

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

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



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Steric effects of substituents in mesogens and phase transition temperatures in uniaxial liquid crystals

E. M. Averyanov<sup>a</sup>

<sup>a</sup> L. V. Kirensky Institute of Physics, U.S.S.R. Academy of Sciences, Siberian Branch, 660036, Krasnoyarsk, U.S.S.R.

**To cite this Article** Averyanov, E. M.(1987) 'Steric effects of substituents in mesogens and phase transition temperatures in uniaxial liquid crystals', *Liquid Crystals*, 2: 4, 491 – 504

**To link to this Article:** DOI: 10.1080/02678298708086305

**URL:** <http://dx.doi.org/10.1080/02678298708086305>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or 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.

## Steric effects of substituents in mesogens and phase transition temperatures in uniaxial liquid crystals

by E. M. AVERYANOV

L. V. Kirensky Institute of Physics, U.S.S.R. Academy of Sciences,  
Siberian Branch, 660036 Krasnoyarsk, U.S.S.R.

(Received 28 April 1986; accepted 30 January 1987)

The influence of steric effects of lateral substituents on the thermal stability of smectic A, nematic and cholesteric mesophases in mesogens with one (biphenyl derivatives) and two (stilbene derivatives, cinnamic acids and their cyanophenyl esters, cholesteryl cinnamates) actual conformational degrees of freedom is considered. The compounds studied differ in the following factors: (i) the length of the aromatic core and the flexible aliphatic chains, (ii) the central or off-central position of the fragment in the core structure and (iii) the presence or absence of  $\pi$ -electronic conjugation of the fragment with other core fragments. A linear dependence of the smectic A—nematic (cholesteric)—isotropic transition temperatures on the generalized coordinate ( $Q = \cos^2 \phi$ ) for the conformational degree of freedom has been confirmed for the compounds studied over the complete range  $Q = 0-1$ ; here  $\phi$  is the dihedral angle between the planes of two  $\pi$ -conjugated fragments, joined by a single chemical bond.

### 1. Introduction

The steric effect of lateral substituents in conjugated mesogenic molecules, i.e. the change of conformation of  $\pi$ -conjugated molecular fragments by means of substitution of one or more atoms, is of great interest. As a result of such substitution the smectic A—nematic (cholesteric)—isotropic ( $S_A-N(\text{Ch})-I$ ) transition temperatures decrease very strongly [1]. There has been active interest to this effect for many years [1-11]; however an interpretation of the influence of the steric effect on the thermal stability of liquid crystals has only been qualitative up to now. The following dependence of the  $S_A-N(\text{Ch})-I$  transition temperatures  $T_c$  on the intramolecular conformational parameters  $Q_k$  has been obtained [8, 12] as a result of the consideration of the interaction of the liquid crystal order parameter with the intramolecular degrees of freedom

$$T_c(Q_i) = T_c(0) + AQ_i, \quad (1)$$

where  $Q_i$  is the average value of the  $Q$  parameter over all molecules in the isotropic phase and  $A$  is a constant. The parameters  $Q_k$  describe different conformations of the molecular fragment. In the case of steric effect the parameter  $Q = \cos^2 \phi$  is related to the biaxiality of the system of two  $\pi$ -conjugated fragments which rotated with respect to each other by an angle  $\phi$  around the single chemical bond joining them [8]. Physically relation (1) means that the  $S_A-N(\text{Ch})-I$  transition temperatures increase with increasing biaxiality of mesogenic molecules. Qualitatively it agrees with the results of molecular statistical theories of the nematic—*isotropic* transition [13, 14].

Equation (1) does not depend on the specific features of the influence of  $Q$  on the geometrical, electronic and other molecular properties which determine  $T_c$ . Therefore

to verify equation (1) for steric effects of substituents in the complete range of  $Q$  for the nematic, cholesteric and smectic A liquid crystals of different chemical classes is the topic of this paper. In this context many of the modern trends in liquid-crystalline compounds (aliphatic rings, heterocyclic, polar end groups) are not included; indeed some of these topics have been discussed previously [6, 7, 9–11].

In §2 the influence of the steric effect on the molecular biaxiality is considered and phenomenological relation (1) is compared with the prediction of the Luckhurst–Zannoni–Nordio–Segre (LZNS) molecular statistical theory of nematics composed of biaxial molecules [13, 15]. In §3 the test compounds are presented and their principal features are outlined. Distinguishing the steric effect contribution to the change of  $T_c$  from the total change of  $T_c$  due to substitution is discussed in detail in §4. Section 5 contains the results of the investigation of the dependence  $T_c(Q)$  for the compounds studied. In §6 the results obtained are discussed and compared with the known data on the influence of terminal substituents on the molecular polarizability of mesogens and on the nematic–isotropic transition temperatures.

## 2. Molecular biaxiality and thermal stability of the nematic phase

In the LZNS theory [13, 15] the molecular biaxiality can be described by the parameter

$$\lambda = \frac{\sqrt{6}}{4} \frac{\alpha_{xx} - \alpha_{yy}}{\alpha_{zz} - (\alpha_{xx} + \alpha_{yy})/2} \equiv \frac{\sqrt{6}}{4} \frac{\Delta\alpha'}{\Delta\alpha}. \quad (2)$$

Here  $\alpha_{ii}$  are the components of a molecular interaction tensor, which is diagonal in the molecular frame  $XYZ$ . Let us consider the model of a molecule consisting of two plane fragments joined by the bond along the molecular  $Z$  axis (cf. figure 1). The 4,4'-substituted biphenyl core may be treated as an example of the molecule considered. We assume that tensors  $\alpha_1$  and  $\alpha_2$  for the fragments are diagonal in the frames  $(xyz)_1$  and  $(xyz)_2$  respectively and  $z_{1,2}$  axes coincide with the  $Z$  axis. To take into account the condition  $C_{200} = \text{constant}$  [13] we also assume that the components of the tensors  $\alpha_{1,2}$  do not depend on the angle  $\phi$ .

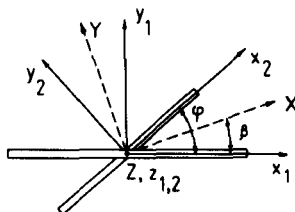


Figure 1. The location of the axes in the fragment  $(x_1 y_1 z_1)$  and  $(x_2 y_2 z_2)$  and the molecular  $XYZ$  reference frames.

