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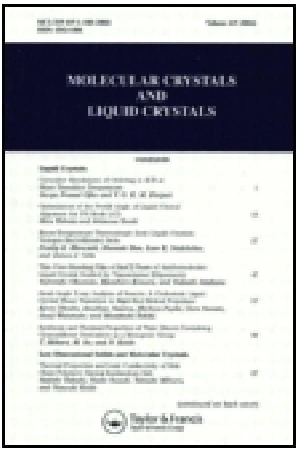

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Dependence of Nematic-Isotropic Phase Transition Temperature Values on Molecular Parameters of Weak-Polar Nematics

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DEPENDENCE OF NEMATIC-ISOTROPIC PHASE TRANSITION TEMPERATURE VALUES ON MOLECULAR PARAMETERS OF WEAK-POLAR NEMATICS

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Abstract Dimensions, shape and polarizability of a weak-polar molecule and a space occupied by it in different molecular coordinate systems have been calculated. For various substances, the dependence of the clearing temperature on a shape of excluded volume is considered. The realistic values of molecular ionization potential are obtained from clearing temperature data according to Maier-Saupe theory.

INTRODUCTION

The progress in Maier-Saupe molecular-statistical theory [1] is known to be the basis of any modern theory of "nematic liquid crystal - isotropic liquid" phase transition (NI). The T_{NI} value can be calculated by the following relationship :

$$A / K_b T_{NI} \quad V^2 = 4.54 \qquad (1)$$

where V is molar volume at transition temperature and the constant A is expressed, according to Ref. [2], as follows :

$$A = (4\pi^2/135)(\alpha_{\parallel} - \alpha_{\perp})^2 I_{ion} \qquad (2)$$

(I_{ion} - molecule excitation energy identified with ionization potential).

In Ref. [2] the right part of Eqn. 1 is reduced by a coefficient B when the contribution of repulsive forces or excluded volume to the interaction of molecules is taken into account . Therefore

$$T_{ni} \square (A/K_b V^2)/(4.54 - B)^{-1} \qquad (3)$$

The excluded volume is determined as a volume of the body which is a locus of centres of the second rod-like molecule moving around the first one and touching it [2]. If molecules are approximated by spherocylinders with length L and diameter D , consideration for the excluded volume made in Ref. 3 leads to the following expression for B :

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$$B = \frac{5\pi}{32} * \frac{2DL^2(1-D/L)^2}{(\pi/4)D^2L(1-D/3L)} = 3.75\frac{(p-1)^2}{(3p-1)} \qquad (4)$$

where $p=L/D$ is a form-factor of a spherocylinder. By differentiating Tni on p one may obtain the following expression :

$$\frac{dT_{NI}}{dp} = \frac{3.75T_{NI}(3p+1)(p-1)}{(3p-1)(-3.75p^2+21.12p-8.29)} \qquad (5)$$

Formulae (3),(4) are considered to be valid only for explanation of a variation in T_{NI} values with a change of the dimensions of the molecular core [4]. The above formulae seem to be not suitable for homologous series if the molecule length is influenced by the dimensions of alkyl substituents but the width not [2,4].

Similar discrepancy was observed when defining the variation of elastic constants ratio K_{33}/K_{11} in homologous series due to van der Meer et al. theory [5]. According to the theory the ratio $K_{33}/K_{11} \sim p^2$, i.e. its value increases as a square of the substituents length. However the experiment shows the decrease of the K_{33}/K_{11} ratio in homologous series.

In Ref. 6 the molecular approach was proposed to avoid the contradictions mentioned. It is based on the calculation of the dimensions of space occupied by a molecule and the suggestion that the form of this space corresponds to the shape of excluded volume. There was also explained a great variety of viscosity and elasticity coefficients, their different ratios in homologous series of tolane derivatives and some other substances.

The purpose of this paper is the further development of a molecular model [6] to calculate both geometric and electronic parameters of a molecule and to applicate it for the description of the T_{NI} change in various bi- and tricyclic nematic mesogens.

CALCULATION OF MOLECULAR DIMENSIONS, FORM AND POLARIZABILITY

The molecular parameters were calculated for some weak-polar substances , mainly for 4-alkyl-4'-alkoxytolanes C_nH_{2n+1}-C_6H_4-C≡C-C_6H_4-OC_mH_{2m+1} which are further designated with the abbreviation nTOm or, in some cases as n-m. As these substances possess low values of dielectric constants ($\varepsilon \simeq n^2 \simeq 3$) [7,8], their polarity is small and the contribution of polar interactions is negligible in many cases.

