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ON THE RELATION BETWEEN MOLECULAR STRUCTURE AND LIQUID-CRYSTALLINE BEHAVIOUR

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The mean polarizabilities of four homologous series of mesogenic esters are computed using the MLSP method. The thermal stabilities of these series of mesogens are correlated with the structural characteristics of the molecules using polarizability data.

О СВЯЗИ МЕЖДУ МОЛЕКУЛЯРНОЙ СТРУКТУРОЙ И СВОЙСТВАМИ СИСТЕМЫ ЖИДКОСТЬ–КРИСТАЛЛ

В работе приведены результаты расчета средних поляризуемостей четырех гомологических серий мезогенных сложных Эфиров, которые получены при помощи MLSP-метода. На основе использования данных о поляризуемости установлено, что термическая устойчивость этих серий связана со структурными характеристиками молекул.

I. INTRODUCTION

Since the discovery of liquid-crystalline of mesomorphic behaviour [1] much attention has been given to its relation with the molecular structure. In the early years Vorlander [2] and his school and Weygand [3] were prominent workers in this field. The melting and clearing points of the liquid-crystalline compounds known up to 1959 were compiled and tabulated by Kast [4] who also discussed the relation with molecular structure [5]. In more recent years there have been general reviews on liquid crystals by Brown et al. [6, 7], Chistyakov [8], Saupe [9], and Sackmann and Demus [10].

A general criterion of the thermal stability of the mesophase is the clearing temperature T_c. At this point the forces responsible for the long-range order can no longer compete with the thermal energy. Maier and Saupe [11] have given a molecular statistic theory based on dispersion forces between anisotropic molecules, predicting nematic behaviour with a first-order transition at T_c. The

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determining factor for nematic behaviour to be correlated with the molecular structure is

$$\sum_{\mu,\nu} \frac{\delta_{0\mu}\delta_{0\nu}}{E_{\mu\nu}-E_{00}} \tag{1}$$

where the summations μ and ν run over different molecules. $\delta_{0\mu}$ is a combination of molecular transition moments

$$\delta_{0\mu} = \langle 0|P_{\parallel}|\mu\rangle\langle\mu|P_{\parallel}|0\rangle - \langle 0|P_{\perp}|\mu\rangle\,\langle\mu|P_{\perp}|0\rangle\,, \tag{2}$$

where $P_{\parallel}$ and $P_{\perp}$ are the operators of the dipole moment parallel and perpendicular to the molecular axis, respectively. The factor (1) is related to the anisotropy of the polarizability, which therefore determines T_c. Possible interactions between induced and permanent dipole moments are included by allowing the value 0 for either μ or ν. Consequently in this model the component of a permanent dipole moment along the molecular axis increases the anisotropy and stabilizes the nematic phase, while the perpendicular component destabilizes.

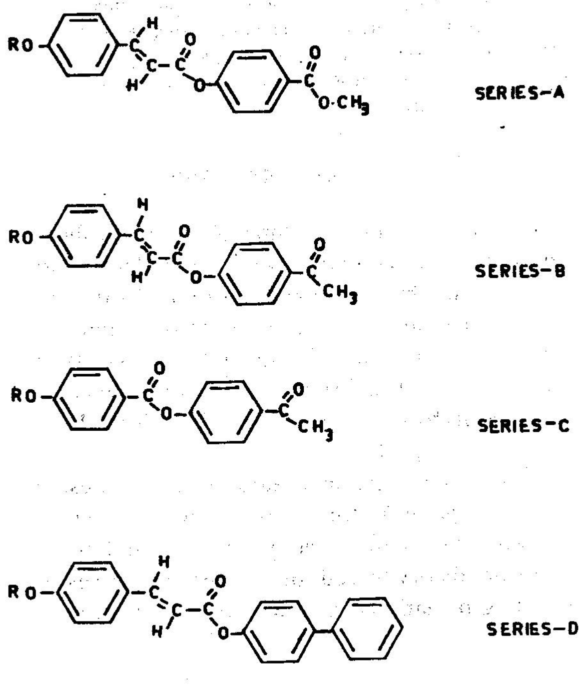

Fig. 1. Structural formulae of the various series of Mesogens.

That the dispersion forces and thus the polarizability of the molecules are an important factor is very likely: many mesomorphic compounds contain benzene rings that are easily polarizable because of the presence of π electrons. To a first approximation the anisotropy of the polarizability is determined by the geometrical anisotropy. Maier and Saupe [12] have also pointed out that with an alkoxy group as p-substituent the nonbonded electrons of oxygen are easily coupled to the π-electron system and this favours the polarizability along the long axis more than an alkyl group of the same length would. When a twist angle is introduced between the benzene rings, the conjugation between the rings is reduced [13]. Consequently the polarizability along the long axis will be reduced.