The molecular tensor  $\alpha$  is diagonalized in the  $XYZ$  frame, where the orientation of the  $X$  axis depends on  $\phi$ . From figure 1 we can obtain

$$\Delta\alpha' = \Delta\alpha'_1 \cos 2\beta + \Delta\alpha'_2 \cos 2(\phi - \beta). \quad (3)$$

Excluding angle  $\beta$  from equation (3) by using the condition  $\alpha_{xy} = 0$ , i.e.

$$\Delta\alpha'_1 \sin 2\beta = \Delta\alpha'_2 \sin 2(\phi - \beta),$$

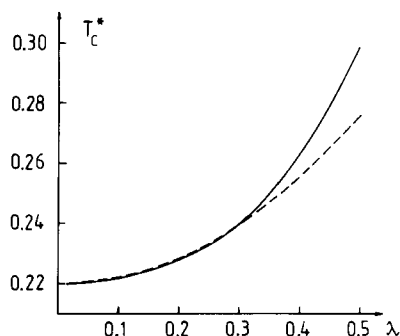


Figure 2. The reduced temperatures  $T_c^* = kT_c/C_{200}$  of the nematic–isotropic phase transition calculated on the basis of the LZNS theory [13] (solid line) and from equation (5) (dashed line) as a function of the biaxiality parameter  $\lambda$  (cf. equation (2)).

we obtain

$$\Delta\alpha' = [(\Delta\alpha'_1 - \Delta\alpha'_2)^2 + 4\Delta\alpha'_1\Delta\alpha'_2\cos^2\phi]^{1/2}. \quad (4)$$

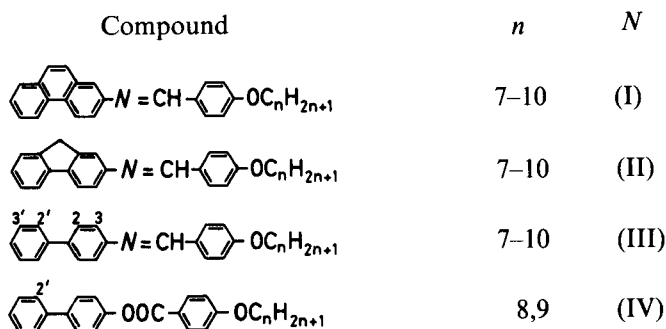
Because the anisotropy  $\Delta\alpha = \Delta\alpha_1 + \Delta\alpha_2$  is independent of  $\phi$  in our model the comparison of equations (2) and (4) shows that  $\lambda^2$  is linearly dependent on  $Q = \cos^2\phi$ , and from equation (1) we obtain

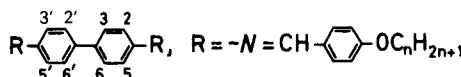
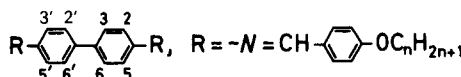
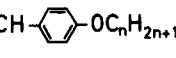
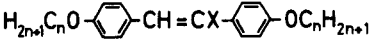


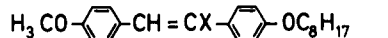


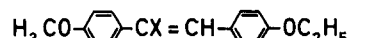


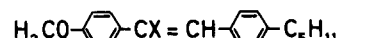





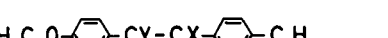


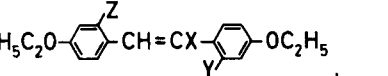

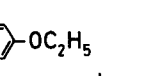
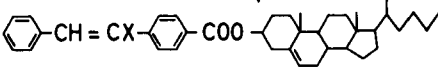
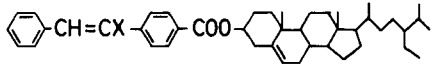




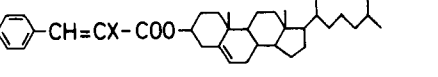
$$T_c(\lambda) = T_c(0) + B\lambda^2. \quad (5)$$

A comparison of the independence of the normalized transition temperatures  $T_c^* = kT_c/C_{200}$  on  $\lambda$  calculated on the basis of the LZNS theory [13] and from equation (5) is given in figure 2. The parameter  $B = 0.2244$  in equation (5) has been obtained by the normalization of  $T_c^*$  at  $\lambda = 0.3$ . For  $\lambda < 0.3$  the agreement between both dependences is quite good. At  $\lambda = 0.1$  and  $0.2$  the difference between the respective values of  $T_c^*$  is only 0.18 and 0.52 per cent. With increasing  $\lambda$  the difference of the dependences discussed increases. However, in the molecular field theory [13] with increasing  $\lambda$  both the jump of the order parameter and the entropy at the transition point  $T_c$  decreases and the nematic–isotropic transition is second order at  $\lambda \simeq 0.47$ . Therefore for the correct comparison of the dependences discussed at large values of  $\lambda$  in the framework of the molecular statistical theory order parameter fluctuations as well as their influence on the renormalization of  $T_c$  must be taken into account. For the pure nematics the experimental values of  $\lambda$  lie in the region 0.1–0.2 [13, 15, 16] where the results of [13] and equation (5) are in a good agreement.