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Let us introduce two molecular coordinate systems (Fig. 1). The main axis of the first one coincides with the direction of the maximal length of a molecule (x(mol)). The main axis of the second system coincides with the long axis of the molecular core (x). We shall call these coordinate systems as the long system and the core one. θ (mol) is the angle between both systems (Fig. 1). We suppose both benzene rings and their substituents in trans-configuration to be in the same plane. So we can easily obtain the directions of y, y(mol) and z axes.

Referring to Fig. 1 we calculated the coordinates of each atom, dimensions of a molecule L(mol), W(mol) and space occupied by this molecule L, W. Some obvious relationships are fullfilled :

$$\mathrm{tg}\,\theta(\mathrm{mol}) \simeq W/L \qquad (6)$$

$$L(\mathrm{mol}) \simeq (L^2 + W^2)^{1/2} \simeq L/\cos\theta(\mathrm{mol}) \qquad (7)$$

The variation of L(mol) in homologous series proved to be monotonous and the average width of a molecule approximately constant. That can be determined with van der Waals volume

$$V_0 = \pi L(\mathrm{mol})W^2(\mathrm{mol})/4(1-1/12p(\mathrm{mol})) \qquad (8)$$

of spherocylindrical molecules. Therefore, the form-factor in long coordinate system p(mol) = L(mol)/W(mol) varies monotonously and does not correspond the change of physical parameters with increase in length of substituents.

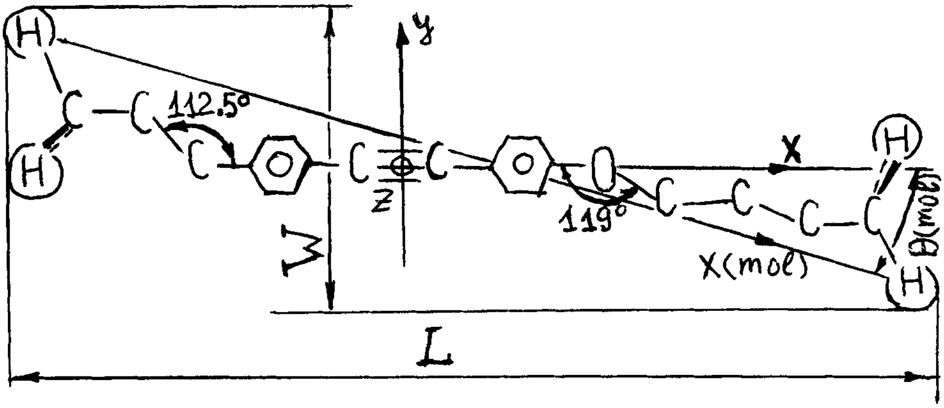

Fig. 1. Definition of molecular coordinate systems for 4-alkyl-4'-alkoxytolanes. x, y, z - rigid core system, x(mol), y(mol) (not shown), z - long coordinate system (see text). L, W - dimensions of a space occupied by a molecule .

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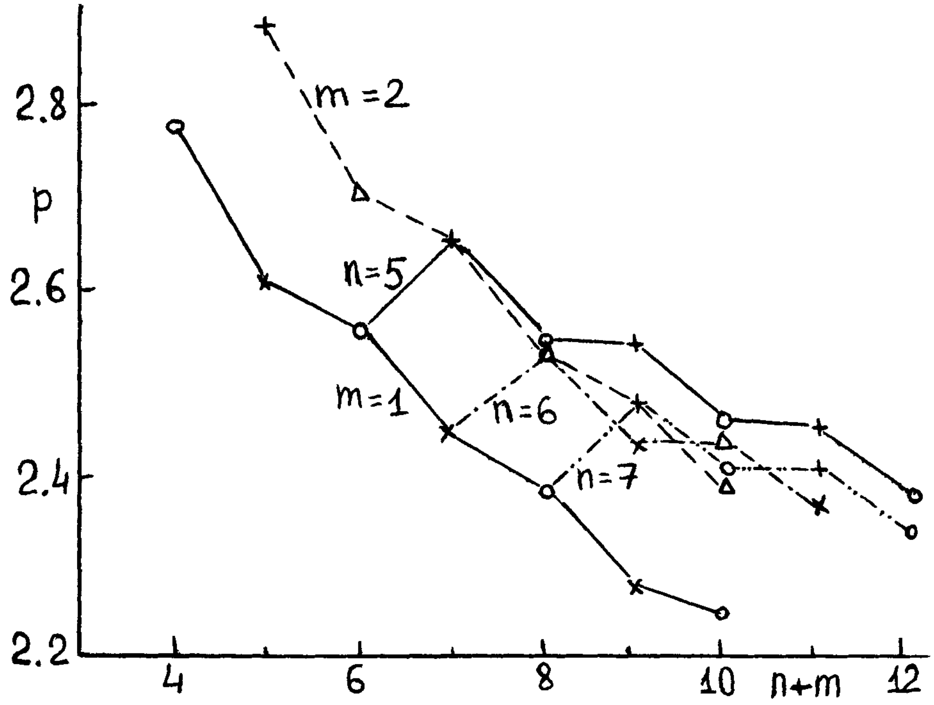