In the present communication we report the mean polarizabilities of four homologous series by using the MLSP method [14—18]. The structural formulae of these series of mesogenic esters are presented in Fig. 1. The thermal stabilities of these series of mesogens are correlated with the structural characteristic of the molecules using these polarizabillity data.

II. METHOD

The MLSP method [14—18] has been used to calculate the mean polarizability in terms of the parallel bond component ($\Sigma\alpha_{\parallel p}$), the perpendicular bond component ($\Sigma\alpha_{\perp}$) and the non-bond region electron contribution ($\Sigma\alpha_{\parallel n}$). The applicable relations are given below

$$\alpha_t = \frac{1}{3}\left(\Sigma\alpha_{\parallel p} + \Sigma\alpha_{\parallel n} + \Sigma 2\alpha_{\perp}\right), \tag{3}$$

where

$$\alpha_{\parallel p} = \frac{4nA\,\exp\,(T-T_c)/T_c}{a_0}\left[\frac{R^2}{4}+\frac{1}{2C_R^2}\right]^2 \exp-\left[\frac{(X_A-X_B)^2}{4}\right]. \tag{4}$$

Here n is the bond order, A the δ-function strength, a_0 the radius of the first Bohr orbit, R the bond length, $C_R = (n_1n_2N_1N_2)^{1/4} \times (A_1A_2)^{1/2}$, where n_1, N_1 and n_2, N_2 represent the principal quantum number and the number of electrons contributing to the bonding in atoms 1 and 2, respectively, and X_A, X_B are Pauling's electronegativities for the atoms A and B in the bond $A-B$,

$$\Sigma\alpha_{\parallel n} = \Sigma f_j\alpha_j\,. \tag{5}$$

Here f_j is the fraction of the non-bonded electrons of the jth atom and α_j is its atomic polarizability.

$$\Sigma 2\alpha_{\perp} = n_{df}\left[\frac{\Sigma x_j^2\alpha_j}{\Sigma x_j^2}\right]. \tag{6}$$

Table 1

Polarizabilities ($\times 10^{24}$ cm^3) of the liquid crystals of series-*A* and series-*B*

Series-*A*					Series-*B*				
R	$\Sigma\alpha_{\parallel p}$	$\Sigma\alpha_{\parallel n}$	$\Sigma 2\alpha_{\perp}$	α	R	$\Sigma\alpha_{\parallel p}$	$\Sigma\alpha_{\parallel n}$	$\Sigma 2\alpha_{\perp}$	α
CH_3	69.59	1.97	31.56	33.96	CH_3	67.96	1.58	31.17	33.32
C_2H_5	73.94	1.97	33.82	36.17	C_2H_5	72.30	1.58	33.43	35.44
C_3H_7	78.28	1.97	36.09	38.43	C_3H_7	76.65	1.58	35.69	37.78
C_4H_9	82.63	1.97	38.35	40.53	C_4H_9	81.01	1.58	37.96	39.90
C_5H_{11}	86.98	1.97	40.61	42.67	C_5H_{11}	85.35	1.58	40.22	41.87
C_6H_{13}	91.33	1.97	42.87	45.21	C_6H_{13}	89.70	1.58	42.48	44.45
C_7H_{15}	95.68	1.97	45.13	47.31	C_7H_{15}	94.05	1.58	44.75	46.51
C_8H_{17}	100.03	1.97	47.39	49.65	C_8H_{17}	98.40	1.58	47.01	48.80
$C_{10}H_{21}$	108.73	1.97	51.91	53.82	$C_{10}H_{21}$	107.09	1.58	51.53	52.81
$C_{12}H_{25}$	117.42	1.97	54.90	57.81	$C_{12}H_{25}$	115.79	1.58	54.52	56.78
$C_{16}H_{33}$	134.82	1.97	65.47	66.81	$C_{16}H_{33}$	133.19	1.58	65.09	65.88
$C_{18}H_{37}$	143.52	1.97	69.98	71.32	$C_{18}H_{37}$	141.89	1.58	69.61	70.24

Here n_{df} is the number of degrees of freedom given by $n_{df}=(3N-2n_b)$, N is the total number of atoms and n_b is the total number of bonds in the liquid crystal and x_j is the electronegativity of the jth atom.

$$\alpha=\alpha_l\left[1-\frac{m}{\varrho_l}(T-T_c)\right]. \tag{7}$$

Here m is the slope of the density versus temperature curve, T_c is the transition temperature, ϱ_l is the density in the liquid phase, α_l is the polarizability in the liquid phase and α is the mean polarizability in the liquid crystalline phase. Details of derivation of Eq. (7) are discussed in our previous paper [14]. The necessary data on bond-lengths are taken from Ref. [19].