### 3. Test compounds and their features

The chemical formulas of the compounds studied are



Compound	<i>n</i>	<i>N</i>
 $R$ -  - $R$ , $R = -N = CH$ -  - $OC_nH_{2n+1}$	7–10	(V)
 $H_{2n+1}C_nO$ -  - $CH = CX$ -  - $OC_nH_{2n+1}$	1–4	(VI)
 $H_3CO$ -  - $CH = CX$ -  - $OC_8H_{17}$	—	(VII a)
 $H_3CO$ -  - $CX = CH$ -  - $OC_2H_5$	—	(VII b)
 $H_3CO$ -  - $CX = CH$ -  - $C_5H_{11}$	—	(VIII a)
 $H_3CO$ -  - $CH \equiv CX$ -  - $C_4H_9$	—	(VIII b)
 $H_5C_2O$ -  - $CY = CX$ -  - $C_5H_9$	—	(VIII c)
 $H_5C_2O$ -  - $CH = CX$ - 	—	(IX)
	—	(X a)
	—	(X b)
$[H_{2n+1}C_n$ -  - $CY = CX - COOH]_2$	4–6	(XI)
$[H_{2n+1}C_nO$ -  - $CY = CX - COOH]_2$	1,3–10,12	(XII)
$H_{2n+1}C_nO$ -  - $CH = CX - COO$ -  - $CN$	1–8	(XIII)
	—	(XIV)

The transition temperatures for the compounds (I)–(IX), (XI)–(XIII) were taken from [17] for (Xa, b) from [18] and for (XIV) from [19]. Several factors made these particular compounds convenient for study. Compounds (I)–(V) have in the molecular core the biphenyl fragment for which values of the angle  $\phi$  between the planes of benzene rings are known for various substituents in positions 2(2') and 6(6') (cf. table 1).

The parameter  $Q$  for the fragment can be changed discretely over the complete range 0–1 by varying the substituent. In compounds (I)–(IV) and (V) the fragments occupy off-central and central positions, respectively. Then, in compounds (I)–(III), (V) and (IV), the biphenyl fragment has joined and has not joined respectively by  $\pi$ -conjugation with other molecular core fragments; that is of interest for the determination of the individual fragments' contributions to the derivative  $dT_c/dQ$ . Finally, the materials chosen give us the possibility to study the dependence of  $dT_c/dQ$  on the flexible chain length at a fixed core length ((I)–(IV)) as well as on the core length at a fixed chain length ((III), (V)).

Stilbene derivatives (VI)–(X) have in their aromatic core two fragments (two single chemical bonds between the bridging group  $CH = CH$  and benzene rings) joined by

Table 1. The dihedral angle  $\phi$  between planes of the benzene rings in the biphenyl fragment and between the benzene ring and the bridging group in the stilbene fragment for various substituents  $X$ .

$N$	Fragment	$X$	$\phi$ /degrees	References	$N$	Fragment	$X$	$\phi$ /degrees	References
1		—	4	[20]	4.1		Cl	67–69	[26]
2		—	0–12	[21–23]	4.2		Br	70–72	[26]
3.1		H	30–36	[23–26]	5.1		CH <sub>3</sub>	67–79	[20, 21, 23, 25, 28, 29]
3.2		F	46–48	[23]	5.2		Cl	69–79	[22, 30, 31]
3.3		CH <sub>3</sub>	47–58	[21, 23, 25]	5.3		Br	70–80	[22]
3.4		Cl	60–63	[23]	6		Cl	87	[32]
3.5		Br	63–66	[23]	7.1		H	0	[21, 23]
3.6		I	83–90	[22, 23, 27]	7.2		CH <sub>3</sub>	35	[21]
					7.3		Cl	39	[21]

strong  $\pi$ -conjugation. The conformation of these fragments can be changed in turn or simultaneously by substituting one or two hydrogen atoms in the bridging group. Here it is interesting to test the equivalency of these fragments for symmetric (VI) and asymmetric (VII) molecules, for the same or different terminal chains (transition from (VI), (VII) to (VIII)) and also to study the influence of the interaction of two conformational degrees of freedom on  $T_c$  in (IX). The compounds ( $X_a, b$ ) differ from (VI)–(IX) in the chemical structure of the aromatic core as well as by the off-central position of the stilbene fragment in the core. The investigation of nematogens (VI)–(IX) and cholesterogens ( $X_a, b$ ) allows us to compare the influence of the steric effect of the same substituents on the change of the nematic–isotropic and cholesteric–isotropic transition temperatures.

In cinnamic acids (XI), (XII) the  $\pi$ -conjugation of the fragments COOH with the bridging group is reduced sufficiently because of the dimerization of the molecules in the mesophase by hydrogen bonds between these fragments and so there is only one degree of freedom in these compounds. From the point of view of the  $\pi$ -conjugation strength of the bridging group with the fragment COO the situation for the compounds (XIII), (XIV) is intermediate between the stilbene derivatives and cinnamic acids. Therefore the comparison of compounds (IX), (XI)–(XIV) allows us to establish a dependence of the derivative  $dT_c/dQ_1$  on the parameter  $Q_2$  as well as on the dimerization ((XI), (XII)) and association (XIII) of the molecules in the mesophase.

#### 4. Estimation of the steric effect contribution of substituents on the change of the mesophase thermal stability

Substitution of the hydrogen atom in the benzene ring or bridging group of the mesogen leads to a change of  $T_c$  at least because of the following reasons: (i) increasing the molecular width and the intermolecular distances in the mesophase with decreasing geometrical molecular shape anisotropy as well as the anisotropy of steric and dispersive intermolecular interactions, (ii) change of the molecular polarizability and

polarity as well as of the corresponding dipolar and dispersion contributions to the intermolecular forces; (iii) perturbation of the substituted fragment electronic structure due to the mesomeric and inductive effects of the substituents; (iv) decrease of the coplanarity and of the  $\pi$ -conjugation of the core fragments with decrease of the molecular polarizability anisotropy; (v) change of the molecular biaxiality parameter (cf. equation (2)) due to the change of the parameters  $\Delta\alpha'$  and  $\Delta\alpha$  depending on  $\phi$ .

The first effect of substitution leads to the similar depression of  $T_c$  for mesogens of approximately the same molecular shape anisotropy in spite of the presence or absence of the  $\pi$ -conjugation chain of the core fragments [1, 4]. If the benzene ring is not connected by the conjugation with the bridging groups ortho- or meta-substitution of this ring will not lead to much change of the molecular polarizability anisotropy [33]. Dipolar interactions cannot be important as far as nematic or cholesteric thermal stability is concerned but they must be taken into account when smectic thermal stability is analysed [1, 4–7, 10]. For the substituents listed in table 1 the mesomeric moments describing the mesomeric influence of the substituents on the electronic system of the benzene ring [34] and the spectroscopic moments describing the inductive effect of the substituents [35] are small. Therefore the total influence of the factors (i)–(iii) on the change of  $T_c$  may be called the geometrical effect of the substituent. This effect leads to the same decrease of  $T_c$  in the cases of ortho- or meta-substitution of the benzene ring to the bridging group [36, 37]. The last two listed reasons are difficult to separate from each other if  $\pi$ -conjugation of the fragments is present because of the strong influence of the core electronic structure on the molecular polarizability components  $\alpha_{ij}$ . Therefore the joint contribution of these to the change of  $T_c$  may be called the steric effect of the substituent.

