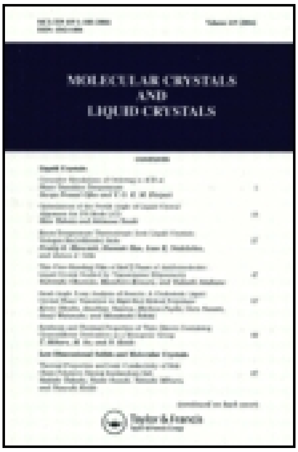

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Crystal-Nematic Transition Temperature Depend on Energy of the Torsion Deformation for Nematogene Molecules

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CRYSTAL-NEMATIC TRANSITION TEMPERATURE DEPEND ON ENERGY OF THE TORSION DEFORMATION FOR NEMATOGENE MOLECULES

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Abstract The linear regression equation determining a dependence between crystal-nematic mesophase transition temperature, T_N, and energy of the torsion deformation, E_T, of the nematogene molecules has been obtained on the strength of calculations by the MM2 molecular mechanics method. It has been performed this transition occurs on reaching such value T_N which corresponds to the average quantity of the heat kinetic energy $<E_K>$ in respect to the two short molecule axes exceeding E_T. The methods of consideration of the intermolecular association have been examined.

INTRODUCTION

A theoretical evaluation of the phase transition temperature with aid of calculated parameters of the mesomorphogene molecules acquires a great interest for understanding of the mesophase transition peculiarities at the molecular level.

RESULTS AND DISCUSSION

The general selection including 24 organic compounds - nematogenes has been considered for the determination of the crystal - nematic mesophase transition temperature, T_N, dependence on the molecular structure parameters. This general selection has been shown in Table 1. The general peculiarity of these compounds consists in the reversed transition from crystalline phase to nematic mesophase escaping the smectic mesophase[1-6]. In addition the interval of the

T_N values is large enough: from 287 K to 551 K. The selected nematogenes belong to various classes of the organic compounds and contain the aromatic (benzene, pyridine, diphenyl) as well as the saturated (1,3-dioxane, pyperidine, cyclohexane) rings in the molecular structure. Such segments as -N=N(O)-, -N=CH-, -OOC-, -C≡C- etc. are the bridges between rings.

The methods of molecular mechanics with the Allinger strength field, MM2, have been used for calculation of the molecular characteristics for the investigated compounds. These methods are good for the determination of the conformational mobility of organic molecules. It allows to calculate their geometric parameters such as a bond length, valence and torsion angles, as well as their energetic and electronic characteristics[7].

Table 1 shows the calculated full energies, E_F, Van der Waals, E_{VW}, and torsion deformation, E_T, energies, distances between the most remote atoms along the principal axis of molecule, L, and dipole moments, μ. The comparison of the experimental T_N values and their molecular parameters shows that only E_T increases monotonously with the T_N rise. The executed multicorrelation analysis has confirmed this conclusion. In one's turn the following regression analysis permits to obtain the linear Eq. (1) connecting the T_N and E_T values:

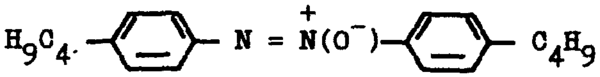
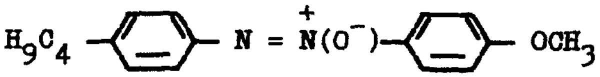
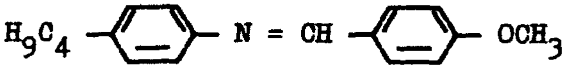
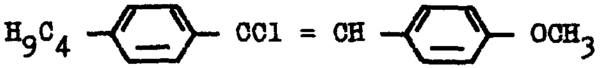
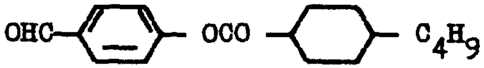
$$T_N = 9.829\ E_T + 183.454 \qquad (R = 0.980,\ S = 14.073) \qquad (1)$$

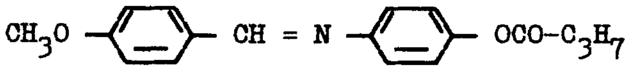
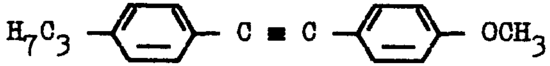
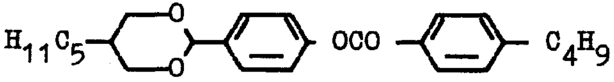
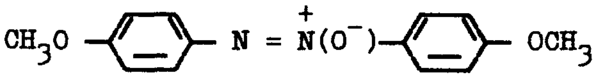
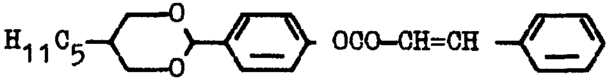
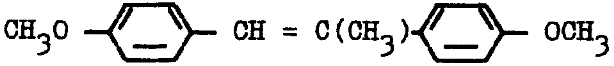
where R is a correlation coefficient and S is a standard deviation (in K).

