This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 07:35
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Studies of Some Heterocyclic Mesogens

J. A. Nash[a] & G. W. Gray[a]

[a] Chemistry Department, University of Hull, Hull, HU6 7RX, England

Version of record first published: 29 Aug 2007.

To cite this article: J. A. Nash & G. W. Gray (1974): Studies of Some Heterocyclic Mesogens, Molecular Crystals and Liquid Crystals, 25:3-4, 299-321

To link to this article: http://dx.doi.org/10.1080/15421407408082809

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1974, Vol. 25, pp. 299-321

Printed in Dordrecht, Holland

Studies of Some Heterocyclic Mesogens[†]

J. A. NASH and G. W. GRAY

Chemistry Department
University of Hull
Hull HU6 7RX, England

(Received November 14, 1972)

New mesogens have been prepared and studied by differential thermal analysis and optical microscopy to elucidate the effects on mesomorphic properties of replacing a benzene ring by different heterocyclic rings.

Earlier workers have assessed the effects on *nematic* properties arising from such changes in the terminal groups of molecules of the type 4-MeO·C_6H_4·C_6H_4·N:CH·R-4′ (where R is phenyl, pyridyl or certain five-membered heterocylic rings). By studying the corresponding *n*-octyl ethers, the relative effects of the different terminal rings on smectic properties have now been established. The compounds exhibit smectic polymorphism and the types of phase have been examined. Compounds of the type 4-R·CH:N·C_6H_4·C_6H_4·N:CH·R-4′ showed some differences in trends compared with those for compounds with only one terminal group, R. Other compounds, including two series of the type 4-X·C_6H_4·CO·O·C_6H_4·CH:CH·R-4′ (where X is methoxy or *n*-octyloxy and R is phenyl, pyridyl or diazinyl), have been examined and show, in addition to the trends observed above, the effect of the heterocyclic system on π-bond interactions within the molecule.

To supplement earlier work and to complement the above studies of changing the terminal groups of molecules, compounds with pyridyl rings in non-terminal positions have also been studied.

The overall results relating to the mesophases formed and the trends in the crystal–mesophase or -amorphous liquid and mesophase-mesophase or -amorphous liquid transition temperatures are discussed in terms of changes in axial molecular polarizability produced by the hetero-atom either directly or indirectly.

[†] Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

INTRODUCTION

The liquid crystalline properties of organic compounds are highly sensitive to changes in chemical structure, and considerable effort has been devoted to the systematic study of closely related compounds in order to establish empirical relationships between structural and other parameters and the thermal stabilities of the various types of mesophase which may be observed.[1] In the past few years, much attention has been devoted to the preparation and study of homologous series of organic compounds which show mesogenic character. In such cases, it has been shown that when the transition temperatures for the various mesophases shown by a particular series are plotted against the number of carbon atoms in the alkyl chain, smooth curve relationships of a limited number of kinds are observed.[1]

Comparatively less systematic work has been carried out to examine the effects of other changes in molecular structure on mesophase thermal stabilities. However, this paper now presents thermodynamic data obtained from several series of structurally related compounds in which the nature of the aromatic ring system is changed, and an attempt is made to relate the changes observed in mesophase thermal stability to these changes in structure. These changes are generally accomplished by replacing a phenyl or *p*-phenylene ring in a known liquid crystalline compound by pyridyl or related rings; in a few cases, five-membered heterocyclic rings are also used. Changes such as these, unlike changes in an homologous series, are likely to have a less obvious effect upon molecular twist, polarizability etc., and hence the changes in mesophase thermal stabilities may be less simply related to the changes in structure. On the other hand, as the dimensions of the molecules will be little altered by such changes, it may be possible to comment upon the observed variations in crystal thermal stabilities, which, in homologous series, are considered to be unpredictable.[1]

Mesogenic compounds containing a heterocyclic ring have been reported by a number of authors, for example, Refs. 2–5. However, little attempt has been made to investigate the effects of the heterocyclic rings on mesophase thermal stabilities. The papers by Schubert[4] and Young, Haller and Williams[5] are of interest however. Schubert reported thermodynamic data for several series of heterocyclic analogues of 4,4″-di-*n*-alkyl- and -di-*n*-alkoxy-*p*-terphenyls, from which it is possible to examine the effects of the various ring systems on mesophase and crystal thermal stabilities (see below). Young, Haller and Williams prepared a series of Schiff's bases derived from simple heterocyclic aldehydes and attempted to relate the observed changes in mesophase thermal stabilities to changes in chemical structure. The latter authors reduced the difficulties with the synthesis of mesogenic compounds containing heterocyclic rings by selecting an aromatic amine which will give mesogens with simple aldehydes, e.g. benzaldehyde. As a result, heterocyclic aldehydes, which are commercially available, may be used directly and are involved in the minimum number of synthetic steps. The results reported by Young *et al.*[5] will be discussed later.

Figures 1(a) and (b) show data taken from the paper by Schubert[4] who reports crystal and mesophase thermal stabilities for homologous series of 4,4''-di-*n*-alkyl- and -di-*n*-alkoxy-*p*-terphenyl compounds and their heterocyclic analogues. By way of illustration, the data for the diethyl and di-*n*-pentyl compounds are presented graphically to show now the effect on crystal and mesophase thermal stabilities of changing the nature of the central aromatic ring, rather than of the alkyl group. We have conluded that the trends shown in mesophase thermal stabilities in plots of this type cannot be interpreted simply in terms of changes in molecular diameter, net dipole or angle of twist between the rings due to differences between *ortho*-proton:*ortho*-proton and *ortho*-proton:hetero-atom lone pair interactions. However it can be seen that compounds containing pyridyl and pyrimidinyl rings differ from those containing the remaining heterocyclic rings in that they appear to favour smectic behaviour, and also that they have the lowest crystal thermal stabilities. While it is normally considered that crystal thermal stability changes are unpredictable,[1] it is significant that of the heterocyclic compounds studied here, those containing pyridyl and pyrimidinyl rings are the only ones in which one of the two phenyl rings is *not* attached to the heterocyclic ring at a position which is adjacent to one of the hetero-atoms.

The hetero-atom in a pyridine or related ring system is known to behave similarly in many respects to an aromatic nitro-group.[7] The hetero-atom has a high electronegativity and will therefore withdraw electrons from the other atoms of the ring system, making the ring deactivated relative to benzene. Electron withdrawal is most pronounced from the 2- and 4-positions because of conjugative interactions with the hetero-atom; these interactions may also involve substituents present in the 2- and 4-positions. A classical example of this well documented effect is the acidity of the methyl protons of 2- and 4-methylpyridine which allows participation in condensation reactions, *e.g.* with benzaldehyde giving a stilbazole (see later). This reaction is given by neither 3-methylpyridine nor 3,5-dinitrotoluene, but occurs readily with 2,4-dinitrotoluene.

Thus when a phenyl ring occupies a 3-position with respect to the hetero-atom, π-bond interactions will be negligible and the phenyl and heterocyclic rings may be twisted due to repulsions between *ortho*-hydrogens. Phenyl rings in the 2- or 4-positions are likely to give π-bond interactions which will be at a maximum when the two rings are co-planar: in this case the axial polarizability of the system will be at a maximum.