If the conjugation of the substituted ring with other core fragments is absent the steric effect of the substituent does not lead to an appreciable additional depression of  $T_c$  [38]. It means that the additivity of the steric and geometrical contributions to the change of  $T_c$  takes place for the conjugated mesogens and is possible to write

$$\Delta T_c(\text{H-X}) = \Delta T_{cs}(\text{H-X}) + \Delta T_{cg}(\text{H-X}), \quad (6)$$

where

$$\Delta T_c(\text{H-X}) = T_c(\text{H}) - T_c(\text{X})$$

is the decrease of the  $S_A$ -N(Ch)-I transition temperatures due to the substitution of hydrogen by X. The subscripts s and g denote the steric and geometrical effects of the substituent X. The additivity in equation (6) only holds for the substituents presented in table 1 since these do not lead to a noticeable change of the molecular electronic structure, polarizability and polarity. For the substituents  $\text{NO}_2$ ,  $\text{NH}_2$ ,  $\text{CN}$ ,  $\text{OH}$  and others which have a strong polarity, large mesomeric and spectroscopic moments, electron-donor and acceptor properties and can form intra- or intermolecular hydrogen bonds, the additivity of equation (6) may not be true. Therefore these substituents are outside our discussion.

Several methods for the determination of  $\Delta T_{cg,s}(\text{H-X})$  used here are presented in table 2, where  $\Delta T_{m(n)}$  ( $\Delta T_{m,n}$ ) is the change  $\Delta T_c(\text{H-X})$  for one (two) atom X in position *m* or *n* (*m* and *n*). Version (b) takes into account the possible differences in the values of  $\Delta T_3$  and  $\Delta T_3$ , for the molecules of type III with an off-central position of the fragment in the core [1]. In the expression  $\overline{\Delta T_{cg}(\text{H-X})}$  and  $\overline{\Delta T_{cg}(\text{Y-X})}$  the bar denotes averaging over molecules of different chemical classes but disregarding the steric effect of the substituents X and Y. To determine the averaged parameters for the nematic-isotropic transition the following compounds have been considered.

Compound	Substituents, X	N	References
	H, F, Cl	(XV)	[1]
	H, F, Cl, Br	(XVI)	[7]
	H, F, Cl	(XVII)	[17]
	H, F, Cl, Br, I, CH3	(XVIII)	[17]
	H, Cl, Br, CH3	(XIX)	[17, 39]
	H, Cl, Br	(XX)	[17]
	H, F, Cl, Br, I	(XXI)	[1]

For the compounds of type (XVI), (XVIII)–(XX) the substituted ring is perpendicular to the COO fragment plane even for  $X = \text{H}$  [40]. The substitution of H by more bulky atoms leads to a change of  $T_c$  due only to the geometrical effect of the substituent. Data on  $\Delta T_c(\text{H}-X)$  for the compound (XVI) are distorted due to the partial screening of the substituent by the features of the core structure [7] so they were not considered when determining the value of  $\overline{\Delta T_{cg}(\text{H}-X)}$ . Data on  $\Delta T_c(Y-X)$  for this compound were taken into account in determining  $\overline{\Delta T_{cg}(Y-X)}$ . The results of the analysis are

X	F	Cl	Br	I	CH <sub>3</sub>
$\overline{\Delta T_{cg}(\text{H}-X)}$ °C	18	43	50	64.3	43.5
Y-X	F-Cl	Cl-Br	Br-I	Cl-CH <sub>3</sub>	
$\overline{\Delta T_{cg}(Y-X)}$ °C	26.2	11	14	1.2	

Due to dimerization in the mesophase, molecules of compounds (XV) and (XXI) contain two and four benzene rings in the core, respectively. The compounds considered differ in the following ways: (i) the geometrical anisotropy of the aromatic core and the length of the aliphatic chains, (ii) the existence of one or two chains and (iii) the position of the substituent. Therefore the average value  $\overline{\Delta T_{cg}(\text{H}-X)}$  may be used to evaluate the geometrical effect of substituents in typical nematogens and cholesterogens containing two or four benzene rings in the core.

Table 2. Methods for estimating the contributions of geometrical and steric effects of substituents to the total change  $\Delta T_c(\text{H}-X)$  of the I-N(Ch)-S<sub>A</sub> transition temperatures (see comments in the text).

N	$\Delta T_{cg}(\text{H}-X)$	N	$\Delta T_{cs}(\text{H}-X)$
a	$\Delta T_{3(3)}$	$\alpha$	$\Delta T_{2(2')} - \Delta T_{cg}$
b	$(\Delta T_3 + \Delta T_{3,3'}/2)/2$	$\beta$	$\Delta T_{2,5} - 2\Delta T_{cg}$
c	$\overline{\Delta T_{cg}(\text{H}-X)}$	$\gamma$	$\Delta T_{2,3'} - 2\Delta T_{cg}$
d	$\Delta T_{cg}(\text{H}-Y) + \overline{\Delta T_{cg}(Y-X)}$	$\delta$	$\Delta T_{2,6(6')} - 2\Delta T_{cg}$
e	$\Delta T_c(\text{H}-Y), X = \text{H}$	$\epsilon$	$\Delta T_{2,2',6} - 3\Delta T_{cg}$
		$\omega$	$\Delta T_c(\text{H}-X) - \Delta T_{cg}$



Table 3. The combinations of methods presented in table 2 which have been used to separate the steric and geometrical effects of the substituents in compounds (III)-(XIV) with the fragments indicated in table 1.