III. RESULTS AND DISCUSSION

Polarizabilities of the four homologous series of mesogens, calculated using the MLSP method are presented in Tables 1 and 2. The relative thermal stabilities of these mesogens [20] are presented in Table 3. From Tables 1, 2 and 3 it appears that the series with a more pronounced mean polarizability has higher thermal stability values. From Table 3 it is evident that smectic-nematic or smectic-isotropic thermal stability for compounds of series *C* is the lowest. Incidentally the members of series-*C* have the lowest values of mean polarizability (Tables 1 and 2). Smectic-isotropic or smectic-nematic thermal stability for compounds of series-*A* is less than that of the compounds of series-*B*. While the non-complanarity and the length of the central bridge of the compounds of series-*A* and *B* are the same, the only difference is in the terminal group attached to the phenyl ring on the right-hand side. The ambiguous lower thermal stability in compounds of series-*A* as compared to that of the compounds of series-*B* may be due to factors such as the linking of the methyl group through the oxygen atom. The latter causes induction effects which result in weaker terminal attractions. The smectic-nematic or smectic-isotropic thermal stability for the compounds of series-*D* is the highest among all the four homologous series. This is perhaps due to the presence of a biphenyl ring which enhances the polarizability greatly.

Table 2

Polarizabilities ($\times 10^{24}$ cm^3) of the liquid crystals of series-*C* and series-*D*

Series-*C*					Series-*D*				
R	$\Sigma\alpha_{\parallel p}$	$\Sigma\alpha_{\parallel n}$	$\Sigma 2\alpha_{\perp}$	α	R	$\Sigma\alpha_{\parallel p}$	$\Sigma\alpha_{\parallel n}$	$\Sigma 2\alpha_{\perp}$	α
CH_3	59.86	1.58	27.91	29.63	CH_3	78.68	1.18	36.06	38.37
C_2H_5	64.21	1.58	30.17	31.69	C_2H_5	83.03	1.18	38.33	40.48
C_3H_7	68.56	1.58	32.43	33.95	C_3H_7	87.38	1.18	40.60	42.84
C_4H_9	72.91	1.58	34.70	35.96	C_4H_9	91.73	1.18	42.87	44.94
C_5H_{11}	77.26	1.58	36.76	38.17	C_5H_{11}	96.08	1.18	45.13	46.89
C_6H_{13}	81.61	1.58	39.22	40.44	C_6H_{13}	100.43	1.18	47.40	49.52
C_7H_{15}	85.96	1.58	41.48	42.53	C_7H_{15}	104.78	1.18	49.66	51.56
C_8H_{17}	90.31	1.58	43.75	44.67	C_8H_{17}	109.13	1.18	51.93	53.86
$C_{10}H_{21}$	99.01	1.58	48.27	49.32	$C_{10}H_{21}$	117.83	1.18	56.46	57.85
$C_{12}H_{25}$	107.71	1.58	52.79	53.86	$C_{12}H_{25}$	126.53	1.18	59.41	61.81
$C_{16}H_{33}$	125.10	1.58	61.82	62.08	$C_{16}H_{33}$	143.92	1.18	70.03	70.92
$C_{18}H_{37}$	133.80	1.58	66.38	66.78	$C_{18}H_{37}$	152.62	1.18	74.55	75.20

Table 3

Relative Thermal Stabilities of the various series of Mesogens [20]

Transition	Average transition temperature (°C) of the series			
	A	*B*	*C*	*D*
Smectic-nematic or Smetic-isotropic	133.7 (C_8—C_{18})	139.6 (C_8—C_{18})	100.1 (C_{12}—C_{18})	148.8 (C_8—C_{18})
Nematic-isotropic	138.25 (C_3—C_6)	135.8 (C_3—C_6)	88.2 (C_5—C_7)	206.0 (C_1—C_4)
Commencement of Smetic phase	C_4	C_5	C_5	C_7

The nematic-isotropic thermal stability for the compounds of series-*A* is higher than that of the compounds of series-*B* and series-*C*. The increased overall polarizability due to the central bridge as well as the increased length of the terminal group may contribute towards the enhanced thermal stability of the compounds of series-*A*. The commencement of the smectic mesophase at the fourth homologue in series-*A* and at the fifth homologue in series-*B* and series-*C* indicates approximately equivalent non-complanarity since the early commencement of the smectic phase is attributed to less non-complanarity of the compounds. The commencement of the smectic phase at the seventh member in series-*D* may probably be due to the biphenyl ring which enhances polarizability.

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