Terminal Groups in the Nematic and Cholesteric Phases: a Thermodynamic Study

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The effects of terminal substituents in the nematic and cholesteric phases have been investigated by examination of the enthalpy and entropy changes of the mesophase–isotropic transition by calorimetric differential thermal analysis. A series of nematic, unsymmetrical *p*-phenylene bis-(*para*-substituted benzoates) were chosen in which one substituent was varied among small, compact groups, and a series of cholesteryl *para*-substituted benzoates were also studied. The nematic series showed that the transition temperature and the transition heat are *not* directly proportional as is quite commonly assumed: $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$ was found to be strongly related to the electron donating character of the substituent. The cholesteric series showed $\Delta H_{\mathrm{Ch}\rightarrow\mathrm{I}}$ which were not correlatable with substituent polarity or electronic donating character; $T_{\mathrm{Ch}\rightarrow\mathrm{I}}$ and $\Delta H_{\mathrm{Ch}\rightarrow\mathrm{I}}$ were also not directly related. The heats and entropies were intimately related along both series suggesting that as intermolecular order increases so does intermolecular binding for these compounds. The nematic and cholesteric phases have very similar terminal group efficiencies when the transition temperature is taken as the criterion for mesophase stability, but they show no such similarities with regard to heats and entropies of the mesophase–isotropic transition.

THE types of terminal substituents in liquid crystalline compounds can be divided into two groups: the homologous series and the small compact type. There is an odd–even effect in most homologous series. [2] The nature of this phenomenon is not completely clear, but it does bear mentioning that for a homologous alkoxy-series the clearing points for even carbon chain members and for odd chain members each fall on a smooth curve. The 'even' curve lies above the 'odd' curve. For homologous alkyl series the same two smooth curves can be drawn, one connecting the even carbons and the other connecting the odd carbon compounds. In this case however the curve for the odd carbons lies above the even curve. It is interesting to note that calorimetric data,[3] heats and entropies of transitions, seem to support both the 'smooth curve' effect and 'odd–even' effect of the mesophase–isotropic transition temperatures. Chain branching in alkyl and alkoxy-groups usually lowers the clearing point due to unfavourable, inefficient packing in the mesomorphic lattice.[4]

Terminal groups with a small, compact structure such as cyano, halogen, methoxy, nitro, *etc.*, comprise the second class of terminal substituents. Although much effort has been put forth to arrive at a relative efficiency order for such substituents in promoting thermal

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[1] Taken in part from the Ph.D. Dissertation of A. C. Griffin, University of Texas at Austin, 1975.

[2] G. W. Gray, 'Molecular Structure and the Properties of Liquid Crystals,' Academic Press, New York, 1962, ch. 9.

[3] J. F. Johnson, R. S. Porter, and E. M. Barrall, II., *Mol. Cryst. Liquid Cryst.*, 1969, **8**, 1.

[4] M. E. Neubert, L. T. Carlino, R. D'Sidocky, and D. L. Fishel in 'Liquid Crystals and Ordered Fluids,' Plenum Press, New York, 1974, vol. 2, p. 293.

persistence of the mesophase, only a general trend is apparent. This is due to the complexity in the contribution of the substituent to molecular properties. Of course terminal substituents can both attract and repel one another. They also can affect the polarizability of the aromatic ring to which they are attached. In addition the terminal substituent may interact with the lateral portion of an adjacent molecule. Representative work in the field by Schroeder and Bristol,[5] Dewar and Goldberg,[6] Gray,[7] and Dave and Dewar[8] is collected in Table 1 and represents an efficiency order for various investigations of the three types of mesophases. These data show that the nematic and cholesteric phases have roughly similar group efficiencies while the smectic phase order is quite at odds with that of the other two phases. In the smectic phase the least thermally persistent terminal groups, methoxy and nitro, are the ones of highest clearing point in the other two phases. For the nematic phase, for which data are most abundant, all of the substituents raise the nematic–isotropic transition temperature relative to hydrogen. Groups which are compact, polar, and polarizable seem to be very effective in creating high clearing points.[5]

TABLE 1

Terminal group efficiencies in the three types of mesophase

Type of compound	Phase	Group efficiencies
p-Phenylene dibenzoates [5]	Nematic	$CH_3O > NO_2 > Br \sim Cl > CH_3 > F > H$
p-Phenylene dibenzoates [6]	Nematic	$CH_3O > NO_2 > Cl > F > H$
Biphenyl anils [7]	Nematic	$CH_3O > NO_2 > Cl \sim Br > CH_3 > F > H$
Anil mixtures [8]	Nematic	$NO_2 > CH_3O > Cl = CH_3 > Br \sim H$
Biphenyl anils[7]	Smectic	$Br > Cl > H > NO_2 > CH_3O$
Cholesteryl benzoates [7]	Cholesteric	$CH_3O \sim NO_2 > Cl > CH_3 > H$
Active cinnamate esters [7]	Cholesteric	$CN > CH_3O > NO_2 > Cl > Br > H$