N	Phase transition			N	Phase transition		
	Fragment	N-S <sub>A</sub>	N-I		Fragment	N-S <sub>A</sub>	N-I
(III)	3.2	—	c-d <sup>†</sup> , α(Y = Cl)	(V)	3.2	—	c-d, α(Y = Cl)
	3.3	a, α	—		3.3	a, α	b, α-γ
	3.4	—	a, α		3.4	b, α	b, α-γ
	3.5	—	a, α		3.5	b, α	b, α, β
	3.6	—	d, α(Y = Br)		3.6	d, α(Y = Br)	c-d, α(Y = Br)
(IV)	3.2	—	c, α	4.1	—	b, δ	
	3.4	—	c, α	4.2	—	b, δ	
(VI), (VII), (IX), (X)†	7.2	—	c, ω	5.1	—	b, δ	
(VIII)	7.2	—	c, ω	5.2	—	b, δ	
	7.3	—	c, ω	5.3	—	b, δ	
(XI), (XII)	7.2	—	e, ω	6	—	b, ε	
(XIII)	7.2	—	c, ω	7.3	—	c, ω	

† Explanations are in the text. ‡ Phase transition Ch-I.

The methods ( $\beta$ - $\delta$ ) in table 2 are the consequences of equation (6) and additivity of the substituent geometrical effects for two-fold substitution of a molecule by the same [1, 4, 6, 38, 41] or different substituents [42]. The method ( $\epsilon$ ) is less exact since by introducing the third substituent the transition temperature  $T_c$  changes slightly less than would be expected from the additivity rule [41]. Combinations of the methods used for separation of steric and geometrical effects are summarized in table 3. For the compound V with the fragment 3.6 the value  $\Delta\overline{T}_{cg}(\text{Br-I}) = 20^\circ$  [1] is used to analyse the N-S<sub>A</sub> transition. If the values  $\Delta T_{cg}(\text{H-X})$  obtained by the methods ( $c$ ) and ( $d$ ) were somewhat different then their mean value was used; this is marked as ( $c$ - $d$ ) in table 3.

## 5. Steric effect of substituents and transition temperatures

### 5.1. Derivatives of phenanthrene, fluorene and biphenyl

For the compounds I-V the dependences of  $\Delta T_{cs}(\text{X-H})$  on the parameter  $Q = \cos^2 \phi$  are shown in figure 3. The parameter  $Q$  for the corresponding fragments from table 1 are localized in figure 3 at the points of the abscissa axis which correspond to the middles of the possible intervals indicated. In accordance with equation (1) a

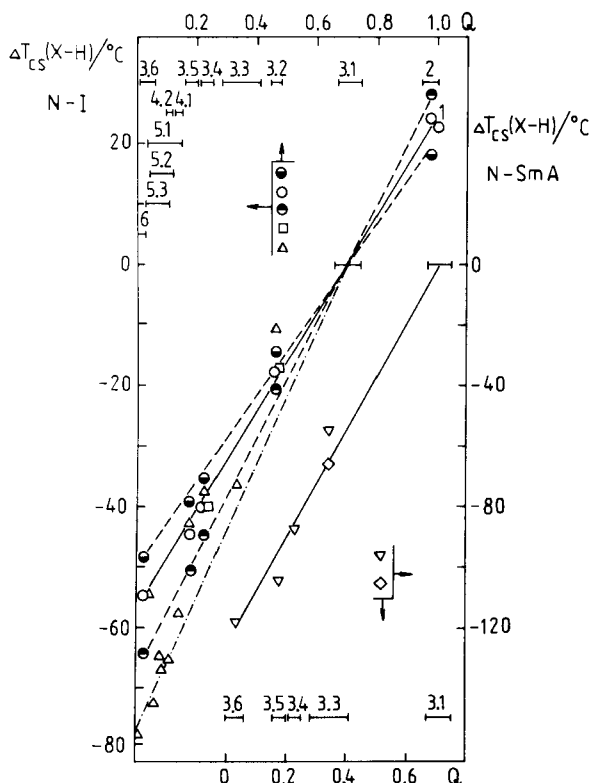


Figure 3. The change of the N-I and N-S<sub>A</sub> transition temperatures due to the steric effect of the substituents in compounds (I)-(III) (the N-I transition: ●,  $n = 7$ ; ●,  $n = 10$ ; ○, an average over  $n = 7$ -10; the N-S<sub>A</sub> transition in (III): ◇, an average over  $n = 9, 10$ ); (IV) (□, an average over  $n = 8, 9$ ) and (V) (the N-I transition: △, an average over  $n = 7$ -10; the N-S<sub>A</sub> transition: ▽, an average over  $n = 9, 10$ ). The segments show the possible intervals of the change of  $Q$  for the fragments listed in table 1.

linear dependence of  $\Delta T_{cs}(Q)$  is observed in the range  $Q = 0-1$  for individual homologues (dashed lines) as well as for the values averaged over  $n = 7-10$  (solid line). The derivative  $dT_c/dQ$  for the nematic-isotropic transition decreases with the increasing length of the flexible chains. This agrees with the well-known fact that within the homologous series the nematic-isotropic transition temperature  $T_c(n)$  approaches the limiting value  $T_1$  which depends weakly on the chemical and electronic structure of the molecular core for increasing  $n$  [1, 4-7, 43].

For the compounds (I)-(III), (V) (an average over  $n = 7-10$ ) and (IV) ( $n = 8, 9$ ) with the same effective chain lengths, the derivative  $dT_c/dQ$  is  $85^\circ\text{C}$  at the nematic-isotropic transition is of the same magnitude. It means that for the biphenyl derivatives the value of  $dT_c/dQ$  does not depend on the  $\pi$ -conjugation of the biphenyl fragment with other fragments of the molecular core (compare the compounds (III) and (IV), (V)), the central or off-central ((I)-(IV) and (V)) position of the fragment in the core, the chemical structure of other fragments and the dimensions of the core ((III)-(V)). Therefore the derivative,  $dT_c/dQ$ , is characteristic of the fragment and does not depend on the absolute value of  $T_c$  which results from the specific features of the geometrical, electronic and chemical structure of the core.

