ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2362–2368. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © T.R. Prosochkina, R.G. Shestakova, E.A. Kantor, K.G. Kichatov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 11, pp. 1910–1916.

Computational Simulation of the Molecular Ordering of 3,6-Bis(4-butylphenyl)[1,2,4,5]tetrazine at the Phase Transition Temperatures

T. R. Prosochkina, R. G. Shestakova, E. A. Kantor, and K. G. Kichatov

Ufa State Petroleum Technical University, ul. Kosmonavtov 1, Ufa, 450062 Russia
e-mail: agidel@ufanet.ru

Received October 11, 2010

Abstract—Computational simulation of 3,6-bis(4-butylphenyl)[1,2,4,5]tetrazine was carried out. Based on the energy of intermolecular interactions of dimers was determined the probability of each configuration (stacking, in-plane and terminal). It was revealed that in the 3,6-bis(4-butylphenyl)[1,2,4,5]tetrazine dimers the sliding of the molecules relative to each other is energetically allowed in the narrow range of distances that provides retaining orientation of the molecules in the mesophase. The relationship between the translational rigidity of the molecules in the dimer and nematic properties was revealed.

DOI: 10.1134/S1070363211110247

In recent decades, the liquid crystal materials characterized by their unique properties were widely used in various fields of science and technology: molecular biology, medicine, cybernetics, microelectronics, optics, etc. [1]. This leads to intense investigation of the structure and physico-chemical behavior of compounds exhibiting mesomorphic properties.

Introduction of a heterocyclic fragment to the molecular structure extends possibility of synthesis of new liquid crystal material and improving their properties [2]. The presence of heteroatoms in the liquid crystal (LC) leads to a change in the steric and electronic structure of the molecule that causes changes in the complex of its properties: polarity, polarizability, fluidity, dielectric anisotropy, and thus affects the type of mesophase and the phase transition temperature [3, 4] . The most of known heterocyclic LC is constructed similarly to the benzene derivatives (e.g., 1,4-terphenyl), but one of the benzene rings is replaced by the pyridine, pyrimidine, pyrazine, pyridazine or 1,2,4,5-tetrazine ring [4, 5].

It is important to reveal the *structure–property* relationship for the LC with the nitrogen-containing heterocyclic compounds, the study of the molecular nature of mesomorphism and the effects of self-organization of molecules in the liquid crystals combining different types of molecular order: the conformational, orientational, and positional, at different levels of structural organization of the LC (from molecular to macroscopic). The approaches associated with the computational simulation of LC includes the methods of molecular mechanics and dynamics [6], Monte Carlo [7], atom–atom potentials [8], quantum-chemical semiempirical and nonempirical [9], perturbation theory [10, 11], and permit predicting the mesomorphic properties in the pre-experimental stage and then directing the synthesis of mesomorphic materials with desired properties [12, 13]. For this purpose is calculated interaction energy of two mesogenic molecules, the dimers of various configurations: the lateral (stacking, St), planar (Pl) and terminal (T), and determined the probability of each configuration [10, 11, 14–16]. One of the issues of computational simulation of LC is the study of their molecular ordering, which affects the type of the mesophase. The mesophase type is determined by the presence of translational freedom along the long axis of the LC molecule, as its quantitative measure can serve the translational rigidity coefficient [11].

We apply this approach to the study of molecular ordering in 3,6-bis(4-butylphenyl)[1,2,4,5]tetrazine (**I**) [17]. We compare the calculated value of the translational rigidity with the type of mesophase.