As the polarity of the group decreases the clearing point seems to fall also. This is attributed by these workers to increased intermolecular attractions as the polarity and polarizability of the substituent is increased.[5-8] As Dewar and Goldberg[6] have pointed out for a series of symmetrical p-phenylene dibenzoates the nematic phase is more persistent as the mesophase-stabilizing effect of mutual conjugation between the *para*-substituent and the ester carbonyl is increased. Thus electron-donating ($-E$) substituents should promote the polarity of the carbonyl which should result in stronger intermolecular attractions. For a corresponding series of bis-(*para*-substituted phenyl) terephthalates they found that electron-withdrawing ($+E$) substituents lowered the clearing points of the mesophase by, they thought, reducing the polarity of the carbonyl.

In view of the successful applications[9-11] to other mesomorphic systems of our use of differential thermal analysis (d.t.a.) we decided to use this method to study nematic and cholesteric terminal groups with an eye toward unravelling factors responsible for mesophase stability.

EXPERIMENTAL

M.p.s (all corrected) were determined with a Thomas–Hoover apparatus or by d.t.a. The d.t.a. measurements were carried out by the procedure previously described.[10,11] The esters were prepared from cholesterol or p-hydroxyphenyl p-anisate[12] by reaction with the appropriate acid chloride in pyridine. The i.r., mass, and n.m.r. spectra were consistent with the assigned structures. Tables 2 and 3 show their m.p. and transition temperatures. Full details will be found in ref. 1. New compounds all gave satisfactory elemental analyses.

TABLE 2

M.p.s and nematic–isotropic (N–I) transition temperatures for p-X $C_6H_4CO_2C_6H_4O_2CC_6H_4OCH_3$-$p$

Compound [a]	X	M.p. (°C) [b]	N–I Transition temperature (°C) [b]
(1)	H	159.0 (157)	171.4 (173)
(2) *	F	155.0	249.0
(3)	Cl	196.1 (196)	277.8 (275)
(4)	Br	213.1 (214)	275.6 (277)
(5)	CH_3	204.1 (199)	269.1 (265)
(6) *	CN	181.1	321.4
(7) *	NO_2	200.2	300.2
(8)	OCH_3	*c*	*c*
(9) *	CF_3	228	231

[a] New compounds indicated by asterisks. [b] Literature[5] value in parentheses. [c] See ref. 10.

DISCUSSION

Terminal Groups in the Nematic Phase.—The nematic compounds chosen to study terminal group effects were the unsymmetrical esters of hydroquinone of the type described by Schroeder and Bristol.[5] These compounds have extremely suitable mesomorphic ranges for thermal studies.

Included in Table 4 are the melting and clearing points of these compounds along with enthalpy and entropy data for the N–I transition. Perhaps the most unexpected result of the transition enthalpies is that the methyl compound (5) has such a large value. This is quite amusing in that the methyl group is only weakly polar and was therefore thought to contribute little to intermolecular attractions.[5] In terms of transition temperatures, compounds containing terminal chlorine

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[5] J. P. Schroeder and D. W. Bristol, *J. Org. Chem.*, 1973, **38**, 3160.

[6] M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, 1970, **35**, 2711.

[7] G. W. Gray, *Mol. Cryst. Liquid Cryst.*, 1969, **7**, 127.

[8] J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 1955, 4305.

[9] M. J. S. Dewar, A. Griffin, and R. M. Riddle in ref. 4, p. 733.

[10] M. J. S. Dewar and A. C. Griffin, *J. Amer. Chem. Soc.*, 1975, **97**, 6662.

[11] M. J. S. Dewar and A. C. Griffin, *J.C.S. Perkin II*, preceding paper.

[12] S. A. Haut, D. C. Schroeder, and J. P. Schroeder, *J. Org. Chem.*, 1972, **37**, 1425.

or bromine almost always have higher values than the analogous methyl terminated compound. This has long been taken as evidence that a strong dipole acting out from the molecular terminus is extremely advantageous in promoting terminal associations whereby intermolecular bonding is increased. Comparisons of (3) and (4) with (5) show that this explanation is invalid. The low enthalpy for the nitro-compound (7) is also in opposition to the idea of strong intermolecular attractions due to terminal dipoles. Likewise the cyano-substituent (6), which like the nitro-compound has a high $T_{N \rightarrow I}$ value, has a relatively small enthalpy for this transition.