For the compound (V) (an average over ( $n = 7-10$ )) with the fragments 4.1-6 containing two or three substituents, the dependence  $\Delta T_{cs}(Q)$  is linear within the range  $0 \leq Q \leq 0.7$  (dashed-dotted line in figure 3), but the derivative  $dT_c/dQ$  is larger in this case than for the fragments 3.1-3.6 with one substituent. It may be caused by such reasons as the change of the valence angles and the length of the central C-C bond as well as the noticeable perturbation of the biphenyl electronic structure by the substituents in addition to the change of  $\phi$ . The value of  $\Delta T_{cs}(Q)$  for the fragment 3.3 of the compound V ( $n = 7-10$ ) is somewhat larger than would be expected from the known value of  $\phi$ . It has also been mentioned earlier by Gray [1]. The value of  $\Delta T_{cs}(Q)$  for the fragment 3.2 of the strong anisotropic compound V ( $n = 7-10$ ) is probably somewhat underestimated because of using the value  $\overline{\Delta T_{cg}(\text{H-F})} = 18^\circ\text{C}$  which does not take into account some decrease of  $\Delta T_{cg}(\text{H-X})$  with the increasing anisotropy [1] of the substituted molecule. The dependences  $\Delta T_{cs}(Q)$  for the N-S<sub>A</sub> transition in compounds III, V are also described by equation (1) with the value  $dT_c/dQ = 185^\circ\text{C}$  which is twice as large as that for the nematic-isotropic transition. It indicates the significant influence of the interaction between the molecular aromatic cores on the thermal stability of the layered smectic structure.

### 5.2. Stilbene derivatives

For compounds (VI)-(XIV) the dependences  $\Delta T_{cs}(Q)$  are presented in figure 4. The change of the derivative  $dT_c/dQ$  within the homologous series (VI) and (VII) is less marked than for compounds (III) and (V). It is probably the consequence of the closeness of  $T_c(n)$  to  $T_1$ . The values  $\Delta T_{cs}(\text{X-H})$  for compounds with two (VI) and one (VII) flexible chain are in good agreement with each other; this has already been noted for compounds (III), (V). Substitution of the molecules (VIII) in positions  $X$  or  $Y$  leads to the same change of  $T_c$  for both substituents  $\text{CH}_3$  and  $\text{Cl}$ , although the electronic-donor properties of the alkyl- and alkyloxy-chains are different [34, 35]. It indicates the equivalency of the two conformational degrees of freedom described by the parameters  $Q_{1,2}$  in the stilbene fragment. The derivative  $dT_c/dQ_{1,2}$  does not depend on the degree of  $\pi$ -conjugation of the benzene rings with other molecular fragments

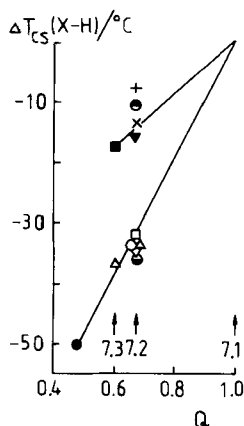


Figure 4. The change of the N(Ch)-I transition temperature due to the steric effect of the substituents in compounds (VI) (○, an average over  $n = 1-4$ ), (VII) (□, an average over (VIIa, b)), (VIII) (Δ, an average over (VIIIa, b, c)), (IX) (●, the Y-substitution of the molecule (IX) with  $X = H$ ,  $Z = CH_3$ ); (◻, the X-substitution of the molecule (IX) with  $Y = H$ ,  $Z = CH_3$ ); (●, the Y,Z-substitution of the molecule (IX) with  $X = H$ ,  $Q = Q_1, Q_2$ ), (X) (▽, an average over (Xa, b)), (XI) (x, an average over  $n = 4-6$ ), (XII) (+, an average over  $n = 1,3-10, 12$ ), (XIII) (▽, an average over  $n = 1,8$ ) and (XIV) (■). The pointers show the values of  $Q$  for the respective fragments listed in table 1.

as occurs for compounds (III), (IV). However, the derivative  $dT_c/dQ_i$  is very sensitive to the value of  $Q_j$  ( $i, j = 1, 2$ ). For example, X-substitution of the (IX) molecule with  $Y = H$ ,  $Z = CH_3$  and consequently decrease of  $Q_1$  at  $Q_2 = 1$  leads to the same value of  $dT_c/dQ_1$  as for (VI)–(VIII). But Y-substitution of the (IX) molecule with  $X = H$ ,  $Z = CH_3$  and decrease of  $Q_2$  at  $Q_1 = 0.67$  leads to the smaller value of  $dT_c/dQ_2$ . Thus there is a strong interaction of two conformational degrees of freedom in the stilbene fragment through  $\pi$ -conjugation with the bridging group and it is possible to introduce the generalized coordinate  $Q = Q_1 Q_2$  to describe the conformational state of the entire stilbene fragment. Then the value  $\Delta T_{cs}(Q)$  for compound (IX) with  $X = H$ ,  $Y = CH_3$  and  $Z = CH_3$  lies on the corresponding plot for compounds (VI)–(VIII) and the contradiction mentioned previously is eliminated. The value  $dT_c/dQ = 93^\circ\text{C}$  for the stilbene fragment is somewhat bigger than that for the biphenyl fragment. The values  $\Delta T_{cs}(H-X)$  for compounds (Xa, b) agree with those for compounds (VI)–(IX). This means that the derivative  $dT_c/dQ$  does not depend on the position of the fragment in the core, or the chemical and electronic structure of the core containing the chiral fragments.

### 5.3. Cinnamic acids, their cyanophenyl esters and cholesteryl cinnamates

Within the homologous series (XI) and (XII) a relatively weak increase and decrease of  $\Delta T_{cg}(H-X)$  is observed for increasing  $n$ . Therefore the use of the average value  $\overline{\Delta T_{cg}(H-X)}$  for the determination of  $\Delta T_{cs}(H-X)$  in a wide interval of  $n$  probably leads to a smaller value of  $\overline{\Delta T_{cs}(H-X)}$  for (XII) if the averaging goes over  $n = 1-12$ . This can be seen in figure 4 by comparison of the values  $\Delta T_{cs}(H-X)$  for compounds (XI) and (XII). The derivative  $dT_c/dQ_1 = 40^\circ\text{C}$  is approximately the same as for compounds (XI)–(XIV) and differs by more than two from that for the stilbene derivatives with  $Q_2 = 1$ , but is comparable with  $dT_c/dQ_2$  for (IX) with  $Q_1 = 0.67$ . Because of the absence of reasons to assume that  $Q_2 < 1$  for compounds (XI)–(XIV),

this consideration shows a weak  $\pi$ -conjugation of the fragments COOH((XI), (XII)) and COO((XIII), (XIV)) with the bridging group in comparison with the conjugation of the benzene ring with the bridging group in stilbene. The agreement between the values of  $dT_c/dQ_1$  for compounds (XI)–(XIV) shows a weak influence of the dimerization of molecules (XI), (XII) and association of molecules (XIII) on the steric effect of substituents.