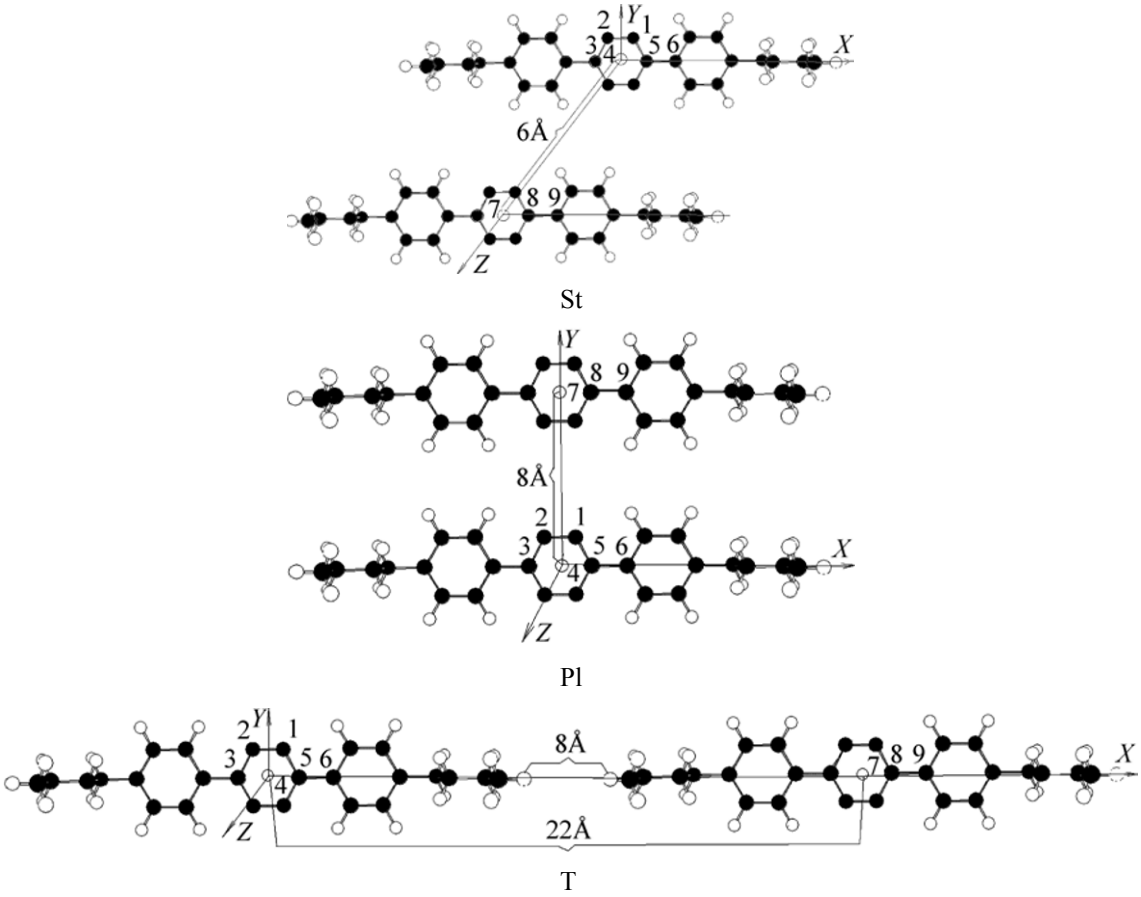

Fig. 1. Geometric configuration of stacking (St), planar (Pl), and teminal (T) conformations of dimer molecule **I** for the calculation.

Computational procedure. The quantum-chemical calculation method adequately describing the structural parameters of the nitrogen-containing heterocyclic compounds is chosen by comparing the overall relative error and using statistical verification of the adequacy of the calculation results with the experimental data, based on regression analysis [18]. For the geometry optimization of the isolated molecule **I** are implemented the methods RHF/STO-3G, RHF/6-31G(d,p), V3LYP/6-31G(d,p), and MP2/6-31G(d,p) within the software PC GAMESS v. 7.1.F [19]. Identification of the stationary points is carried out by solving the vibrational problem (in the Hessian diagonal matrix all the force constants have positive eigenvalues only).

The conformational analysis is performed by RHF/STO-3G method. To establish a preferred orientation of butyl substituents to the benzene rings in the molecule **I** is performed scanning the potential energy surface (PES) varying the torsion angles corresponding to the rotation angles of alkyl chain around the C_{Ar}–C_{Alk} bonds with the 10º increment in the range from –180º to 180º. The values of torsion angles corresponding to stationary points are refined with the 1º increment. The values of total energy at stationary points are refined by RHF/6-31G(d,p), V3LYP/6-31G(d,p) and MP2/6-31G(d,p) methods with full optimization of geometric structure. A similar scan of the PES is conducted over two torsion angles corresponding to the rotation angles of the benzene rings relative to the heterocyclic fragment. The barrier of internal rotation is refined by means of thermochemical calculations.