In the heterocyclic analogues of the substituted terphenyl compounds of Schubert,[4] the only compounds in which both phenyl rings occupy positions in the heterocyclic ring from which π-bond interactions can occur contain tetrazinyl, pyrazinyl or pyridazinyl rings. In these cases, the overall axial polarizabil-

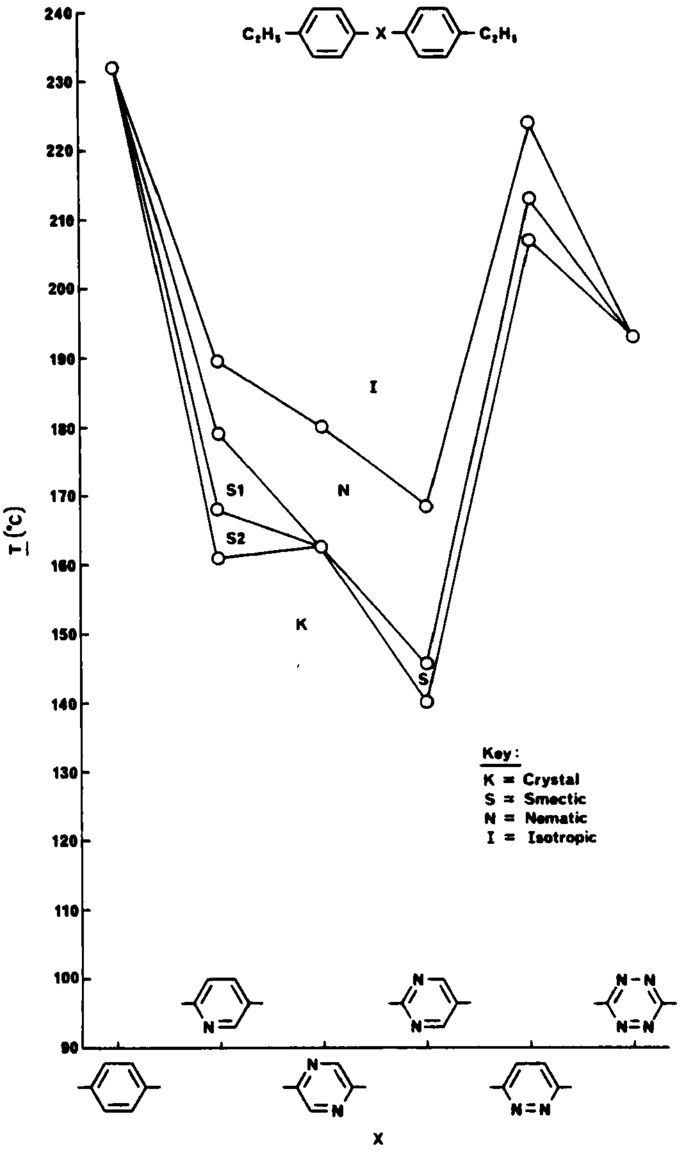


FIGURE 1(a) Thermodynamic data for 4,4″-diethyl-*p*-terphenyl and heterocyclic analogues from Schubert.[4]

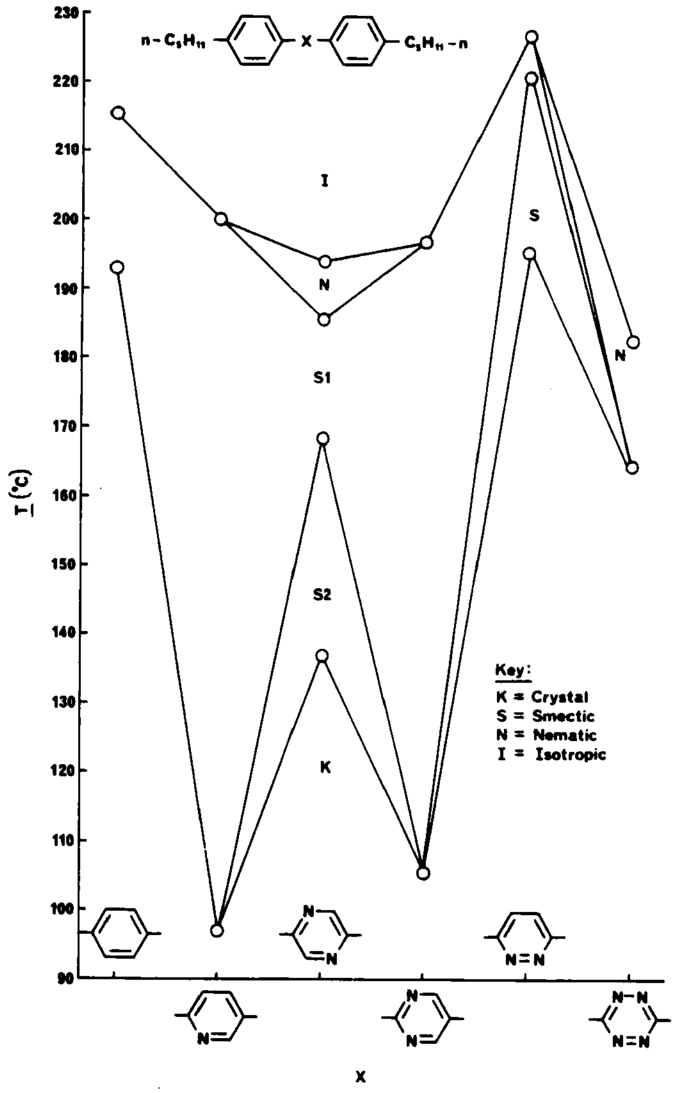


FIGURE 1(b) Thermodynamic data for 4,4″-di-*n*-pentyl-*p*-terphenyl and heterocyclic analogues from Schubert.[4]

ity of the molecule will be high, and crystal and mesophase thermal stabilities comparable with those of the analogous terphenyl compounds are likely. In the pyridyl and pyrimidinyl analogues however, one of the phenyl rings occupies a 3-position with respect to the hetero-atom(s); this will minimize π-bond interactions in the molecule, reducing the molecular axial polarizability. This may alter the thermal stabilities of the crystal lattices resulting in the observed low melting points for these compounds. The changes in mesophase thermal stabilities in these compounds may be a product of several effects, and are less readily related to the chemical structural changes involved.

RESULTS AND DISCUSSION

The compounds discussed in this paper fall into three groups:

1) Schiff's bases derived from heterocyclic aldehydes—this study represents a development of the earlier work of Young *et al.*[5]

2) Esters containing a stilbene or stilbazole unit—this work was prompted by the work of Young *et al.* on stilbenes and chlorostilbenes.[6,8]

3) Compounds containing a heterocyclic ring in a non-terminal position—this represents preliminary work carried out to apply the conclusions reached in Secs. 1 and 2 to systems of a type more likely to have technological applications.

Schiff's bases

Young *et al.*[5] reported data on a series of Schiff's bases, derived from 4-amino-4′-methoxybiphenyl, which showed only nematic mesophases (Fig. 2(a)); the analogous *n*-octyloxy compounds were therefore examined here to determine the effects of the various heterocyclic rings on smectic behaviour (Fig. 2(b)). A series of di-Schiff's bases derived from benzidine was also prepared in order to establish the effects of the rings when occupying both terminal positions in the molecule (Fig. 3). It can be seen from the graphical presentation of the thermodynamic data that these three series of compounds show a number of striking similarities. In order to simplify this section, the results obtained for compounds containing five- and six-membered heterocyclic rings will be discussed separately.

In the series of compounds containing six-membered rings, it should be noted (Figs. 2(a) and 2(b)) that the effects on mesophase thermal stabilities of replacing a phenyl ring by a pyridyl ring are generally less than those which occur when the phenyl ring gains a 4-substituent (see also Fig. 5). This is in accord with the fact that, in the former case, no great change in molecular size is involved.

