4-cyanophenyl)ethyl)pyrimidines. The amide (0.001 mole) was suspended in D.M.F. (10 cm^3; dried over type 4A molecular sieves) and thionyl chloride (0.004 mole) in D.M.F. (5 cm^3; dried as above) was added dropwise at 0°C. Stirring and cooling were continued for 15 h. Dilute (2M) hydrochloric acid was then added and the mixture was poured onto ice (10 g), and shaken with ether (3 × 20 cm^3). The combined organic extracts were washed with water (3 × 20 cm^3), dried ($MgSO_4$), and filtered; the solvent was then removed. The crude product was chromatographed on a column of *neutral* alumina (1 × 30 cm^3) eluted with chloroform; the appropriate fraction was obtained and recrystallised from hexane. Yields were between 30 and 40%. Physical data are given in Table V.

Physical measurements

Transition temperatures (T_{C-I}, T_{N-I} etc) for the materials in Tables III, IV and V were measured by optical microscopy using a Nikon LKe polarising microscope in conjunction with a Mettler heating stage (FP52) and control unit (FP5).

Enthalpies of fusion for the C_5H_{11} homologues of compounds (VII) and (VIII) were obtained by differential scanning calorimetry (Perkin Elmer DSC-2C) using a heating rate of 10° min^{-1}. The viscosities and permittivity values of the materials were measured by standard procedures at R.S.R.E., Malvern.

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