Intermolecular interaction energy (IIM) is calculated for the equilibrium geometric configurations of dimers of the molecules in different layers of the LC (St) and in one LC layer (Pl and T) (Fig. 1) [11].

The orthogonal coordinate system *XYZ* origin is placed to the center of mass of the first molecule, the *X* axis is directed along its long axis, the *XY* plane coincides with the plane of the molecule. In the stacking configuration the initial distance between the

centers of mass of isolated molecules is 6 Å along the *Z* axis, in a planar configuration 8 Å along the *Y* axis, in the terminal configuration 22 Å along the *X* axis [11].

While calculating the changes in the relative probability of the dimer configurations associated with the displacement of a molecule along its long axis (*X* axis), one molecule of the dimer in the calculated equilibrium configuration is fixed, and another molecule is shifted relative to the fixed along this axis with 0.5 Å steps.

In the calculation by the RHF/6-31G(d,p) method, all contributions to the IIM energy, $E_{\text{interaction}} = E_{\text{dimer}} - 2E_{\text{monomer}}$, except for the dispersion energy, is already accounted for. Accounting for the dispersion component can be carried out in various ways: either by refining the interaction energy by the MP2/6-31G(d,p) method [19], or using modified Kitaigorodskii formula [11]:

$$E_{\text{disp}} = \frac{1}{2}\sum_{k=2}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n}(-A_{ij}/R_{ij}^{6}),$$

where *k* is the number of a neighboring molecule *N* is the number of molecules in the immediate environment (in our case *N* = 2); *n* is the number of atoms in the molecule; *i* is number of an atom in the first molecule; *j* the same in the *k*th molecule; A_{ij} is the parameter of the atom-atom potentials; R_{ij} is the distance between *i*th and *j*th atoms. The relevant parameters of atom-atom potentials are given in [20]. The obtained values of IIM energy are used as inputs for calculating the relative probability of each configuration with the Maxwell–Boltzmann formula:

$$P = \frac{\exp(-\beta\varepsilon_i)}{\Sigma_i \exp(-\beta\varepsilon_i)},$$

where *P* is the probability of a given configuration, $\beta = 1/kT$, *k* is Boltzmann constant, *T* is absolute temperature, ε_i is the energy of *i*th configuration relative to the energy minimum obtained for a series of configurations for which the probability distribution is calculated.

To estimate the translational freedom along the long axis of the molecule in the dimer, that is, the possibility of free displacement of molecules in the dimer relative to each other, we propose the following approach. The most probable (equilibrium) configuration (expectation) is calculated as the first initial statistical moment [21]:

$$M_1 = \frac{\int_{X_0}^{X_k}(X)Pd(X)}{\int_{X_0}^{X_k}Pd(X)},$$

where M_1 is the first initial statistical moment; *X* is displacement of molecules in the dimer relative to each other along the long axis of the molecule; *P* is probability of a given configuration of the dimer.

The resistance to the movement of molecules relative to each other (dispersion) is calculated as the second central statistical moment:

$$\mu_2 = \frac{\int_{X_0}^{X_k}(X - M_1)^2 Pd(X)}{\int_{X_0}^{X_k}Pd(X)}.$$

The reciprocal of μ_2 characterizes the translational rigidity of the system.

At the computational simulation is important to choose a calculation method that adequately describes the condensed state of matter (crystalline, liquid crystal, liquid). This problem can be solved by comparing the results of quantum-chemical calculations with the experimental data, such as XRD, reflecting the conformational features of the molecules (bond lengths and torsion angles) due to the presence of intermolecular interactions.

In order to select the calculation method describing adequately the molecular structure of heterocyclic liquid crystals with the central nitrogen-containing fragment we carried out full optimization of geometry and determined the structural parameters using the following methods: MM+, CNDO/2, MNDO/d, AM1, PM3, RHF/STO-3G, RHF/3-21G, RHF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) [19]. Were calculated the molecules of 3,6-biphenyl-1,2,4,5-tetrazine (**II**), 2,5-bifenilpyrazine (**III**) and 2-(4-*p*-butoxyphenyl)-5-phenylpirimidine (**IV**), -pyridazine (**V**), 1,3-diazine (**VI**), pyrazine (**VII**), 1,3,5-triazine (**VIII**), pyridine (**IX**), as well as benzene (**X**) and biphenyl (**XI**). The calculation results are compared with XRD data [22–26]. The choice of molecules is defined by the fact that they are structural fragments of liquid-crystalline nitrogen-containing compounds, and for them there are experimental data. We conducted a