In Fig. 2(b), the order of mesophase thermal stabilities is, in ascending order: 2-pyridyl; phenyl; 4-pyridyl; 3-pyridyl; 4-fluorophenyl; 4-chlorophenyl, assuming that nematic- and smectic-amorphous isotropic liquid transition temperatures may be compared in this manner. The position in the order for the 4-pyridyl compound, relative to phenyl, is what might be expected if the lone pair of electrons of a terminal hetero-atom is considered equivalent to a 4-substituent in that it can enhance molecular axial polarizability. The relative positions of 3- and 4-pyridyl groups are discussed below. The low mesophase thermal stability for the 2-pyridyl compound may, by analogy with certain substituted Schiff's bases,[9] arise from interaction between the lone pair of electrons of the hetero-atom and

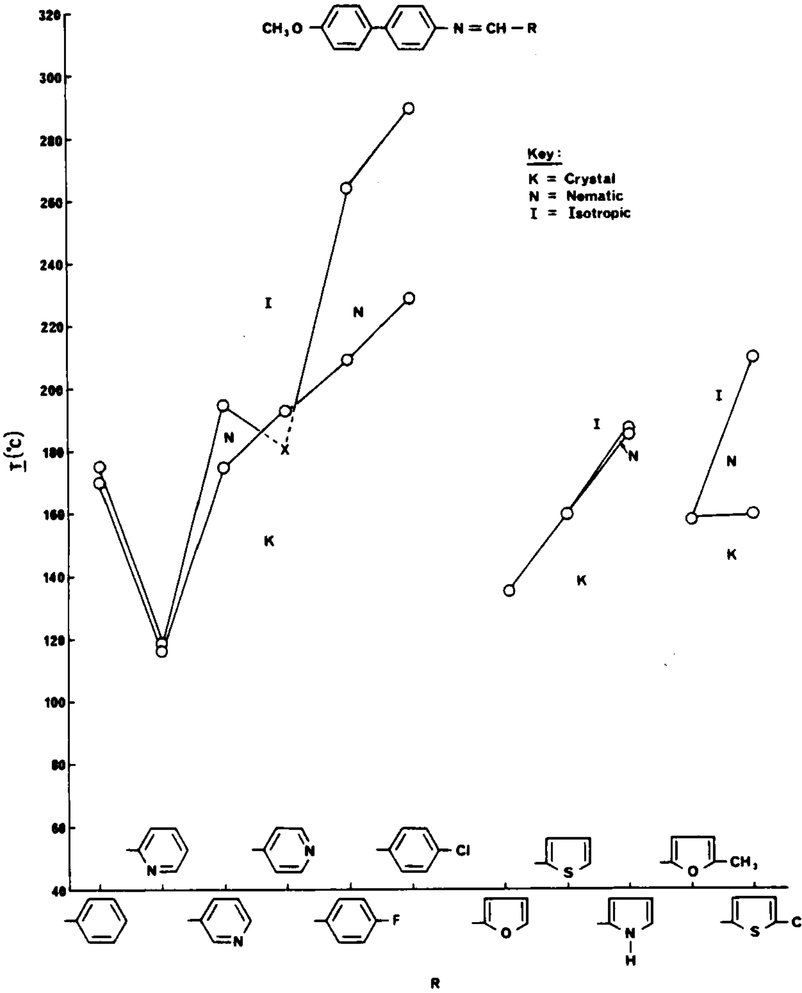


FIGURE 2(a) Thermodynamic data for Schiff's bases derived from 4-amino-4'-methoxybiphenyl and heterocyclic analogues[5] (Tables I and II).
The point defined by (X) is for a monotropic transition.

the bonding electrons of the Schiff's base linkage; this would weaken π-bond interaction and thereby further increase the angle of twist between the rings.[10] In this situation, the smectic thermal stability may be very markedly reduced, with the result that this compound is the only member of the series to show a nematic phase, which would be less seriously affected in thermal stability by such a steric effect. The decreased axial molecular polarizability resulting from these effects will also contribute to the relatively low nematic thermal stability.

It is of interest that, in addition to a reduction in mesophase thermal stability, there is also a reduction in crystal thermal stability for the 2-pyridyl compound. This would suggest that the earlier emphasis placed on the crystal thermal stability data for the compounds reported by Schubert, as reflecting

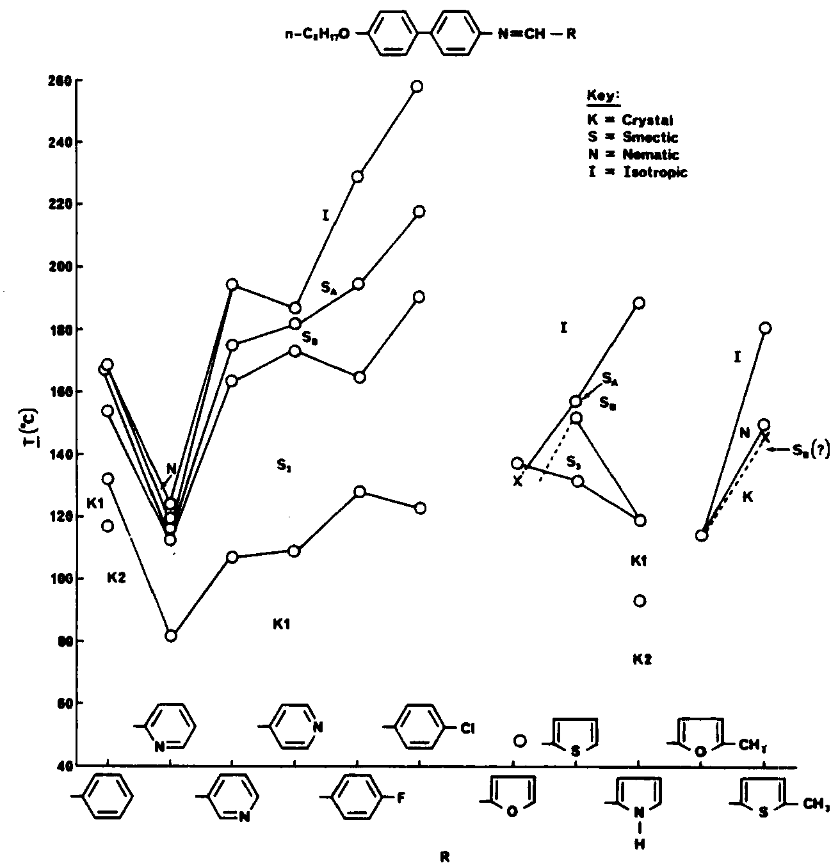


FIGURE 2(b) Thermodynamic data for Schiff's bases derived from 4-amino-4′-*n*-octyloxybiphenyl and heterocyclic analogues (Tables I and II). A point defined by (X) is for a monotropic transition.

TABLE I Thermodynamic data for Schiff's bases of heterocyclic aldehydes. Transition temperatures are quoted in °C and below these in parenthesis are the enthalpy values quoted in k cal mol^{-1}