Fig. 2. Dependence of the form-factor p=L/W on the sum (n+m) of carbon atoms in alkyl and alkoxysubstituents.

It is quite different with the form-factor p=L/W defined in the core coordinate system (Fig. 2). The p value is strongly dependent on both the length of a substituent and its configuration. Moreover different nTOm isomers with constant (n+m) sum have different p values. E. g., the p value increases in series of substances (9-1)<(8-2)<(7-3)<(6-4)<(5-5)<(3-7). The isomeric effect is due to the difference of (CCC) and (COC) valent angles (Fig. 1). The alkoxy chain in this coordinate system is closer to the x axis than the alkyl one.

The core coordinate system was also used for calculation of polarizability tensor components and its anisotropy $\Delta\alpha / \bar{\alpha}$ ($\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = \alpha_{xx} - 0.5(\alpha_{yy} + \alpha_{zz})$, $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$) according to Vuks procedure [9]. The results are shown in Fig. 3a, b. Obviously

$$\Delta\alpha\,(\mathrm{mol}) = \Delta\alpha / \cos 2\theta\,(\mathrm{mol}) \qquad (9)$$

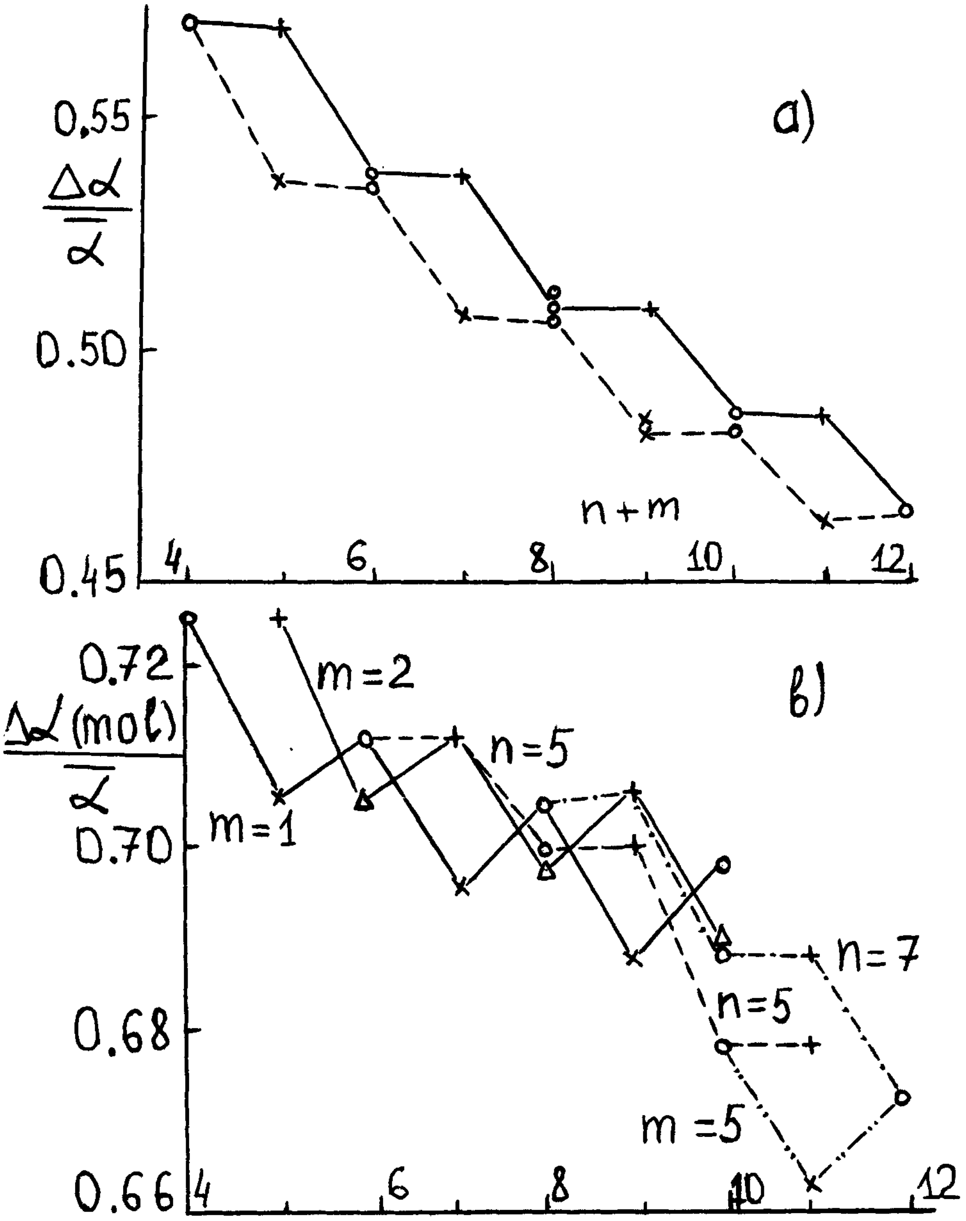

Fig. 3. Dependence of the relative anisotropy of polarizability $\Delta\alpha / \bar{\alpha}$ on the sum (n+m) for nTOm in core (a) and long (b) coordinate systems. In Fig. 3a m is even - continous line , m is odd - dashed line.

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It should be mentioned that values of $\bar{\alpha}$ calculated by us and experimentally determined by the data of refractive indices and density for 5TO1 and 7TO3 [10, 11] coincide.

The isomeric effect in $\Delta\alpha/\bar{\alpha}$ (n+m) variation is absent in the core coordinate system and well pronounced in the long one. The pecularity of $\Delta\alpha/\bar{\alpha}$ change is its quantization. We can see later it may be sequence of variaton of the orientational part of the interaction energy in homologous series [6].