Table 1. Total relative error *a*, %, and relative integral errors *b* of the quantum-chemical methods at the calculation of the structural parameters of molecules **II–XI**

Method	For interatomic distances	For bond angles	For torsion angles	Over all structural parameters
MM+	6.62 (*a*)	1.11	6.30	4.68
	0.25 (*b*)	0.04	–	–
CNDO/2	5.02 (*a*)	0.83	17.20	7.68
	0.13 (*b*)	0.10	–	–
MNDO/d	6.17 (*a*)	0.71	15.34	7.41
	0.13 (*b*)	0.07	–	–
AM1	1.48 (*a*)	0.67	7.95	3.37
	0.11 (*b*)	0.04	0.18	0.11
PM3	1.17 (*a*)	1.06	5.73	2.65
	0.03 (*b*)	0.12	0.92	0.36
RHF/STO-3G	0.94 (*a*)	0.63	0.16	0.58
	0.03 (*b*)	0.06	0.01	0.03
RHF/3-21G	0.87 (*a*)	0.79	0.20	0.62
	0.03 (*b*)	0.06	0.11	0.07
RHF/6-31G(d,p)	1.04 (*a*)	0.59	0.19	0.61
	0.09 (*b*)	0.01	0.12	0.07
B3LYP/6-31G(d,p)	0.75 (*a*)	0.40	0.15	0.43
	0.02 (*b*)	0.01	0.02	0.02
MP2/6-31G(d,p)	0.86 (*a*)	0.60	0.19	0.55
	0.04 (*b*)	0.03	0.12	0.06

quantitative estimation of the differences between the calculated and experimental data using a comparison of the overall relative error and statistical verification of the adequacy of the calculation results with the experimental data based on regression analysis.

The calculated values of relative integral errors indicate that for the nitrogen-containing heterocyclic compounds the least error between the calculated data and the data of XRD shows the B3LYP/6-31G(d,p) method, the largest PM3, to use the methods MM+, CNDO/2, and MNDO/d is impractical because the analysis of results of calculations of the Fisher *F*-criterion by these methods showed that the regression equation for the torsion angles is statistically insignificant (Table 1) [18].

In general, quantitative estimation of discrepancy between the calculated and experimental data shows that the methods RHF/STO-3G, RHF/3-21G, RHF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) describe the experimental data adequately (Table 1), while semiempirical methods and the method of molecular mechanics are inappropriate.

Comparison of the of the structural parameters of molecules **I** and **II** calculated by nonempirical methods shows that terminal substituent does not introduce significant changes in the bond lengths and angles in the heterocyclic fragment, the bond lengths changes in benzene rings do not exceed 0.01 Å, and angles 1.5º. while simulating the molecule **I** should be taken into account that to a certain limit the alkyl substituents of the mesogenic molecules in the crystalline state is preferably in a zig-zag fully transoid conformation with the location of a regular chain in a plane, while in the nematic phase the value of torsion angle between the benzene ring plane and the plane of the terminal substituent is 90° [27]. Thus, the [B3LYP/6-31G(d)] quantum-chemical analysis of conformations of the 4-*n*-pentyl-4'-cyanobiphenyl (5CB) shows that the preferred conformation of the molecule corresponds to the torsion angle between benzene ring and the plane

Table 2. The rotation barriers of molecules **I** and **II** with the torsion angles τ_1 and τ_2, kJ mol^{-1}

Method	ΔE_0	ΔH_{298}	ΔG_{298}
RHF/STO-3G	25.1	23.0	25.6
RHF/6-31G(d,p)	27.7	24.3	25.1
B3LYP/6-31G(d,p)	32.3	25.1	33.1
MP2/6-31G(d,p)	31.4	28.5	32.3

of the alkyl fragment 90° [28], which is fully consistent with XRD data. The maximum energy barrier at the rotation around the bond connecting benzene ring and alkyl substituents, is 09.05 kJ mol^{-1}.