Group R	$(R.CH = N.C_6H_4.)_2$	$CH_3O.C_6H_4.C_6H_4.N = CH.R$[5]	n-$C_8H_{17}O.C_6H_4.C_6H_4.N = CH.R$
phenyl	K 241 N 268 I (6.85) (0.06)	K 170 N 175.5 I (8.41) (0.09)	K2, 117 K1, 132 S$_3$ 154 S$_B$ 167 S$_A$ 169 I (0.71) (3.02) (0.30) └(2.18)┘
2-pyridyl	K 2, 117 K1, 177 I[a] (0.92) (2.24)	K 116.8 N 118.8 I (4.89) (0.05)	K 82 S$_3$ 112.5 S$_B$ 116 S$_A$ 119.5 N 123.5 I (3.10) (0.33) (1.34) └(0.16)┘
3-pyridyl	K2, 144 K1, 244 N 324 I (1.31) (3.86) (0.09)	K 175.7 N 195.2 I (3.72) (0.09)	K 107 S$_3$ 164 S$_B$ 175 S$_A$ 194 I (6.21) (0.66) (0.39) (2.48)
4-pyridyl	K 256 I (–)[d]	K 193.8 I (181.3 N) (8.65)	K 108 S$_3$ 173 S$_B$ 182 S$_A$ 187.5 I (6.67) (0.48) (0.56) (2.28)
2-furyl	K 257 I (–)[d]	K 138.6 I (–)[c]	K2, 49 K1, 137 I (132 N) (1.39) (9.30)
2-thienyl	K 258 I (5.83)	K 160.2 I (–)[c]	K 132 S$_3$ 152 S$_B$ 157 S$_A$ 157 I (2.68) (0.09) └(3.95)┘
2-pyrrolyl	-[b]	K 186.0 N 187.5 I (–)[c] (–)[c]	K2, 94 K1, 119 S$_A$ 189 I (1.92) (3.65) (3.69)
5-methyl-2-furyl	K 179 I (7.79)	K 158.5 I (–)[c]	K 114.5 I (10.46)
5-methyl-2-thienyl	K2, 179 K1, 214 N 280 I (1.10) (5.01) (–)[d]	K 160.1 N 211.0 I (7.51) (0.15)	K 150 N 181 I (2.96) (0.13)

[a] On cooling, crystal K3 forms; on reheating a transition K3, 168 I (4.02) is observed.
[b] Compound decomposes rapidly on heating and no reliable data could be obtained.
[c] No data are quoted by these authors.
[d] – means enthalpy unreliable or very small.

changes in molecular polarizability, is not misplaced.

Figure 2(a) presents the data reported by Young *et al.*[5] together with data for the analogous 4-fluoro- and 4-chloro-phenyl compounds (see Table II). These compounds show only nematic mesophases whose thermal stabilities follow the order given above. It is suspected that the lower mesophase thermal stability for the 4-pyridyl compound relative to the 3-pyridyl compound arises from an intermolecular repulsion between the lone pairs of electrons of the nitrogen hetero-atom in one molecule and those of the oxygen atom of the methoxy group of another, colinear molecule, which will weaken the forces maintaining order in the nematic state. This effect was observed to a smaller extent in the analogous *n*-octyloxy-compounds, possibly due to the greater shielding of the oxygen atom by the *n*-octyl group, an effect which is presumably achieved mainly by the increased physical separation between the oxygen and nitrogen atoms.

In the di-Schiff's bases derived from benzidine (Fig. 3), the 'nematic' thermal stability for the di-4-pyridyl compound is reduced possibly by intermolecular repulsions between the unshielded lone pairs of electrons of the ring nitrogens; the phase is presumably monotropic but unobservable. It is noticeable that this effect is not reflected in any relative change in crystal thermal stability, *cf.* Figs. 2(a) and 2(b). Thus it would perhaps seem that, in certain cases, changes in crystal thermal stability are a less ambiguous guide to changes in molecular polarizability than changes in mesophase thermal stability, *cf.* the discussion of the data reported by Schubert.[4] The 2-pyridyl compound has, as before, a very low 'nematic' thermal stability, which, like that of the 4-pyridyl compound, makes this phase unobservable. In this case, there is again a concurrent reduction in crystal thermal stability relative to those of the other members of the series. The large variations in nematic thermal stability shown by this series suggest that the interactions which occur in the 2- and 4-pyridyl ring systems may be cumulative.

Figures 2 and 3 also show data for a number of compounds containing five-membered heterocyclic rings. These compounds cannot easily be compared with their phenyl or pyridyl analogues as a result of the change in ring size, and moreover, the orientation of the hetero-atom in these compounds resembles that found only in the 2-pyridyl compounds. As a result, only the general comment can be made that these five membered ring systems appear to have little nematogenic character (Figs. 2(a) and 3), although, as might be expected, this is increased by methyl substitution. Smectic behaviour on the other hand, is, in the *n*-octyloxy series (Fig. 2(b)), rather more pronounced. However, a clearer assessment of the effects on the mesophase behaviour shown by compounds of this type due to the smaller ring size, the position, polarizability and dipolarity of the hetero-atom and the presence, in an off axial position, of the methyl group (when present) must await the examination of a wider range of compounds. These

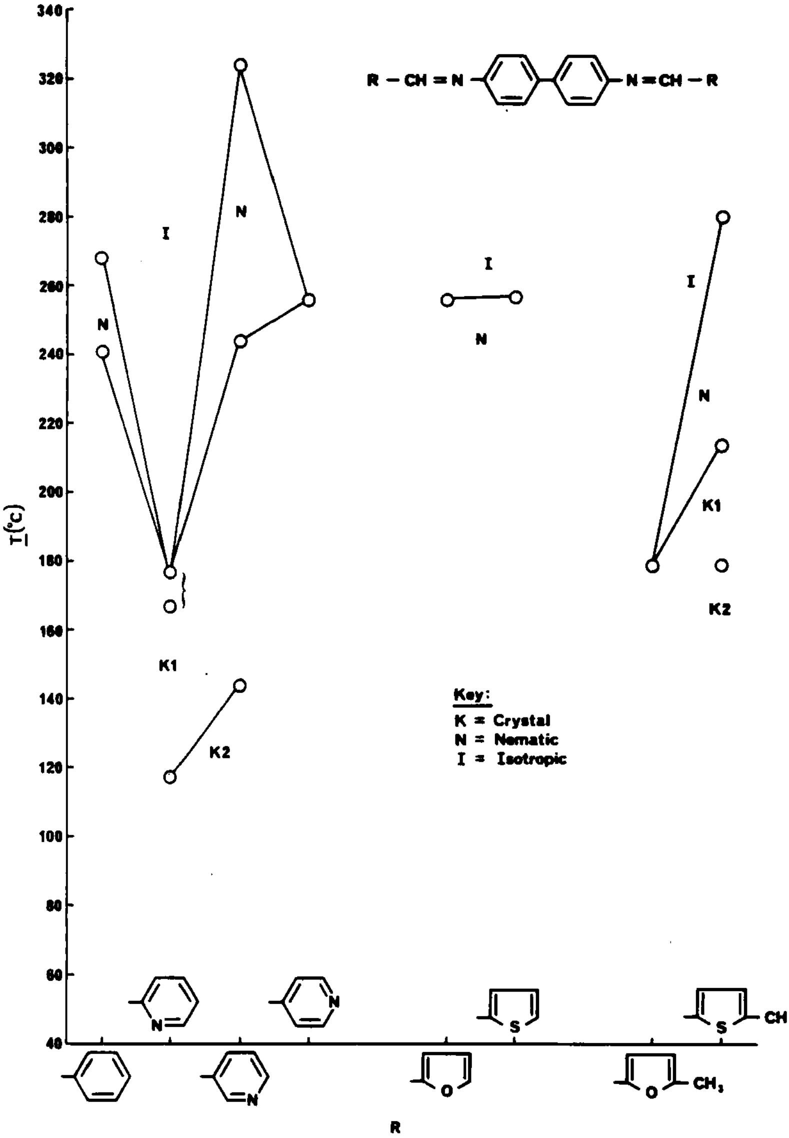


FIGURE 3 Thermodynamic data for di-Schiff's bases derived from benzidine and heterocyclic aldehydes (Table I).

should include those in which the five membered ring carries a 4-methyl substituent and those with the ring linked *via* the 3-position.