More detailed procedure of calculation of molecular dimension, polarizability and discussion will be published later [12, 13].

Here we applicate these results to explain the T_{NI} dependence in frames of the excluded volume model [2, 3].

DEPENDENCE OF CLEARING TEMPERATURE ON FORM-FACTOR P AND ANISOTROPY OF POLARIZABILITY

Fig. 4 shows nTOm clearing temperatures T_{NI} with a change of n+m from 4 to 12. Temperature values were measured for some substances in the Laboratory of LC of the University of Vilnius (Lithuania) and taken from Refs. 7, 14 for other tolane substances. The even-odd alteration of the T_{NI} value is pronounced when both n and m vary. Let us consider the T_{NI} variation in isomeric substances. For substances with the odd sum of (n+m), a difference of T_{NI} values seems to be a natural consequence of orientation of both end C-C bonds like in PAA (4,4'-dialkoxyazoxybenzene) series. When the sum of (n+m) is even the isomeric effect of another type is observed. So, the T_{NI} values for compounds with m=2 are higher than these for substances with m=1 or m=3. For (n+m)=10 isomers, the following sequence is valid : $T_{NI}(9-1) < T_{NI}(7-3) < T_{NI}(6-4) < T_{NI}(5-5) < T_{NI}(3-7)$, i. e., the sequence of changing of the form-factor p is observed except for substance 8TO2 .

Fig. 5 presents relationships of $T_{NI}(p)$ for various bi- and tricyclic derivatives of tolane, butadiyne, phenylpyrimidine and biphenyl. The cores of molecules of these substances have pronounced long axis . It makes possible to vary the quantity of p in a wide range (from 2 to 3.45). This dependence is disintegrated into several branches with various steepness which is compared with one calculated from formula (5).