In order to study the steric structure of the molecule **I** we performed its conformational analysis. The calculation results confirm the greater stability of the conformer with the torsion angle between the plane of the ring and the plane of the alkyl chain carbon skeleton is 90°, therewith the location of substituents at the same or at the different sides of the benzene ring planes is equally probable. A similar scan of the PES was carried out over the torsion angles τ_1 and τ_2 that correspond to rotation angles of the benzene rings relative to the heterocyclic fragment (Fig. 2).

On the PES of **I** and **II** there is a global minimum corresponding to the location of the benzene rings nearly coplanar with the heterocyclic fragment. The barrier of internal rotation was refined by the thermochemical calculations (Table 2). We revealed

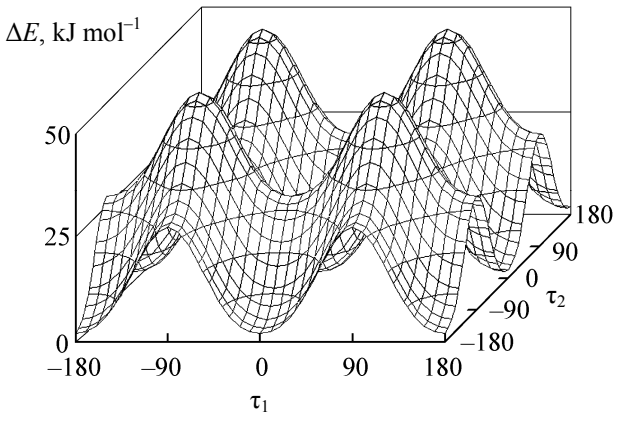

Fig. 2. Potential energy surface (PES) at the internal rotation of molecule **I** in the range of torsion angles τ_1 and τ_2 from –180º to 180º (RHF/STO-3G).

that the molecules **I** and **II** are characterized by adequate conformational rigidity of the central three-ring aromatic fragment. These calculations show that this molecular fragment in the temperature range 0 to 500 K remains almost unchanged. The results can be applied in the analysis of the properties of the studied LC at the temperatures of the phase transition (melting point with transition to the nematic phase T_N = 443 K, the temperature of transition in the isotropic liquid T_I = 445 K [17]).

To understand the mezomorphic behavior of the system is necessary to investigate the effect of displacements of molecules in the dimer on the configurational probability, since the nature of the nematic LC often is determined by the presence of the possibility of translational movement along the long axes of the molecules. A number of papers have reported on the calculations of the IIM energy in the LC dimers of various configurations of lateral (stacking St), planar (Pl), and terminal (T) performed using the Rayleigh–Schrödinger perturbation theory [10, 11, 14–16]. To calculate the electrostatic contribution to the total energy of pairing interaction of molecules by the semiempirical CNDO/2 method were calculated atomic charges and dipole moments at each atomic center of the molecule. The contributions to the IIM energy corresponding dispersion interactions and repulsive forces are defined with the Kitaigorodskii empirical formula, which is a modified Buckingham "6-exp" potential for hydrocarbon molecules. Further, the values of the IIM energy were used to calculate the probability of each configuration at various temperatures and the coefficient of translational rigidity.

Since we established the unreasonableness of semiempirical calculations for the molecules of nitrogen-containing heterocyclic compounds, in order to calculate the probability of each configuration (St, Pl, and T) of the molecule **I** dimer at different temperatures we applied the nonempirical RHF/6-31G(d,p) method.

We revealed that at any temperature is observed a distinct advantage of a specific configuration corresponding to the energy minimum (Fig. 3). In order to estimate the translational freedom along the long axis of the molecule in the dimer, that is, the possibility of free displacement of molecules in the dimer relative to each other, we determined the equilibrium configuration of molecules in the dimers and their rigidity using the methods of mathematical statistics.