The Schiff's bases derived from 4-amino-4′-*n*-octyloxybiphenyl (Figure 2(b)) show three types of smectic mesophase: S_A, S_B and S_3, all of which possess characteristic textures when observed under the polarizing microscope. The S_B and S_3 phases of the compound derived from thienyl-2-aldehyde and the S_A, S_B and S_3 phases of the compound derived from pyridine-3-aldehyde have been shown to be miscible with the corresponding smectic phases of 1-methylpropyl 4-(*p*-phenylbenzylideneamino)cinnamate, the S_A and S_B phases of which are known to be miscible with phases defined by Sackmann.[11] The S_3 phase, however, has previously been observed[11] only in cinnamate esters of the above-mentioned type, which, like the compounds reported here, possess a terminal aromatic ring. An examination to gather more data concerning the particular role of the terminal aromatic ring in relation to the S_3 mesophase is now in progress. In particular we are examining the effect on S_3 thermal stability of substituents in the terminal ring to see if S_3 thermal stability decreases with increasing substituent size or if the S_3 phase gives way to some other type of smectic phase at some particular substituent size. Our preliminary findings show that a certain degree of substitution can be tolerated by the S_3 phase. A preliminary study has also been carried out on compounds of the types shown in

TABLE II

Thermodynamic Data for Schiff's Bases Derived from *p*-substituted Benzaldehydes

Compound	Constants (temperatures in °C; enthalpies given in parenthesis in k cal mol^{-1})
$CH_3O.C_6H_4.C_6H_4.N=CH.C_6H_4F$	K 209 N 262 I (6.00) (–)[a]
„ $=CH.C_6H_4.Cl$	K 229 N 290 I (6.70) (0.03)
$n\text{–}C_8H_{17}O.C_6H_4.C_6H_4.N=CH.C_6H_4.F$	K 128 S_3 164 S_B 194 S_A 228 I (5.75) (0.46) (0.54) (1.41)
„ $=CH.C_6H_4.Cl$	K 122 S_3 190.5 S_B 219 S_A 258 I (5.45) (0.22) (0.43) (1.40)
„ $=CH.C_6H_4.CN$	K 124 S_A 139 N 263 I (107 S_B 105 S_3) (6.10) (1.13) (0.14)
„ $=CH.C_6H_4.C_6H_5$	K2, 114 KI, 179 S_3 214 S_B 251 S_A 288N (1.32) (4.17) (1.20) (0.83) (0.37) 302 I (0.15)

[a] means enthalpy unreliable.

Table II containing *p*-methyl and *p*-methoxy groups in the benzylidene ring; both types show complex smectic polymorphism, but no mesophase has been visually identified as a S_3.

Sackmann has recently shown that the S_3 phases of two cinnamate esters reported by Gray and Harrison[11] are miscible with a phase defined by him as a S_E phase.[12] Previously only four compounds had been reported which showed this phase.[13] It is curious that these are of two distinct types; (*a*) those that are symmetrical systems and (b) those that are unsymmetrical and have, like the compounds discussed here, a terminal aromatic ring. It seems strange that two such dissimilar types of molecule should give smectic phases of identical structure. A possible explanation might be that in certain circumstances terminal rings may give intermolecular association (perhaps even with a vertical stacking of the terminal rings) giving the smectic phase a highly symmetrical double layer structure. Such a structure may possibly only be stable for compounds having small substituents. If a model such as this is correct, the difference between the two types of compound mentioned above loses much of its significance since the double layer structure is equivalent to a single layer structure of symmetrical molecules.

Stilbene esters

The decision to examine the relationship between mesophase thermal stabilities and the nature of heterocyclic rings present in molecules of the type shown in Figures 4 and 5 was prompted by the work of Young *et al.* They showed that the stilbene system has a high nematogenic character[8] and also that replacement in this system, of an *ortho* or olefinic hydrogen by a bulky group caused a molecular twist which produced large reductions in crystal thermal stability.[6] A further factor was the ease with which most of the stilbazole systems could be prepared from commercially available materials.

Figure 4 shows, in the usual graphical form, the transition temperature data for a series of methoxy- and *n*-octyloxy-benzoate esters of stilbene; Figure 5 shows the corresponding data for analogous cyano-stilbene esters. It can be seen that the pairs of plots are remarkably similar and show a number of distinct variations from the trends shown by the three series of Schiff's bases.

The order of nematic thermal stability shown by the compounds in Figure 4, omitting the two diazinyl compounds, is, in ascending order: 3-pyridyl; 2-pyridyl; phenyl; 4-pyridyl. As in the Schiff's bases, the order of nematic thermal stability for the phenyl and 4-pyridyl compounds reflects the increase in molecular axial polarizability due to the lone pair of electrons of the heteroatom. In the methoxy-series, the difference in nematic thermal stabilities for these two ring systems is much reduced due, possibly as in the Schiff's bases, to an intermolecular repulsive interaction between the lone pair of electrons of the terminal nitrogen and those of the oxygen of the methoxy group. Compared with the Schiff's bases, the repulsive interactions in this series may be enhanced by the π-bond interaction between the heterocyclic ring and the remainder of the system which will allow the highly electronegative nitrogen hetero-atom to acquire an enhanced negative charge.

The nematic thermal stabilities for the 2-pyridyl compounds are, as in the Schiff's bases, lower than those for the phenyl compounds and, as before, this may be ascribed to a steric interaction between the lone pair of electrons of the hetero-atom and the electrons of the olefinic bond; this will produce a molecular twist and thereby reduce π-bond interactions, the molecular axial polarizability and the nematic thermal stability relative to those of the phenyl compounds. It is of interest that this order is again followed by the changes in crystal thermal stabilities.

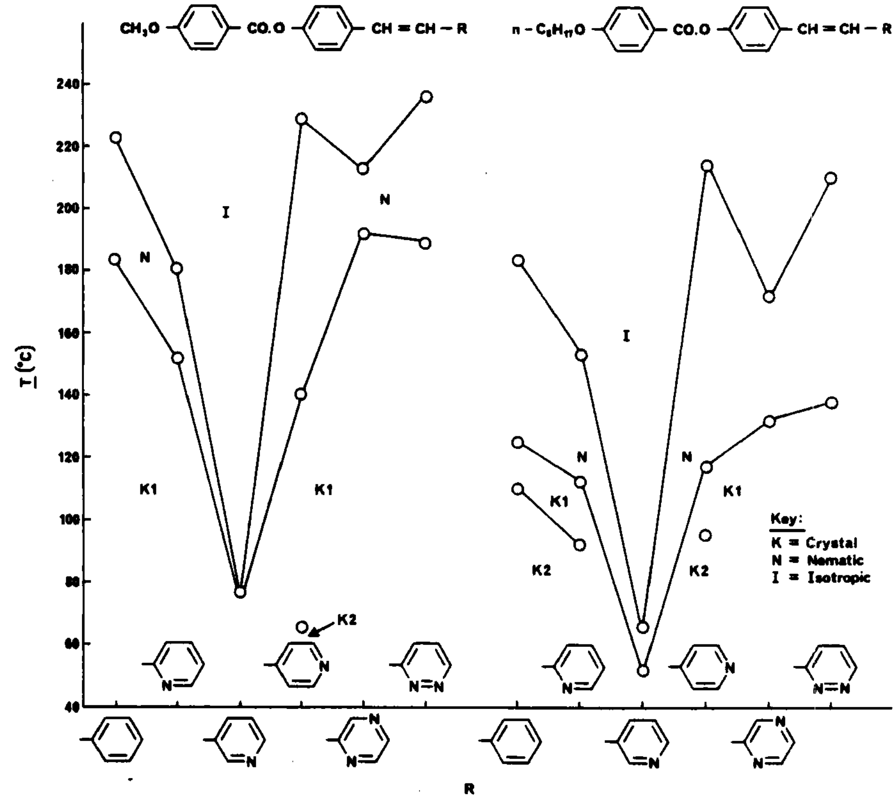


FIGURE 4 Thermodynamic data for stilbene and stilbazole esters derived from: (a) *p*-methoxybenzoic acid (Table III)–left of fig.; (b) *p*-*n*-octyloxybenzoic acid (Table III)–right of fig.