## 6. Discussion

The results presented here confirm the dependence in equation (1) of the  $S_A$ –N(Ch)–I transition temperatures on the intramolecular conformation parameter  $Q$  in the complete range  $Q = 0$ –1. For the materials studied the derivative  $dT_c/dQ$  does not depend on the following factors:

- (i) The central or off-central position of the fragment in the aromatic molecular core;
- (ii) the degree of the  $\pi$ -configuration of the fragment with other fragments of the core;
- (iii) the chemical structure of other fragments of the core, containing, in particular, the chiral fragments;
- (iv) geometrical anisotropy of the core at fixed lengths of the flexible end chains;
- (v) the absolute value of  $T_c$  determined by the chemical, electronic and geometrical core structure.

Therefore the value  $dT_c/dQ$  is characteristics of the fragment and it is the same for various mesogens containing this fragment in the core. This result shows that the intermolecular interaction energy in the mesophase is probably the sum of interaction energies between the force centres distributed discretely over such a molecule. The biphenyl and stilbene fragments may be considered as an example of such centres. A many-centred molecular model of the mesogens improves an estimate of the nematic–isotropic transition temperature  $T_c$  in the framework of the molecular–statistical theory [44] and has been successfully used in the Luckhurst theory of nematics with flexible molecules [15].

The independence of the derivative  $dT_c/dQ$  on the absolute value of  $T_c$  is correlated with the observed additivity of the contributions of the molecular fragments to the value of  $T_c$  for nematics [5, 45]. For the  $S_A$ –N transition the possibility of such additivity has not been examined up to now. There is an analogy between the dependence of  $\Delta T_{cs}$  on  $Q$  and a linear dependence of the nematic–isotropic transition temperature  $T_c$  on the increment  $\Delta\alpha_x$  of the molecular polarizability anisotropy for small terminal substituents  $X$  which do not lead to noticeable changes in the shape anisotropy and the volume of the substituted molecule [5, 33, 46]. As for the steric effect, the derivative  $dT_c/d(\Delta\alpha_x)$  does not depend on the absolute value of  $T_c$ . This analogy shows that the change of the actual fragment polarizability anisotropy is a probable reason for the influence of the substituents' steric effect on the transition temperatures in the compounds studied. In this case the linear dependence  $\Delta T_{cs}(Q)$  correlates with the linear dependence of the increments  $\Delta\alpha_Q$  of the biphenyl and stilbene polarizability anisotropies on the parameter  $Q$  [8, 47, 48]. The special feature of the compounds studied is a sufficient change of  $T_c$  and probably the large change of the polarizability anisotropy, while for terminal substitution the relative changes of these values are small [33, 46].

On the other hand, for the large changes of the polarizability anisotropy  $\Delta\alpha$  due to substitution of the benzene rings by the saturated rings the correlation between

$T_c$  and  $\Delta\alpha$  does not hold [6, 7, 49, 50]. However, in contrast to the steric effect, substitution of the benzene ring by saturated rings changes the electronic structure, the character of the intermolecular correlations and the spectrum of the possible molecular conformations [7, 49]. Moreover, in alkyl cyanobiphenyl molecules ( $nCB$ ) [49] substitution of one benzene ring by cyclohexane or bicyclo-octane rings results in the decrease of  $\Delta\alpha$  and some increase of the mean polarizability  $\bar{\alpha}$  [51], but with decreasing  $Q$  for  $nCB$  both values  $\Delta\alpha$  and  $\bar{\alpha}$  are decreased [8, 47]. This is of importance, since in the generalized van der Waals theory of nematics [52] the main part of the constant  $C_{200}$  in the molecular field potential and consequently the nematic-isotropic transition temperature are determined by the isotropic dispersion attractive forces and hence by the parameter  $\bar{\alpha}$ . Therefore the steric effect of substituents is probably caused by variation of both  $\Delta\alpha$  and  $\bar{\alpha}$ .

The author wishes to express his gratitude to Professors D. Demus, D. A. Dunmur, R. Eidenschink, W. M. Gelbart, G. W. Gray, W. H. de Jeu, G. R. Luckhurst and E. T. Samulski and Drs D. J. Byron, L. D. Field, M. A. Osman, R. Shashidhar and S. Takenaka for the reprints of their papers used in this work.