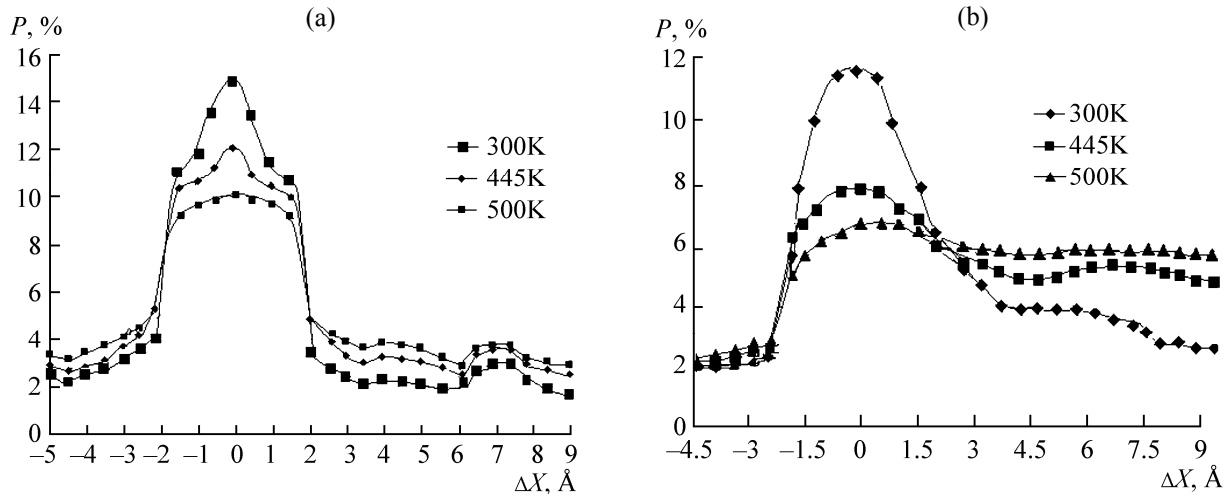

Fig. 3. Changing the probability P (%), associated with movement along the X axis (ΔX, Å) for (a) St- and (b) Pl-interactions in the dimers formed by molecules **I** (T = 300, 445, and 500 K).

The equilibrium configuration falls to the range of shifts 1.3 to 2.4 Å. This indicates that the sliding of one molecule relative another is allowed energetically in the narrow range of distances to retain the orientation of the molecules in the mesophase.

Since Pl interaction is somewhat weaker than St interaction, one should expect greater freedom for the displacements of the molecules at the Pl interaction (lower rigidity), which is actually observed at the T_N = 443 K [$1/\mu_2$ (Pl) = 0.08 Å^{-2}, $1/\mu_2$ (St) = 0.11 Å^{-2}) (Table 3). With increasing temperature, the molecules acquire sufficient freedom to slide relative to the long axis, which is slightly more pronounced in the case of Pl interactions. Since the values of the rigidity of the molecules in the St and Pl configurations of the dimer are comparable in value at the same temperature, for **I** one can expect appearing the properties of nematic liquid crystals, and this is confirmed by experimental data [17].

Thus, it is shown that at the computational simulation of nitrogen-containing heterocyclic compounds, including 3,6-bis(4-butylphenyl)[1,2,4,5]tetrazine, can be used the methods RHF/STO-3G, RHF/3-21G, RHF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p), which adequately describe the experimental data, while the semiempirical methods and the method of molecular mechanics are inappropriate. We revealed that in the temperature range 0 to 500 K the studied molecule is characterized by the conformational rigidity of the central three-ring aromatic fragment. In the 3,6-bis(4-butylphenyl)[1,2,4,5]tetrazine dimers, sliding of one molecule relative to another energetically allowed in the narrow range of distances that provides retaining the orientation of the molecules in the mesophase. The relationship between the translational rigidity of the molecules in St (stacking) and Pl (planar) configurations of the dimer and nematic properties is revealed.

Table 3. Calculated positions of equilibrium and rigidities of the dimers of molecule **I**

Temperature, K	St-interaction		Pl-interaction	
	equilibrium configuration, M_1, Å	rigidity, $1/\mu_2$, Å^{-2}	equilibrium configuration, M_1, Å	rigidity, $1/\mu_2$, Å^{-2}
300	1.3	0.15	1.4	0.09
445	2.0	0.11	1.8	0.08
500	2.4	0.09	2.0	0.07