TABLE 3

M.p.s and cholesteric–isotropic (Ch–I) transition temperatures for *para*-substituted cholesteryl benzoates, *p*, X $C_6H_4CO_2(C_{27}H_{45}O)$

Compound [a]	X	M.p. (°C) [b]	Ch–I Transition temperature [b]
(10)	H	154.4 (145.8 [c])	179.9 (180.7 [c])
(11) *	F	150.7	193.1
(12)	Cl	170.1 (165.0 [c])	252.8 (245—6;[7] 240.0 [c])
(13)	Br	177.6 (175.3 [c])	251.6 (245.3 [c])
(14)	CH_3	183.9 (180 [d])	243.1 (241 [d])
(15) *	CF_3	160.8	194.6
(16)	NO_2	184.9 (156 [e])	Decomp. (265 [e])
(17) *	CN	173.4	287.0 (Decomp.)
(18)	OCH_3	181.0 (163;[e] 181.5 [f])	267.0 (236 [e], 268 [f])

[a] Asterisk denotes new compound. [b] In °C; literature values in parentheses. [c] Ref. 14. [d] C. Weigand, *Z. Naturforsch.*, 1949, **46**, 249. [e] H. Stoltzenberg, Dissertation, Halle, 1911. [f] E. M. Barrall, II., J. F. Johnson, and R. S. Porter, *Mol. Cryst. Liquid Cryst.*, 1969, **8**, 27.

TABLE 4

Thermodynamic properties for some unsymmetrical *p*-phenylene dibenzoates (1)—(9)

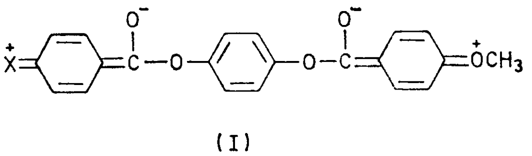
Compound	$T^a_{C \rightarrow N}$/ °C	$T^b_{N \rightarrow I}$/ °C	$\Delta H^c_{N \rightarrow I}$/ kcal mol^{-1}	$\Delta S^d_{N \rightarrow I}$/cal mol^{-1} K^{-1}
(1)	159.0	171.4	0.158	0.355
(2)	155.0	249.0	0.244	0.466
(3)	196.1	277.8	0.282	0.511
(4)	213.1	275.6	0.248	0.451
(5)	204.1	269.1	0.387	0.713
(6)	181.1	321.4	0.228	0.383
(7)	200.2	300.2	0.192	0.334
(8)	217.0	301.0	0.408	0.711
(9)	228	231		

[a] M.p. [b] N–I Transition temperature. [c] Heat of N–I transition. [d] Entropy of N–I transition.

All the halogen compounds (2)—(4) have approximately the same N–I enthalpies. In every case the enthalpies for the halogens are greater than those for both cyano (6) and nitro (7) even though the halogens have considerably lower $T_{N \rightarrow I}$. The methoxy-compound (8) gave rise to the highest transition enthalpy and hydrogen the lowest.

The N–I transition entropies for this series are significant in that there should be to a first approximation no obvious differences in gross molecular geometry in the series. The entropies seem to roughly parallel the enthalpies of the N–I transition implying that the ordering of the molecules in the nematic phase is, for this series, intimately related to the strength of the intermolecular associations.

It is readily seen that the enthalpies of transition do not seem to correlate well with either the polarity of the substituent nor with $T_{N \rightarrow I}$. The most probable explanation may be found in the conjugative interaction of the substituent with the carbonyl carbon through the intervening aromatic ring.[5,6] Thus with the exception of hydrogen the electron-releasing ($-E$) substituents increase $\Delta H_{N \rightarrow I}$. Such a conjugation would involve the highly polar structure (I).



(I)