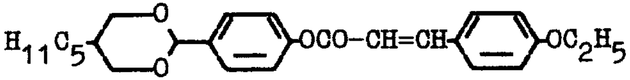
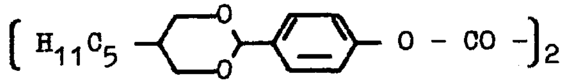
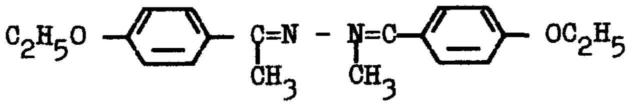
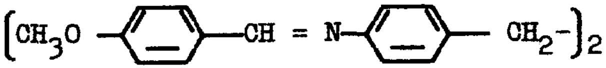
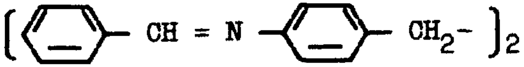
Table 1 shows also the T_N values calculated by Eq. (1) besides the experimental values. Taking into consideration first of all the fact that kT_N value (where k is the Boltzmann constant) is the average kinetic energy of molecules, $\langle E_K \rangle$, relating to the two degrees of freedom (relatively to the two molecular axes unlike the principal), one can write Eq. (1) in the more general form Eq. (2):

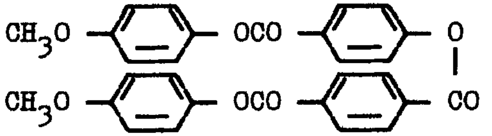
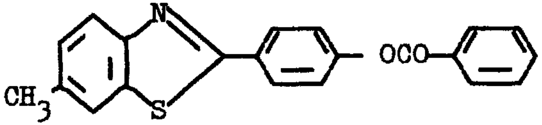
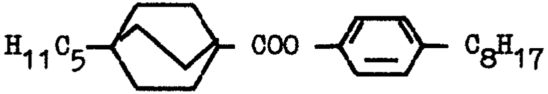
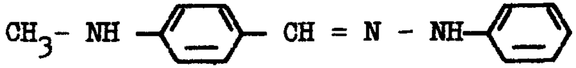
$$\langle E_K \rangle = k\ T_N = \alpha\ E_T + \beta \qquad (2)$$

TABLE 1 The considered nematogenes, their energetic parameters, and T_N values.

No	Compound	E_F kcal/mole	E_{VW} kcal/mole	E_T kcal/mole	L Å	μ D	T_N, K exper.	T_N, K calc.	Ref.
1	2	3	4	5	6	7	8	9	10
1		44.34	17.84	11.58	17.2	8.34	287.2	297.3	[1]
2		52.39	22.01	11.18	16.3	7.01	289.2	293.3	[2]
3		30.00	11.09	13.66	15.9	1.92	295.2	317.7	[1]
4		47.34	20.76	13.18	16.7	2.85	313.2	313.0	[6]
5		32.30	10.34	12.83	16.6	4.65	316.3	309.6	[7]
6		37.61	12.83	14.05	18.4	4.31	321.2	321.6	[3]

1	2	3	4	5	6	7	8	9	10
7		40.43	13.42	15.08	17.4	3.27	323.2	331.7	[2]
8		24.45	6.69	15.86	15.1	1.05	339.2	339.3	[6]
9		56.94	13.86	20.19	22.7	2.57	367.9	381.9	[4]
10		53.94	16.12	20.79	24.3	2.91	384.3	387.8	[7]
11		51.71	15.16	20.56	13.0	7.50	389.2	385.5	[6]
12		54.25	17.82	20.52	21.8	2.37	393.2	385.1	[6]
13		52.81	18.14	21.77	14.6	2.14	395.2	397.4	[7]

1	2	3	4	5	6	7	8	9	10
14		59.50	20.24	20.60	25.5	1.90	401.2	386.0	[7]
15		174.59	22.78	26.09	32.3	1.33	411.1	439.9	[7]
16		47.44	14.50	21.29	16.5	0.06	415.2	392.7	[6]
17		46.60	16.11	22.00	18.2	0.08	424.2	399.7	[6]
18		55.19	19.59	25.88	27.3	0.06	435.2	437.8	[6]
19		48.26	15.50	25.17	15.5	2.11	443.2	430.8	[6]
20		57.24	20.46	26.28	22.1	0.21	444.2	441.8	[6]

1	2	3	4	5	6	7	8	9	10
21		50.52	16.08	26.23	15.1	2.35	467.0	441.3	[6]
22		68.42	15.17	30.11	20.0	0.19	473.2	479.4	[7]
23		60.80	10.73	29.92	18.1	1.85	477.2	477.5	[6]
24		294.44	44.32	39.14	24.0	0.82	551.2	568.2	[6]
25		46.08	16.13	21.08 10.19	25.3	1.37	284.8	– 283.6	[9]
26		25.92	6.56	19.52	12.1	2.46	443.2	440.2	[6]

where $\alpha = 9.829$ k and $\beta = 183.454$ k. Taking into account the circumstance that a value of the torsion deformation energy, E_T, is the integral characteristic immediately connected with energetic barriers of the internal rotation about the all bonds in the molecular structure, the physical sense of the Eq. (1) will be clear.