First let us consider the results for molecules containing two short substituents (n, m≤3) which are characterized by little emergence of gauche-conformations. The line passing through the points corresponding to T_{NI} 3CT2 and 3CT3 , 3PBD3 , 3TO2 has the incline value close to the theoretical one. When m≥2 all the points fall on a straight line for any nTOm, nPyPOm and nBPn compounds. The magnitude of the derivative dT_{NI}/dp decreases to a half of the magnitude

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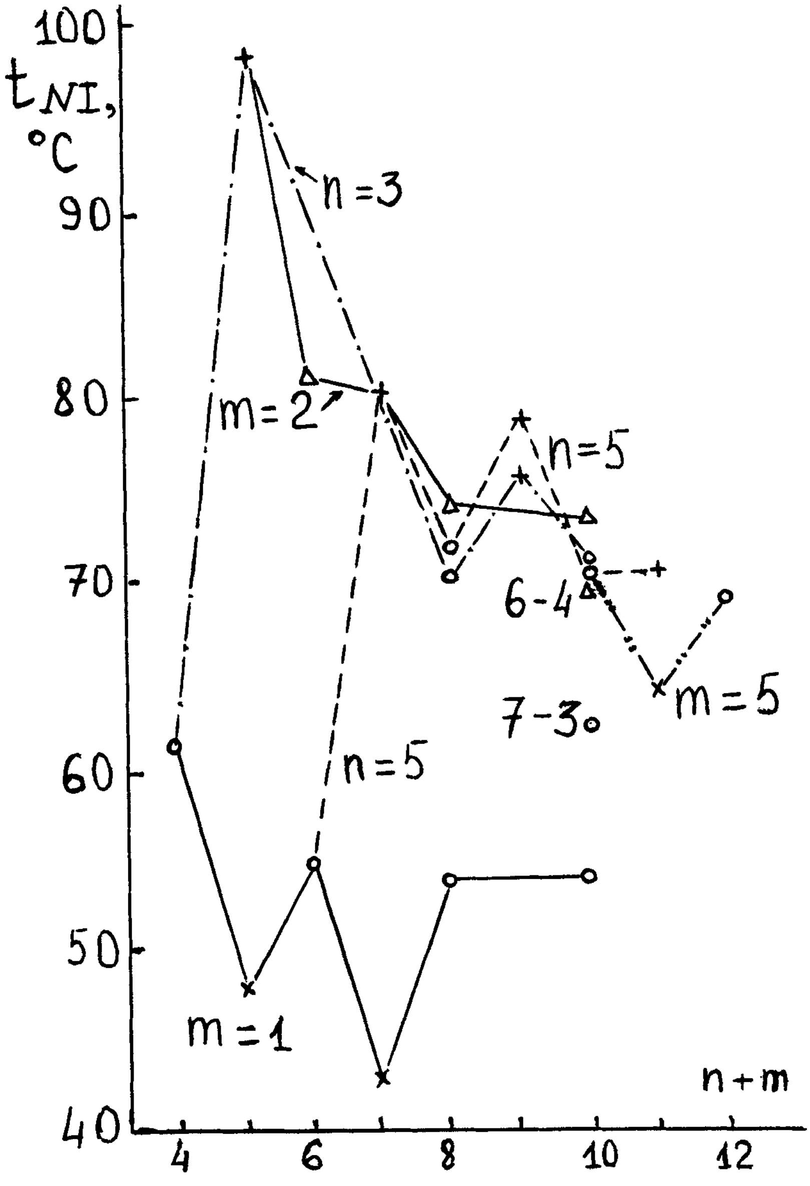

Fig. 4. Clearing temperatures T_{NI} of nTOm. Here and after the orientation of end C-C bonds in substituents is designated as + (--), x (\\), o (_\), (_).