There exists also as an explanation of the transition enthalpies the possibility alluded to by Chandler [13] that in the liquid crystal phase the only forces operative in determining mesophase properties are repulsive forces. This argument seems to be valid for the liquid state. Since the liquid crystalline state is very much more (thermodynamically) like the liquid than the solid state, it appears that an explanation of properties based at least in part on the importance of such repulsive forces may well be appropriate for liquid crystals. Thus the very low $\Delta H_{N \rightarrow I}$ for the nitro-compound (7) can be seen as arising from repulsions between nitro-groups themselves and with other strongly negative ends of dipoles. The low $\Delta S_{N \rightarrow I}$ for (7) is also in accord with the concept of repulsion, the adjacent molecules being forced apart making the nematic arrangement more random and less anisotropic. It is felt that the forces constituting the mesophase energetics are actually a mixture of attractive and repulsive coulombic forces. The attractive forces consist primarily of polar carbonyl units and terminal dipoles interacting with appropriately charged polar groups of other molecules in the mesophase; the repulsive forces being constituted primarily of interactions between protruding negative ends of dipoles. In the case of the nitro-compound (7) and to lesser extents the cyano-compound (6) and the halogen-compounds (2)—(4) the repulsive contribution dominates and thereby lowers both $\Delta H_{N \rightarrow I}$ and $\Delta S_{N \rightarrow I}$. The effect of the methoxy-group in (8) seems explicable in terms of a ' shielding ' effect on the oxygen lone pairs by an ' insulator,'[7] the methyl group. The repulsive forces involving the oxygen lone pairs are thereby substantially reduced. It is also interesting to note that the compounds with large enthalpies, (5) and (8), also have the largest entropy values. Increased lateral attractions due to the strongly polar carbonyl are probably responsible for this. Alternatively the lack of strong repulsive forces could simply allow a close approach of neighbouring molecules increasing bonding forces.

The hydrogen substituent presents something of a dilemma. The question arises as to why it produces a

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[13] D. Chandler, *Accounts Chem. Res.*, 1974, **8**, 246.

compound, (1), with such low $\Delta H_{N\rightarrow I}$ and $\Delta S_{N\rightarrow I}$ values. The answer does not seem to be molecular length since the fluoro-compound (2) which is about the same size as (1) gives a liquid crystal with much greater enthalpy and entropy values. The hydrogen substituent offers little in the way of conjugative interaction with the carbonyl and also little in the way of dipolar attractions. Thus simply on the basis of no strong attractions, although no excessive repulsions are present, the mesophase is weakened (low $\Delta H_{N\rightarrow I}$) and not highly ordered (low $\Delta S_{N\rightarrow I}$). The trifluoromethyl compound (9), although an enantiotropic liquid crystal, was not amenable to thermal analysis due to such a short mesomorphic range.

Terminal Groups in the Cholesteric Phase.—The compounds used to examine terminal group effects in the cholesteric phase were the cholesteryl esters of *para*-substituted benzoic acids. The compounds have suitable mesomorphic ranges for purposes of thermal analysis.

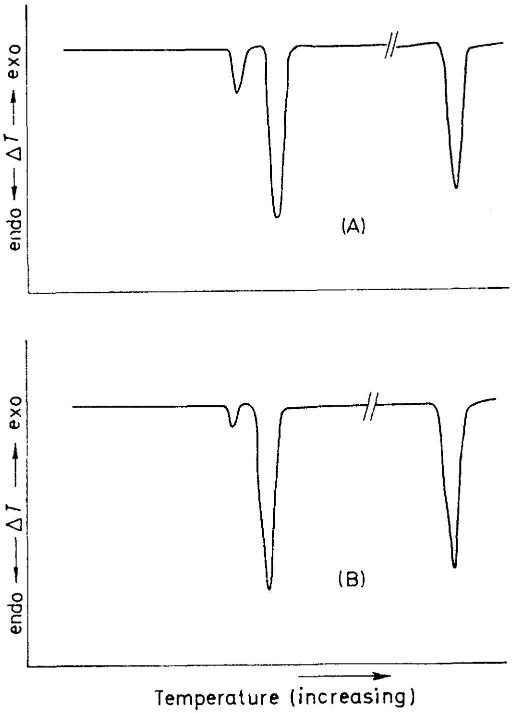
TABLE 5

Thermodynamic properties of some cholesteryl *para*-substituted benzoates (10)—(19)

Compound	$T_{C\rightarrow Ch}$/ °C	$T_{Ch\rightarrow I}$/ °C	$\Delta H_{Ch\rightarrow I}$/ kcal mol^{-1}	$\Delta S_{Ch\rightarrow I}$/cal mol^{-1} K^{-1}
(10) [a]	154.4	179.9	0.124	0.274
(11)	150.7	193.1	0.121	0.259
(12) [b]	170.1	252.8	0.184	0.350
(13) [c]	177.6	251.6	0.159	0.303
(14)	183.9	243.1	0.183	0.354
(15)	160.8	194.6	0.113	0.241
(16)	184.9	Decomp.		
(17)	173.4	287.0		
(18) [d]	181.0	267.0	0.186	0.344