The most striking feature of both plots (Figure 4) is the very low nematic and crystal thermal stabilities shown by the 3-pyridyl compounds. In the phenyl analogous of these compounds there is likely to be considerable conjugation between the terminal phenyl ring and the remainder of the system. With reference to the 3-pyridyl compounds, and, as has already been argued, the hetero-atom in the 3-position will inhibit such interaction so reducing the molecular axial polarizabilities of these compounds relative to their phenyl or 4-pyridyl analogues.

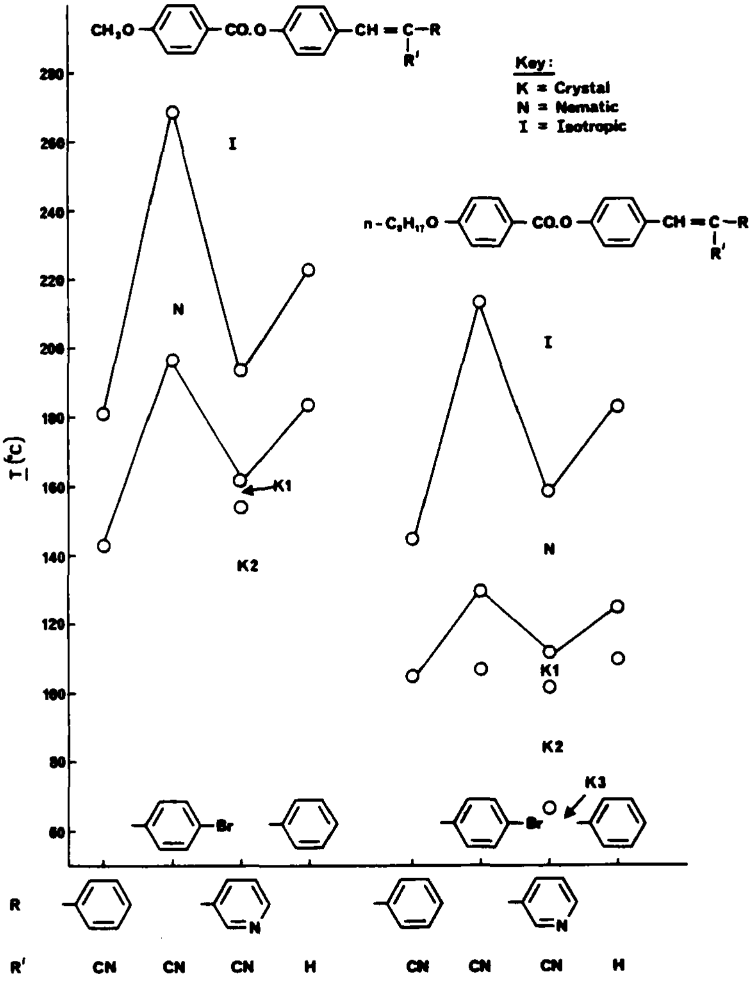


FIGURE 5 Thermodynamic data for cyano-stilbene and -stilbazole esters derived from: (a) *p*-methoxybenzoic acid (Table III)—left of fig.; (b) *p*-*n*-octyloxybenzoic acid (Table III)—right of fig.

TABLE III

Thermodynamic data for stilbene and stilbazole esters of the form $RO.C_6H_4.COO.C_6H_4CH{:}CR'R''$. Transition temperatures are quoted in °C and below these in brackets are the enthalpy values quoted in k cal mol^{-1}.

R'	R''	$R = CH_3$	$R = n\text{-}C_8H_{17}$
H	phenyl	K 182 N 225 I (5.88) (0.09)	K2, 110 Kl, 125 N 183 I (3.08) (7.48) (0.16)
H	2-pyridyl	K 151 N 179 I (6.11) (0.07)	K2, 92 Kl, 112 N 153 I (4.40) (2.34) (0.14)
H	3-pyridyl	K 77 I (7.82)	K 54 N 65 I (7.61) (0.06)
H	4-pyridyl	K2, 65 Kl, 140 N 230 I (4.31) (5.63) (0.28)	K2, 95 Kl, 117 N 214 I (4.58) (0.32) (0.25)
H	2-pyrazinyl	K 192 N 213 I (8.39) (0.09)	K 132 N 172 I (9.05) (0.16)
H	3-pyridazinyl	K 189 N 238 I (8.80) (0.02)	K 139 N 210 I (8.41) (0.21)
CN	phenyl	K 143 N 181 I (–) (–)[a]	K 105 N 145 I (10.21) (0.04)
CN	3-pyridyl	K2, 154 Kl, 162 N 194 I (4.59) (3.03) (0.07)	Kl, 112 N 159 I[b] (11.66) (0.09)
CN	4-bromophenyl	K 197 N 268 I (7.61) (0.11)	K2, 107 Kl, 130 N 214 I (2.37) (6.70) (0.05)

[a] Enthalpies of transition are not available.

[b] On cooling, two new polymorphic forms are produced; on reheating the sample gives the transitions: K3, 67 K2, 102 N 159 I.

This effect is not observed in Schiff's bases in which the heterocyclic ring is attached to the carbon of the Schiff's base linkage. The aromatic rings of Schiff's bases are known to be non-coplanar.[10] Moreover, as the nitrogen of the Schiff's base linkage is highly electronegative and may therefore acquire the major portion of the π-electron density of the double bond, it may therefore be that significant π-bond interaction occurs only between the Schiff's base nitrogen and an aromatic ring attached to it.

The non-coplanarity of the aromatic rings would then arise mainly from a twisting of the bond between the Schiff's base carbon and an aromatic ring attached to it, there being a much smaller degree of π-bond interaction along this bond. The elimination of π-bond interaction can apparently only be observed in the 2-pyridyl compounds, where this arises from an enhanced molecular twist; in the 3-pyridyl compounds the effect of this π-bond interaction may be masked by the increase in polarizability due to the lone pair of electrons of the heteroatom.[14]

The high nematic thermal stabilities of the diazinyl compounds (Figure 4) can also be explained in terms of an increased molecular axial polarizability due to the hetero-atom in the 3-position, conjugation between the heterocyclic ring and the remainder of the molecule being retained due to the presence of a second hetero-atom in the 2-position. Since only four diazinyl compounds have been prepared, it is difficult to comment on the observed differences in nematic thermal stability shown by the pyrazinyl and pyridazinyl compounds. A possible explanation might be that the polarizabilities associated with each hetero-atom can be considered as vector quantities. This would mean that the net polarizabilities of the pyridazinyl compounds would be greater than those of the pyrazinyl compounds; this is in accord with the observed higher nematic thermal stabilities of the pyridazinyl compared with the pyrazinyl compounds.

During the course of the syntheses of the compounds described above, a number of compounds containing a cyano-group attached to the olefinic unit were prepared. These compounds (Figure 5) showed nematic mesophases whose thermal stabilities were examined in the light of the conclusions drawn above. NMR investigation has shown that, in these compounds, the two phenyl rings are trans, i.e., the dipole of the cyano-group acts in a direction perpendicular to the molecular axis and should therefore enhance the negative dielectric anisotropy of the molecule.†

These compounds are analogous to the chloro-stilbenes described by Young *et al.*[6], and it may be that the cyano-group also imparts a twist to the molecule, reducing nematic and crystal thermal stabilities compared with the unsubstituted analogue. However, unlike a chloro-substituent, a cyano-group may give strong π-bond interactions with the olefinic bond so that, although the aromatic rings may be non-coplanar, the molecule as a whole may be highly conjugated and have a high polarizability. The fact that the nematic thermal stability of the cyano-compound is lower than that of its unsubstituted analogue would then be explained by the fact that although the net polarizabilities of the two molecules may not differ greatly, the axial component of the polarizability of the cyano- compound is relatively low.