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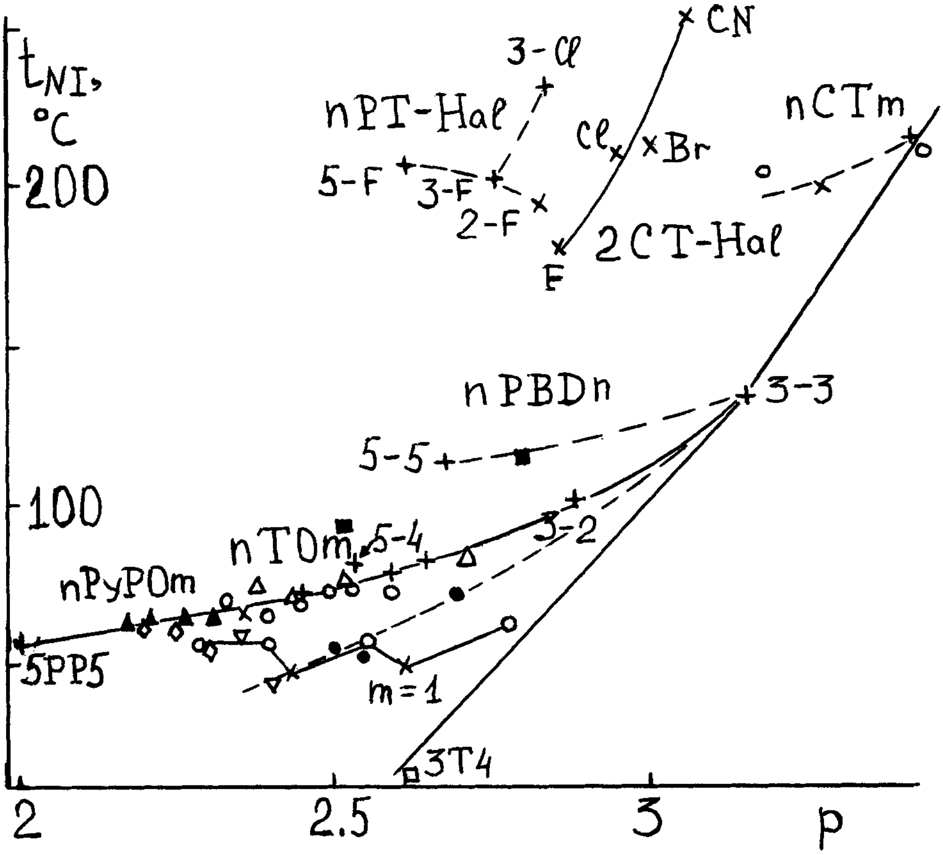

Fig. 5. The dependence of the clearing temperature T on form-factor p for various weak-polar nematic LC consisting of molecules with rigid linear core.
3T4 - $C_3H_7-C_6H_4-C\equiv C-C_6H_4-C_4H_9$ (□);
● - $C_nH_{2n+1}-C_6H_4-C\equiv C-\underset{F}{\text{⌬}}-OC_mH_{2m+1}$;
▽ - $C_nH_{2n+1}-C_6H_4-C\equiv C-\underset{CH_3}{\text{⌬}}-OC_mH_{2m+1}$;
5PP5 - $C_5H_{11}-C_6H_4-C_6H_4-C_5H_{11}$ [15] ;
■ - $CH_2=CH-(CH_2)_{m-2}-C_6H_4-C\equiv C-C_6H_4-CF_3$, m=3 or 6[16];
nPyPOm- $C_nH_{2n+1}-\underset{N}{\overset{N}{\text{⌬}}}-C_6H_4-OC_mH_{2m+1}$[17] (▲ -m odd, ◇ -m even);
nPBDn - $C_nH_{2n+1}-C_6H_4-C\equiv C-C=C-C_6H_4-C_nH_{2n+1}$ [18];
nCTm - $C_nH_{2n+1}-C_6H_{10}-C_6H_4-C\equiv C-C_6H_4-C_mH_{2m+1}$;
2CT-Hal - $C_2H_5-C_6H_{10}-C_6H_4-C\equiv C-C_6H_4$-F, Cl, Br or CN;
nPT-Hal - $C_nH_{2n+1}-C_6H_4-C_6H_4-C\equiv C-C_6H_4$-F or Cl.

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calculated according to (5). A decrease in steepness of the $T_{NI}(p)$ dependence becomes the more pronounced, the shorter alkoxysubstituent (m=2 and m=1). It would be quite natural to explain this phenomenon by the emergence of rotational isomers with a small width W of a space occupied by such molecules. In this case the "y"-coordinates of each atom in a short rigid alkoxysubstituent are less than these ones in aromatic core. The rotation around even C_j-C_{j+1} bonds in a long alkyl chain results in gauche-conformations with smaller width of a molecule too.

A change in T_{NI} with increase of flexible substituents of other classes of substances may also be explained by the changing of the form of rotational isomers. So, for the third and fifth PBD homolougues there is found a decrease in T_{NI} by 20K with a decrease in p by 0.46. This corresponds to a change in T_{NI} by -20K with a decrease in p by 0.34 for substances with nearly equal dimensions of substituents (3TO2 and 5TO4). When comparing the pairs 3TO2 and 4TO2, 3CT3 and 4CT3 one can see that values of $\Delta T_{NI}/\Delta p$ are close to them in terms of the order of magnitude (-17.5/0.17 = -103 K and -11/0.23 = -55 K respectively).