### References

- [1] GRAY, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (Academic Press).
- [2] WIEGAND, CH., 1951, *Z. Naturf. (b)*, **6**, 240.
- [3] DE JEU, W. H., and VAN DER VEEN, J., 1972, *Philips Res. Rep.*, **27**, 172.
- [4] GRAY, G. W., 1974 *Liquid Crystals and Plastic Crystals*, Vol. 4, edited by G. W. Gray and P. A. Winsor (Ellis Harwood), p. 103.
- [5] KOVSHEV, E. I., BLINOV, L. M., and TITOV, V. V., 1977, *Usp. Khim.*, **46**, 753.
- [6] GRAY, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chaps. 1 and 12.
- [7] GRAY, G. W., 1983, *Phil. Trans. R. Soc. A*, **309**, 77.
- [8] AVERYANOV, E. M., 1982, *Soviet Phys. solid St.*, **24**, 1609; 1983, *Ibid.*, **25**, 166.
- [9] FEARON, J. E., GRAY, G. W., and IFILL, A. D., 1985, *Molec. Crystals liq. Crystals*, **124**, 89.
- [10] OSMAN, M. A., 1985, *Molec. Crystals liq. Crystals*, **128**, 45.
- [11] EIDENSCHINK, R., 1985, *Molec. Crystals liq. Crystals*, **123**, 57.
- [12] AVERYANOV, E. M., 1984, *Nelineinaya Optika i Spektroskopiya Molekulyarnykh Sred* (in Russian), edited by V. P. Shabanov (IP SB AS U.S.S.R., Krasnoyarsk), p. 59.
- [13] LUCKHURST, G. R., ZANNONI, C., NORDIO, P. L., and SEGRE, U., 1975, *Molec. Phys.*, **30**, 1345.
- [14] STRALEY, J. P., 1974, *Phys. Rev. A*, **10**, 1881.
- [15] LUCKHURST, G. R., 1985, *NMR of Liquid Crystals*, edited by J. W. Emsley (Riedel), Chap. 3.
- [16] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1981, *Molec. Phys.*, **44**, 565.
- [17] DEMUS, D., DEMUS, H., and ZASCHKE, H., 1974, *Flussige Kristalle in Tabellen*, Vol. 1 (Veb Deutscher Verlag); 1984, *Ibid.*, Vol. 2.
- [18] TAKENAKA, S., KODEN, M., and KUSUBAYASHI, S., 1986, *J. phys. Chem.*, **90**, 660.
- [19] GALATINA, A. I., DERKACH, L. G., KRAMARENKO, N. L., CYGULYOVA, O. M., and SHKARABA, N. M., 1984, *Kristallografiya*, **29**, 1114.
- [20] AVOYAN, R. L., STRUCHKOV, YU. T., and DASHEVSKII, V. G., 1966, *Zh. strukt. Khim.*, **7**, 289.
- [21] SUZUKI, H., 1967, *Electronic Absorption Spectra and Geometry of Organic Molecules* (Academic Press), Chaps. 12 and 14.
- [22] GRAY, G. W., (editor), 1958, *Steric Effects in Conjugated Systems* (Butterworth).
- [23] ZAITZEV, B. A., and KHRAMOVA, G. I., 1974, *Izv. Akad. Nauk SSSR, ser. Khim.*, **12**, 2722; 1973, *Ibid.*, **9**, 1968.

- [24] AVERYANOV, E. M., ZHUIKOV, V. A., and ADOMENAS, P. V., 1981, *Soviet Phys. JETP Lett.*, **33**, 248; 1981, *Soviet Phys. JETP*, **54**, 106.
- [25] SCHMID, E. D., and TOMPSON, R. D., 1983, *J. Raman Spectrosc.*, **14**, 191.
- [26] FIELD, L. D., STERNELL, S., and TRACEY, A. S., 1977, *J. Am. chem. Soc.*, **99**, 5249; 1981, *Ibid.*, **103**, 738.
- [27] LITTLEJOHN, A. C., and SMITH, J. W., 1953, *J. chem. Soc.*, p. 2456; 1954, *Ibid.*, p. 2552.
- [28] MODELLI, A., DISTEFANO, G., and JONES, D., 1983, *Chem. Phys.*, **82**, 489.
- [29] MAIER, J. P., and TURNER, D. W., 1973, *Faraday Discuss. chem. Soc. A*, **5**, 149.
- [30] SMARE, D. L., 1948, *Acta crystallogr.*, **1**, 150.
- [31] ROMMING, G., SEIP, H. M., and AANESSEN FYNNO, A. M., 1974, *Acta chem. scand. A*, **28**, 507.
- [32] REDERSEN, B. F., 1975, *Acta crystallogr. B*, **31**, 2931.
- [33] DE JEU, W. H., and VAN DER VEEN, J., 1977, *Molec. Crystals liq. Crystals*, **40**, 1.
- [34] HIGASI, K., BABA, H., and REMBAUM, A., 1965, *Quantum Organic Chemistry* (Wiley), Chap. 8.
- [35] SVERDLOVA, O. V., 1985, *Elektronnye Spektry v Organicheskoi Khimii* (Khimiya), gl. 5.
- [36] VAN METTER, J. P., and SEIDEL, A. K., 1975, *J. org. Chem.*, **40**, 2998.
- [37] DAVE, J. S., and VORA, R. A., 1973 *Indian J. Chem.*, **11**, 19.
- [38] VAN METTER, J. P., and KLAUDERMAN, B. H., 1973, *Molec. Crystals liq. Crystals*, **22**, 285.
- [39] WEISSFLOG, W., and DEMUS, D., 1984, *Cryst. res. Technol.*, **19**, 55.
- [40] GRAMSBERGEN, E. F., DE JEU, W. H., and ALS-NIELSEN, J., 1986, *J. Phys., Paris*, **47**, 711.
- [41] YOUNG, W. R., HALLER, I., and GREEN, D. C., 1972, *J. org. Chem.*, **37**, 3707.
- [42] DUBOIS, J. C., and BEGUIN, A., 1978, *Molec. Crystals liq. Crystals*, **47**, 193.
- [43] AVERYANOV, E. M., 1985, *Zh. fiz. Khim.*, **59**, 2145.
- [44] WARNER, M., 1980, *J. chem. Phys.*, **73**, 5874.
- [45] KNAAK, L. E., ROSENBERG, H. M., and SERVE, M. P., 1972, *Molec. Crystals liq. Crystals*, **17**, 171.
- [46] VAN DER VEEN, J., 1975, *J. Phys., Paris, Coll.*, C **1**, **36**, C1-375.
- [47] AVERYANOV, E. M., ZYRYANOV, V. YA., ZHUIKOV, V. A., and RUOLENE, YU. I., 1983, *Soviet J. struct. Chem.*, **24**, 740.
- [48] AVERYANOV, E. M., ZHUIKOV, V. A., ZYRYANOV, V. YA., and SHABANOV, V. P., 1986, *Zh. srukt. Khim.*, **27**, 73.
- [49] CARR, N., GRAY, G. W., and KELLY, S. M., 1981, *Molec. Crystals liq. Crystals*, **66**, 287.
- [50] TORIUMI, H., and SAMULSKI, E. T., 1983, *Molec. Crystals liq. Crystals*, **101**, 163.
- [51] DUNMUR, D. A., and TOMES, A. E., 1983, *Molec. Crystals liq. Crystals*, **97**, 241.
- [52] GELBART, W. M., 1982, *J. phys. Chem.*, **86**, 4298.