In the case of the 3-pyridyl compound and its cyano-substituted analogue, the situation is complicated by the deconjugative effect of the hetero-atom. In the cyano-substituted compound, the situation is similar to that of the phenyl analogue – the only influence of the hetero-atom being to increase the axial polarizability and the nematic thermal stability. (A similar explanation may be used to explain the higher nematic thermal stability of the cyano-substituted

---

† Since this was written, it has been shown experimentally[23] that a compound of this type has a strong negative dielectric anisotropy.

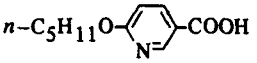
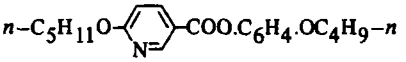
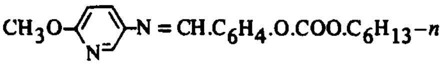
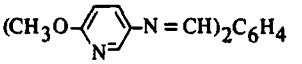
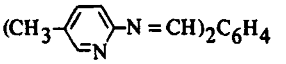
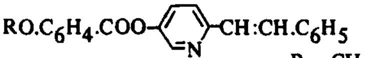
4-bromophenyl compound relative to that of its cyano-substituted phenyl analogue.) However, if the cyano-group is removed from the 3-pyridyl compound, the molecular polarizability would be considerably reduced, as the hetero-atom is inhibiting any conjugation between the ring and the olefinic unit. The nematic thermal stability should therefore decrease. In this respect, the cyano-group plays a similar role to the hetero-atom in the 2-position in the diazine compounds discussed above.

Compounds containing a heterocyclic ring in a non-terminal position

The synthesis of compounds of this type is considerably more complex than that of the monosubstituted heterocyclic systems described above, due to the scarcity of suitably substituted, commercially available precursors. As a result, only a

TABLE IV

Thermodynamic data (Column A) for compounds containing a heterocyclic ring in a non-terminal position. Transition temperatures are quoted in °C and below these in parenthesis are the enthalpy values quoted in k cal mol⁻¹. The data in Column B refer to the phenyl analogous.

Structure[b]	A	B
	K2, 79.5 K1, 125 I (0.11) (4.31)	K 124 N 152 I (4.31) (0.44)
	K 91 I (9.49)	K 67 N 82 I (7.19) (0.21)
	K 64 I (5.28)	K2, 68 K1, 71 N 82 I (4.04) (5.56) (0.16)
	K2, 166 K1, 190 N 267 I (1.11) (8.14) (0.18)	K 224 N 330 I (6.45) (0.15)
	K2, 179 K1, 215 N 258 I (–)[a] (4.90) (0.14)	K 188 N 283 I (6.28) (0.13)
 $R = CH_3$	K2, 45 K1, 53 I └ (11.20) ┘	K 182 N 225 I (5.88) (0.09)
$R = n\text{-}C_8H_{17}$	K2, 49 K1, 62 S_A 64 I (3.06) (9.96) (2.18)	K2, 110 K1, 125 N (3.08) (7.48) 183 I (0.16)

[a] The enthalpy for this transition was unreproducible.

[b] In these structures, C_6H_4 refers to a *p*-phenylene ring.

few compounds of this type are reported here; their transition temperatures, together with those of their phenyl analogues, are shown in Table IV.

The nematic phase of compound 1B* exists due to the formation of a linear dimer, the N–I transition probably occurring when this structure breaks down, as shown by the very high enthalpy of this transition. In the non-mesorphic compound 1A the lone pair of electrons of the heteroatom is capable of hydrogen bonding and simple linear dimerization may not occur. The K–I temperature of compound 2A is greater than the N–I temperature of compound 2B, and also the melt shows little supercooling; hence further comment is impossible.

In compounds 3A and 4A a hetero-atom is present in a 3-position relative to the Schiff's base linkage and should inhibit π-bond interaction between the aromatic ring and the linkage. This may reduce the nematic thermal stabilities of these compounds relative to compounds 3B and 4B, respectively. Also, as discussed earlier, there is a concurrent, though smaller reduction in crystal thermal stabilities. In compound 5A the hetero-atom is now in a 2-position relative to the Schiff's base linkage and conjugation may occur. This would explain the smaller reduction in nematic thermal stability relative to compound 5B, although the conjugative effect may be reduced if any steric interaction results from repulsion between the lone pair of electrons of the hetero-atom and the linkage (see earlier).

In compounds 6A and 7A, the hetero-atom is in a 2-position with respect to the olefin unit (possibly giving a molecular twist) and in a 3-position with respect to the ester function (deconjugating the acyloxy group). The greater conjugative interactions in compounds 6B and 7B may therefore be considerably reduced giving the observed reductions in crystal and mesophase thermal stabilities. The formation of a smectic phase in compound 7A is unexpected and may arise from the presence of an extra dipole within the molecule.

CONCLUSIONS

The above studies on a limited number of heterocyclic mesogens strongly suggest that the dominant effect of the hetero-atom is to produce changes in conjugative interactions within the molecule which affect factors such as polarizability and dipolarity. Intermolecular effects produced by the lone pair of electrons are apparently, in certain cases, also significant. However, further studies will have to be made if a clearer understanding of the influence of heterocyclic rings on crystal and mesophase thermal stabilities is to be gained.

---

† In the following text, numbers 1-7 refer to the sequence in Table IV.

EXPERIMENTAL

Optical microscopy

Thin films, prepared by melting a few crystals between a glass microscope slide and a cover slip, were examined using a polarizing microscope in conjunction with a heated stage (C. Reichert, Optische Werke A.G., Wien, Austria). The mesophases detected during heating and cooling cycles were identified by their textures and the temperatures of transition determined to within ± 0.25°C.

Differential thermal analysis

This process was carried out using a low temperature thermal analyser (Stanton Redcroft Ltd., Copper Mill Lane, London S.W.17). A 5°C min.^{-1} programme was used for heating, cooling and reheating cycles; the temperatures of transition agreed to within ± 2°C of those determined by optical microscopy.

Values for enthalpies of transition, ΔH, were obtained from thermograms by graphical measurement of peak areas and with reference to data obtained with an indium standard. The accuracy of this method of determination is believed to be no better than ± 0.03 k cal mol^{-1}. However, enthalpies of transitions involving crystalline phases tend to be less reproducible than those involving mesophases, due to variations in the packing of the samples used for determinations and, in some cases, to variations in the proportions of various crystal forms within a particular sample.

Materials

Thermodynamic data for all the mesogens whose preparations are described below are contained in the Tables.† Verbit's system of notation for transition temperatures[22] is used in these Tables; data in round brackets at the end of a line relate solely to monotropic transitions. These products and also all intermediate compounds gave satisfactory elemental analyses.

Schiff's bases

Starting materials for the preparation of Schiff's bases were either available commercially or were prepared using standard methods. A sample of 4-amino-

---

† In all tables and figures transition temperatures involving crystalline solids were measured by DTA. All other transition temperatures were measured by optical microscopy.

4′-*n*-octyloxybiphenyl, prepared by the method of Gray[15], and samples of the Schiff's bases derived from the above amine and also its methoxy- analogue with 4-fluoro- and 4-chloro-benzaldehyde were available to us. In all cases, commercially available materials were used without further purification.