Let us consider a rigid substituent of a substance (m=1) or a molecule containing the lateral moiety which distance to the long (x) axis, i.e. the "y"-coordinate, exceeds the corresponding distance of any atom in alkoxy chain. If m=1 even-odd change in $T_{NI}(n+m)$ takes place. For odd n, the T_{NI} value appears to be constant. It may be also explained by the emergence of rotational isomers that stabilize the molecule's orientation in long homolougues. If a molecule contains o-F or o-CH lateral substituent, the tilt of $T_{NI}(p)$ dependence is close to that calculated by (5) when this dependence is extrapolated from the section of 3PBD3-3TO2 of the main line (Fig. 5).

For bicyclic substances, the right branch of $T_{NI}(p)$ dependence is a line running in the vicinity of 3PBD3, 3TO2, 3TO1, 3T4 points with the incline dT_{NI}/dp = 193 K. Taking into account the weak polarity of tolane derivatives one may assume that the extreme line along the whole Fig. 5 (plane "clearing temperature-molecule's form-factor") separates the zones where "nematic-isotropic liquid" phase transition is possible . We may call this line as the geometrical border of nematic mesophase.

Above the extreme line the transition temperature rises due to the influence of rotational isomers or higher polarizability of the molecular core or its terminal substituents, e.g., halogens, CN-group etc. In this case a change in T_{NI} may be result of increasing the molecular length or anisotropy of polarizability. So, for nCT-Hal the observed increase in T_{NI} with a rise in p (dT_{NI}/dp=227K) corresponds to the calculated one (200-220K). For 2CTCN and 3PTHal,

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the value of T_{NI} is also affected by anisotropy of polarizability, apart from the size.

From Eq. 5 it follows the thermostability of mesophase with any values of $p > 5.21$. For thermotropic LC, significant variation of the form-factor seems to be slightly variable. Lyotropic LC have much wider range of the form-factor variation whose micelles form may be controlled by the change of concentration of one of the components [19]. Many phase diagrams in lyosystems have a sharp change in the transition temperature under a slight change in the mesophase composition. We think it may explained to a great extent by the variation of the geometric shape of a miscelle [20].

Let us consider the suitability of the calculated values of anisotropy to estimate the ionization potential Iion of a particular molecule from (1), (2) equations from which it follows :

$$I_{ion} = \frac{135}{4\pi} k_b T_{NI} \left(\frac{V}{N_a \Delta\alpha} \right)^2 \qquad (10)$$

where N_a is Avogadro's number. The molar volume in the nematic phase V was determined for nTOm from the average refractive index <n> when comparing refractions of 5TO1, 7TO3 and other substances [8, 10, 11]. To make calculations it was assumed that anisotropy of polarizability is equal to $\Delta\alpha$(mol).

From the data presented in Fig. 6 it follows that addition of a methylene group to any alkyl or alkoxysubstituent results in increasing the I_{ion} value by $1.2-1.4*10^{-18}$ J = 7.5-8.3 eV per one molecule.

The C-C bond ionization energy is equal to E(C-C) = 343 KJ/mole [18] and for C-H bond it is equal to E(C-H) = 395 KJ/mole [19]. For CH_2 group the ionization energy seems to be equal to E(CH)=E(C-C)+2E(C-H)=1133 KJ/mole=12 eV, which exceeds slightly the values obtained from T_{NI}.

The ionization potential I_{ion} amounts to 130-180 eV, which is 16-22 times more than the estimations obtained in Ref.1, 23. It is worth emphasizing for the truth that in [2] the I_{ion} value is presented only for certain molecules which are cores of ordinary mesogen molecules.

Thus, geometric and electronic parameters of weak-polar molecules with two flexible substituents may be conveniently described in the coordinate system related to a rigid core of a particular molecule. This enables to explain the influence of substituents configuration and molecular polarizability on the values of NLC clearing temperature and other physico-chemical parameters.