REFERENCES

1. Amerik, Yu.B. and Krentsel', B.A., *Khimiya zhidkikh kristallov i mezomorfnykh polimernykh sistem* (Chemistry of Liquid Crystals and Mesomorphic Polymeric Systems), Moscow: Nauka, 1981, p. 288.
2. Gilcrist, T.L., *Heterocyclic Chemistry*, Moscow: Mir, 1996, p. 464.
3. Aver'yanov, E.M., *Stericheskie effekty zamestitelei i mezomorfizm* (Steric Effects of Substituents and Mesomorphism), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2004, p. 469.
4. Titov, V.V., Kovshev, E.I., and Karamysheva, L.A., *Khim. Geterotsikl. Soedinin*., 1975, vol. 10, p. 1364.
5. Schubert, H. and Wiss., *Z. Univ. Halle*, 1970, vol. 19, p. 1.
6. Wilson, M.R. and Allen, M.P., *Mol. Cryst. Liq. Cryst*., 1992, vol. 12, no. 1, p. 157.
7. Yailoyan, S.M. and Bezhanova, L.S., Abramyan, E.B., *Zh. Strukt. Khim*., 2001, vol. 42, no. 2, p. 222.
8. Sarkar, P., Paul, S., and Mandal, P., *Mol. Cryst. Liq. Cryst*., 2001, vol. 365, p. 535.
9. Sizova, O.V., Sokolova, E.P., Baranovskii, V.I., Rozmanov, D.A., and Tomashenko, O.A., *Zh. Strukt. Khim*., 2004, vol. 45, no. 5, p. 807.
10. Ajeetha, N., Ojha, D.P., and Pisipati, V.G.K.M., *J. Mol. Model*., 2006, vol. 12, p. 152.
11. Ojha, D.P., *Z. Naturforsch., A*, 2002, vol. 57, p. 194.
12. Zorkii, P.M., Timofeeva, T.V., and Polishchuk, A.P., *Usp. Khim*., 1989, vol. 58, no. 12, p. 1971.
13. Kuleshova, L.N. and Antipin, M.Yu., *Usp. Khim*., 1999, vol. 68, no. 1, p. 3.
14. Ojha, D.P. and Pisipati, V.G.K.M., *Z. Naturforsch., A*, 2002, vol. 57, p. 977.
15. Ojha, D.P and Pisipati, V.G.K.M., *Zh. Fiz. Khim*., 2005, vol. 79, no. 4, p. 600.
16. Ojha, D.P., *J. Struct. Chem*., 2006, vol. 47, no. 3, p. 443.
17. Demus, D., Demus, H., and Zaschke, H., *Flüssige Kristalle in Tabellen*, Leipzig, VEB Deutscher Verlad Grundstoffindustrie, 1976, p. 360.
18. Kichatov, K.G., Shestakova, R.G., Prosochkina, T.R., Kantor, E.A., and Kantor, O.G., *Bash. Khim. Zh.*, 2010, vol. 17, no. 1, p. 23.
19. Granovsky, A.A., *PC GAMESS, Firefly version 7.1.F., http://classic.chem.msu.su/gran/gamess/index.html.*
20. Timofeeva, T.V., Chernikova, N.Yu., and Zorkii, P.M., *Usp. Khim*., 1980, vol. 49, no. 6, p. 966.
21. Gmurman, V.E., *Rukovodstvo k resheniyu zadach po teorii veroyatnostei i matematicheskoi statistike: Ucheb. posobie* (Manual for Solving Tasks on the Probability Theory and Mathematic Statistics: Tutorial), Moscow: Vysshee Obrazovanie, 2006, 11 ed., p. 394.
22. Ahmed, N.A. and Kitaigorodsky, A.I., *Acta Cryst., B*, 1972, vol. 28, p. 739.
23. Laing, M. and Sommerville, P., *Acta Cryst., B*, 1976, vol. 32, p. 2764.
24. Winter, G., Hartung, H., and Brandt, W., *Mol. Cryct. Liq. Cryct., B*, 1987, vol. 150, p. 289.
25. Winter, G. and Hartung, H., *Mol. Cryst. Liq. Cryst*., 1987, vol. 149, p. 17.
26. *Computational Chemistry Comparison and Benchmark Database, http://cccbdb.nist.gov.*
27. Walz, L., Nepveu, F., and Haase, W., *Mol. Cryst. Liq. Cryst.,* 1987, vol. 148, p. 111.
28. Clark, C.J., Adam, C.J., Cleaver, C.J., and Crain, J., *Liq. Cryst*., 1997, vol. 22, p. 477.