The Schiff's bases were prepared by suspending the appropriate aldehyde and a 10% molar excess of the amine in ethanol to which two drops of glacial acetic acid had been added. The suspensions were heated until solution was complete, further solvent being added if necessary, and then, after $\frac{1}{2}$ h, the solutions were filtered while hot and allowed to crystallize. The solids were recrystallized from benzene, toluene or monoglyme, depending upon their solubilities, until constant melting points and N–I transition temperatures were achieved. For the Schiff's bases derived from benzidine the quantities used were 2.1 moles of aldehyde and 1 mole of amine; these quantities were reversed for the Schiff's bases derived from terephthalaldehyde.

Stilbene esters

4-Hydroxystilbene and its analogues. The preparations of compounds of the form 4-HO.C_6H_4. CH=CH.R, where R is phenyl[16] and 2- and 4-pyridyl,[17] are reported in the literature; these methods were used without modification.

2-(4′-hydroxystyryl)pyrazine. The method of Franke[18] was modified as follows. 2-Methylpyrazine (94 g, 1 mole), 4-hydroxybenzaldehyde (122 g, 1 mole) and zinc chloride (4 g) were heated at 170°C for 18 h. The crude black oil was allowed to cool and repeatedly heated with toluene (4 x 75 ml) to extract organic material. The toluene extracts were cooled giving yellowish crystals of the required product which was crystallized from toluene. The pure material (15%) had m.p. 176°C.

3-(4′-hydroxystyryl)pyrimidine was prepared similarly in a yield of 15%, m.p. 190°C (decomp.).

5-hydroxy-2-styrylpyridine. Benzaldehyde (106 g, 1 mole), 5-hydroxy-2-methylpyridine (109 g, 1 mole) and acetic anhydride (102 g, 1 mole) were heated together at 150°C for 12 h. The crude reaction mixture was cooled, dilute HCl (50 ml) added and the whole refluxed for a further $\frac{1}{2}$ h to hydrolyze any acetate ester. On cooling, the mixture was made alkaline with dilute aqueous NaOH; dilute acetic acid was than added until the mixture was slightly acidic. The aqueous solution was then shaken with chloroform (5 x 100 ml), and the combined extracts were washed with water and dried. After evaporation, the brown solid was crystallized from monoglyme-ethanol, crystals, m.p. 168°C (7%) forming on standing at 0°C for two days.

4-Hydroxy-α-phenylcinnamonitrile and its analogues. 4-Hydroxy-α-phenylcinnamonitrile was prepared by the method of Colonge *et al.*[19] 4-Hydroxy-α(4′-bromophenyl)cinnamonitrile and 4-hydroxy-α(3′-pyridyl)cinnamonitrile were prepared similarly, except that the latter compound was crystallized from monoglyme.

Bromophenyl compound, m.p. 206-7°C; yield, 40%.
3-Pyridyl compound, m.p. 143-4°C; yield, 35%.

3-(4′-hydroxystyryl)pyridine. 4-Hydroxy-α(3′-pyridyl)cinnamonitrile (11 g bracket, 0.05 mole) was suspended in aqueous NaOH (8 g in 25 ml of water) and heated under reflux until ammonia had ceased to be evolved (about 4 h). The aqueous solution was cooled, acidified with dilute acetic acid and shaken with chloroform (4 x 25 ml). The combined extracts were washed with water and dried; on evaporation, the crude 4-hydroxy-α(3′-pyridyl)cinnamic acid was suspended in cumene and heated under reflux for 10 h. Toluene (50 ml) was then carefully added and heating continued for 1/4 h. The mixture was then allowed to settle, and the solution decanted from the solid residue and allowed to cool. Crystals of 3-(4′-hydroxystyryl)pyridine, m.p. 153-5°C (40%), were obtained.

Preparation of esters. The esters of the above hydroxy-compounds were prepared using commercially available 4-methoxybenzoyl chloride and 4-*n*-octyloxybenzoyl chloride prepared by standard methods.

In all cases, the esters were prepared by suspending equimolar quantities of the phenol and acid chloride in dry pyridine as solvent; the mixture was left to stand at room temperature for 24 h with occasional shaking. The mixture was then poured into water (2 volumes) and the whole shaken with chloroform (6 x 50 ml). These extracts were combined, washed with dilute aqueous NaOH (2 x 50 ml) and then with water until the washings had a pH of 6. The chloroform solution was dried and evaporated; the dry residue was crystallized from petroleum ether (b.p. 60-80°C) and/or benzene until constant transition temperatures were achieved.

Additional compounds

6-n-Pentyloxynicotinic acid and 4′-n-butoxyphenyl 6-n-pentyloxynicotinoate. 6-*n*-Pentyloxynicotinic acid was prepared from 6-hydroxynicotinic acid by the method of Gray *et al.*[20] and crystallized from ethanol. The ester was prepared as described above using 4-*n*-butoxyphenol which had been prepared by the method of Klarmann *et al.*[21]

References

1. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, N.Y., 1962.
2. Champa, R. A., *Mol. Cryst. and Liq. Cryst.* 16, 175 (1972):
   Fishel, D. L., Patel, P. R., *Mol. Cryst. and Liq. Cryst.* 17, 139 (1972).
3. Diele, S., Brand, P. and Sackmann, H., *Mol. Cryst. and Liq. Cryst.* 17, 163 (1972).
4. Schubert, H., *Wiss. Z. Univ. Halle*, XIX '70 M, H. 5, S.1.
5. Young, W. R., Haller, I., Williams, L., *Liquid Crystals and Ordered Fluids*, J. F. Johnson and R. S. Porter, Eds., Plenum, N.Y. (1970), p. 383.
6. Young, W. R., Aviram, A. and Cox, R. J., *Angew Chem.*, 1971, 83, 399; *I.B.M. Research Report, RC3559*, Sept. 30, 1971.
7. Mosher, H. S., *Heterocyclic Compounds*, Vol. 1, R.C. Elderfield, Ed., Wiley, N.Y., 1950, p. 397.
8. Young, W. R., Haller, I. and Aviram, A., *Mol. Cryst. and Liq. Cryst.* 15, 311 (1972).
9. Teucher, I., Paleos, C. M. and Labes, M. M., *Mol. Cryst. and Liq. Cryst.* 11, 187 (1970).
10. Bürgi, H. B. and Dunitz, J. D., *Helv. Chim. Acta* 53, 1747 (1970).
11. Gray, G. W. and Harrison, K. J., *Symposium of the Chemical Society, Faraday Division* 5, 54 (1971).
12. Sackmann, H., private communication.
13. Diele, S., Brand, P. and Sackmann, H., *Mol. Cryst. and Liq. Cryst.* 17, 163 (1972).
14. Similar explanations may be offered for the changes in mesophase thermal stability produced by reversing a Schiff's base linkage, e.g., Rosenberg, H. M. and Champa, R. A., *Mol. Cryst. and Liq. Cryst.* 11, 191 (1970).
15. Gray, G. W., Unpublished work using synthetic route quoted in Ref. 5.
16. Hewitt, J. T., Lewcock, W. and Pope, F. G., *J. Chem. Soc.*, 1912, 606.
17. Ming-Chien Chiang and Hartung, W. H., *J. Org. Chem.*, 10, 21 (1954).
18. Franke, R., *Ber.*, 38, 3724 (1905).
19. Colonge, J. and Frank, P., *Bull. Soc. Chim. Fr.*, 1964, 3090.
20. Gray, G. W. and Jones, B., *J. Chem. Soc.*, 1954, 678.
21. Klarmann, E., Gatyas, L. W. and Shternov, V. A., *J. Amer. Chem. Soc.* 54, 298 (1932).
22. Verbit, L., *Mol. Cryst. and Liq. Cryst.* 15, 89 (1971).
23. Raynes, E. P., private communication.