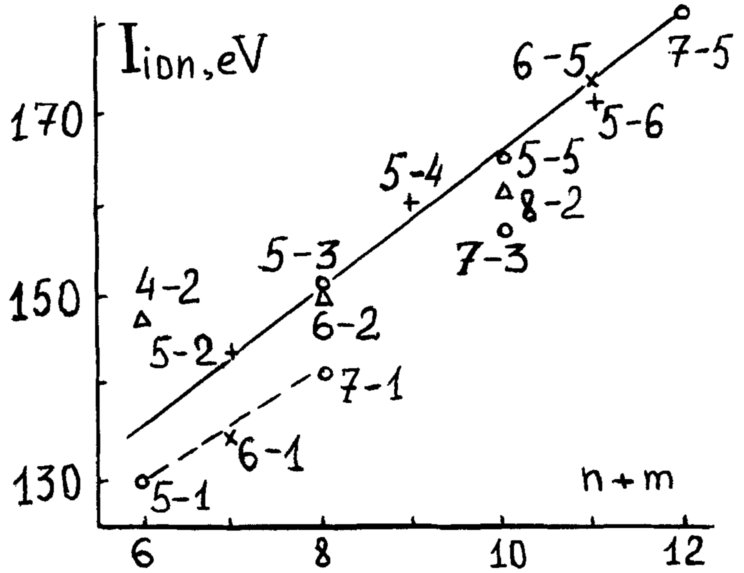

Fig. 6. Dependence of ionization potential I_{ion} of nTOm molecules calculated according to (10) on the sum (n+m).

REFERENCES

1. W. Maier, A. Saupe, Z. Naturforsch., 14a, 882 (1959); 15a, 287 (1960).
2. W.H. de Jeu, J. van der Veen, Mol. Cryst. and Liquid Cryst., 40, 1 (1977).
3. H. Kimura, J. Phys. Soc. Japan., 36, 1280 (1974).
4. E.M. Averyanov "Steric effects of substituents in mesogens and molecular aspects of thermotropic mesomorphysm. Parts 1-3" : Preprints of Institute of Physics of Syberian Department of Academy of Sciences of USSR 493F-495F. Krasnoyarsk. 1988.
5. B.W. van der Meer, F. Postma, A.J. Dekker, W.H. de Jeu, Mol. Phys., 45, 1227 (1982).
6. V.V. Belyaev, S.A. Ivanov, Sov. Phys. Crystallography, 37, 123 (1992).
7. DIC Recent Liquid Crystal Materials, Dai Nippon (Japan) 1988.
8. V.V. Belyaev, A.B. Kuznetsov, Sov. J. Opt. Technology, 60, 25 (1993).
9. M.F. Vuks "Electrical and optical properties of molecules and condensed matter". Leningrad University Edition. 1984 (in Russian).

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10. G. Labrunie, M. Bresse, C. R. Acad. Sci. Paris Ser. B, 276, 647 (1973).
11. M. Brunet, C. Cabos, J. Sicart, C. R. Acad. Sci. Paris Ser. B, 281, 109 (1976).
12. V. V. Belyaev, Izvestiya RAN (1995), be published.
13. V. V. Belyaev, Rus. J. Phys. Chem. (1995), be published.
14. "Sources of thermodynamic data of mesogens", Mol. Cryst. and Liquid Cryst., 115, 1 (1984).
15. K. Czuprynski, J. Przedomski, J. W. Baran, 15th Int. LC Conf., Budapest, 1994. Abstracts, B-P8, V. 1, P. 138.
16. C.-J. Hsieh, G.-H. Hsiue, Liq. Cryst., 16, 469 (1994).
17. A. Hauser, Ch. Selbmann, R. Rettig, D. Demus, Cryst. Res. Technol., 21, 685 (1986).
18. S.-T. Wu, U. Finkenzeller, V. Reifenrath, J. Appl. Phys., 65, 4372 (1989).
19. A. V. Kaznacheev, Izvestiya RAN (1995), be published.
20. N. V. Usol'tseva, Izvestiya RAN (1995), be published.
21. A. F. Skryshevskii "Structural analysis of liquids and amorphous matter". Moscow, Ed. "Vysshaya Shkola". 1980 (in Russian).
22. A. A. Askadskii, Yu. A. Matveev "Chemical structure and physical properties of polymers". Moscow, Ed. "Khimiya". 1983 (in Russian).
23. T. Kobayashi, K. Yokota, S. Nagakura, J. El. Spectr. Rel. Phen., 6, 167 (1975).

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