Really in conformity with the foregoing it can be concluded that the transition of nematogene molecules from crystalline phase to nematic mesophase is possible on reaching such T_N temperature for which the average kinetic heat energy, $\langle E_K \rangle$, relatively the two short molecular axes becomes quite enough for overcoming the total barrier, E_T. The same follows from Eq. (2). The internal rotation around the single bonds gets possible after this overcoming. By that the molecular orientation along the principal axis stays practically identical to the same for crystalline phase. However statistical discovering of the various structural segments relatively the two short axes for the nearest molecules springs up at once.

Hence a formation of the liquid-crystal nematic mesophase has been conditioned by 'thawing' of the internal mobility for nematogene molecules by overcoming of the internal rotation barriers about bonds taking part in ones. The kinetic energy of molecules by their heat motion about the two short axes is consumed for that. Such transition from crystalline phase to nematic mesophase may be called the rotational transition.

The dependence of crystal-nematic transition on the internal rotation of nematogene molecules has been confirmed indirectly by the experimental data of their different reaction ability in crystal and nematic mesophase[8].

One can consider few examples of the molecular structure peculiarities influence on the T_N value. As the first example the two isomeric diphenyl derivatives (Table 1, compounds 19 and 21) are examined. The T_N value for the compound 21 is on 23.8 K more than the same for the compound 19. This one can be explained by the torsion deformation energy for the compound 21 being more than that for the compound 19 because of the potential barrier increase. The last is stipulated by the mutual repulsion between hydrogen atoms of the pyridine carbon, C_3, and CH=N-bridge.

For the compound 25 the torsion deformation energy for the adamantyl fragment makes the significant increment to the E_T value. Moreover this increment is not caused with a rotation of the adamantyl fragment in the whole. The energetic parameters for adamantane have been calculated for an appreciation of the torsion deformation in the above mentioned fragment. The torsion deformation energy for adamantane is great and amounts to 10.89 kcal/mole. Therefore in agreement with the above-mentioned in Eq. (1) we must utilize the difference of $E_T = 21.08 - 10.89 = 10.19$ kcal/mole. By this substitution the calculated value of $T_N = 283.6$ K is in conformity with the experimental value[9].

This example permits to conclude that only that part of the torsion deformation energy, which is stipulated by the rotation of the conformationally 'hard' molecular fragments relative another must be used as E_T in Eq. (1). The part of this torsion deformation energy depending on the deformation energy in such fragments must be eliminated, since it is not connected with the internal rotation arising by the considered phase transition. This condition is necessary, but it is not enough for the prediction of the nematic mesophase realization of the potential nematogenes.

In conclusion we are obliged to note that Eq. (1) allows to obtain the sure T_N values only for the nematogenes which molecules do not form the stable associates in a crystalline phase, for example, connected by H-bonds. This one incidentally occurs extremely seldom.

However the intermolecular association may be taken into account by calculation using Eq. (1). For instance, the calculated E_T value for the compound 26 equals with 19.52 kcal/mole. By Eq. (1) we obtain that the T_N value equals with 375.3 K. However the experimental value equals[6] with 443.2 K. Such difference can be explained by the additional quantity of the heat energy that is needed for the rupture of the intermolecular N-H...N H-bonds. It may be achieved by the essentially more temperature.

It was discovered[10] by IR spectroscopy that the 2-aroyl aminepyridine molecules form dimers in a crystalline phase connected by the N-H...N H-bonds. We can assume that this one is the case for a crystalline phase of the compound 26. If these H-bond are broken by the transition into nematic mesophase with the simultaneous rise of the internal rotation one can write Eq. (1) in form Eq. (3):

$$T_N = 9.829\ (E_T + n\ E_H) + 183.454 \qquad (3)$$

where n and E_H are the number and the energy of H-bonds. If we profit by the N-H...N H-bond energy value equals 3.30 kcal/mole[11] one can calculate by Eq. (3) the T_N value equals 440.2 K. It agrees well with the experimental value.

Thus a consideration of the energetic effects depending on an intermolecular association allows to calculate the T_N values for the organic nematogenes having associated molecules in crystalline phase.

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