[a] E. M. Barrall, II., J. F. Johnson, and R. S. Porter, (*Mol. Cryst. Liquid Cryst.*, 1969, **8** 27) give $\Delta H_{Ch\rightarrow I}$ 0.17 kcal mol^{-1} and $\Delta S_{Ch\rightarrow I}$ 0.38 cal mol^{-1} K^{-1}. [b] This compound underwent a change in crystal form at 161.0° not reported by Barrall *et al.*[14] who found $\Delta H_{Ch\rightarrow I}$ 0.16 kcal mol^{-1} and $\Delta S_{Ch\rightarrow I}$ 0.31 cal mol^{-1} K^{-1}. [c] This compound also underwent a change in crystal form at 169.4° not reported in ref. 14. The polymesomorphism noted there was not seen here. They report $\Delta H_{Ch\rightarrow I}$ (total) 0.23 kcal mol^{-1} and $\Delta S_{Ch\rightarrow I}$ 0.43 cal mol^{-1} K^{-1}. [d] Ref. in note *a* gives $\Delta H_{Ch\rightarrow I}$ 0.29 kcal mol^{-1} and $\Delta S_{Ch\rightarrow I}$ 0.54 cal mol^{-1} K^{-1}.

Shown in Table 5 are the appropriate transition temperatures along with enthalpy and entropy values for the Ch–I transition for the compounds studied. One of the notable features from Table 5 is the lack of well defined trends in $\Delta H_{Ch\rightarrow I}$ and $\Delta S_{Ch\rightarrow I}$. There seems to be little difference in the energetics of the Ch–I transition for the methyl (14), methoxy (18), chloro (12), and bromo (13) compounds. The hydrogen (10), fluoro (11), and trifluoromethyl (15) compounds have significantly lower $\Delta H_{Ch\rightarrow I}$, but are all three themselves approximately the same. It is felt that the cholesteric compounds investigated here are uniquely different from the nematic compounds described in the previous section. This difference is seen as arising from the reduction of aromatic and polar structures in the cholesterol derivatives. The hydrophobic saturated portion of the cholesteryl compounds comprises the bulk of the molecular structure. The polarity and polarizability associated with the benzoate system is comparatively dwarfed by the relatively non-polar saturated portion. Thus the primary interactions in the cholesteric compounds studied here are the interactions (dispersion forces) between hydrophobic portions of adjacent molecules, the polarity due to the carbonyl being of secondary importance. The effect of the terminal substituent seems to be likewise relatively unimportant in an attractive sense, but of significance in a repulsive sense. This is in accord with the theory[13] of liquids noted above. The strongly repulsive fluorine atoms, (11) and (15), produced lower enthalpies than the more polarizable, softer lone pairs of other substituents. The hydrogen substituent again seems to have a low transition enthalpy, but not as comparatively low as in the nematic series. It seems that the hydrogen confers a moderate amount of stability on the mesophase by simply not being repulsive to polar groups in neighbouring molecules. There should not be much in the way of attractive interactions due to the polarity of the terminal group in (10) since the C–H dipole should be weak. Likewise the carbonyl is not made significantly more polar by the terminal hydrogen. Thus by a combination of factors (10) has as stable a mesophase as the strongly polar fluoro and trifluoromethyl compounds.



D.t.a. thermograms of (A) compound (12) and (B) compound (13)

The entropies for the Ch–I transition seem, as in the nematic series, to parallel the enthalpies along the series. The association and binding strength again appear closely related. The nitro-compound (16) and the cyano-compound (17) decomposed in the mesophase. Unfortunately no thermodynamic data could be obtained for these potentially interesting compounds.

It should be noted that in the work of Barrall *et al.*[14] polymesomorphism was observed in the bromo-compound (**13**) and no mention of a change in the crystal structure was made. No observation was recorded of a change in crystal form of the chloro-compound (**12**) by these authors. In the studies reported here both of these compounds underwent a modification in crystal structure before melting. The bromo-compound gave no evidence of two cholesteric forms and had a higher Ch–I transition temperature (251.6 *vs.* 245.3°). The chloro-compound also had a higher $T_{\mathrm{Ch}\rightarrow\mathrm{I}}$ (252.8 *vs.* 240.0°). The Figure shows the d.t.a. thermograms of the chloro- and bromo-compounds. The compounds used by Barrall were commercial samples recrystallized from ethanol. Spectral data and combustion analyses were not given. It is felt the differences in the thermograms of the bromo- and chloro-compounds from that study compared with this are significant, but not yet well understood. The purity of the bromo- and chloro-compounds reported here was checked by combustion analysis, t.l.c., and n.m.r. spectroscopy. These methods gave results consistent with a high purity, single component sample.

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[5/871 *Received, 9th May,* 1975]

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[14] E. M. Barrall, II., K. E. Bredtfeldt, and M. J. Vogel, *Mol. Cryst. Liquid Cryst.*, 1972, **18**, 195.