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Conformational Analysis of the Structure of *p*-Butoxybenzylidene-*p*'-propionyloxyaniline at Temperatures of Crystal → Nematic and Nematic → Isotropic Liquid Phase Transitions

T. G. Volkova, E. G. Nebukina, N. N. Usanova, and M. V. Klyuev

Ivanovo State University,
ul. Ermaka 39, Ivanovo, 153025 Russia
e-mail: Duraushe@yandex.ru

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Abstract—The molecular structure and conformational properties of the *p*-butoxybenzylidene-*p*'-propionyloxyphenylaniline molecule in the crystalline state and at temperatures of the crystal → nematic and nematic → isotropic liquid phase transitions were examined by AM1 calculations. It was found that the nematic → isotropic liquid phase transition is accompanied by a change in the molecular conformation.

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Quantum-chemical methods acquire growing importance in studies of molecular structure of organic substances, as revealing specific features of geometric and electronic structure that cannot be revealed by experimental methods, or whose experimental determination is extremely difficult or too expensive. One of problems of the physical chemistry of liquid crystals is elucidation of regular trends in the influence of the molecular structure of mesogens on mesomorphic and physical properties of mesophases [1], e.g., on the phase transition temperature, dipole moment, and position of bands in the photoelectron spectra [2]. One of the main structural characteristics is the conformational state of mesogenic molecules [3, 4]. It is noted that "rigid" cores of the majority of mesogens are acoplanar (Fig. 1), with the extent of acoplanarity, described by dihedral angles, strongly depending in many cases on the electronic properties and volume of substituents. Klopov [5] believes that the conformation of molecules affects the mechanism of the nematic–isotropic transition. According to the suggested hypothesis, molecules of liquid crystals in different aggregation states exist as different conformers.

Our goal was conformational analysis of the molecular structure of a nematic liquid crystal, *p*-butoxybenzylidene-*p*'-propionyloxyaniline (Fig. 2), at temperatures of phase transitions crystal → nematic (*C* → *N*) and nematic → isotropic liquid (*N* → *I*).

Calculations were performed using the HyperChem software (version 7.5). The geometry was optimized by the AM1 semiempirical method [6, 7] in the approximation of an isolated molecule. The gradient norm did not exceed 0.001 kcal mol^{-1}. In calculations of individual molecules, we checked the type of the stationary point on the potential energy surface. This method is intended for calculating molecules that consist of atoms of the first two rows of the periodic table. It is well suited for organic substances containing nitrogen [8]. It fairly well reproduces the heats of formation, geometries, vibration frequencies, and activation barriers.

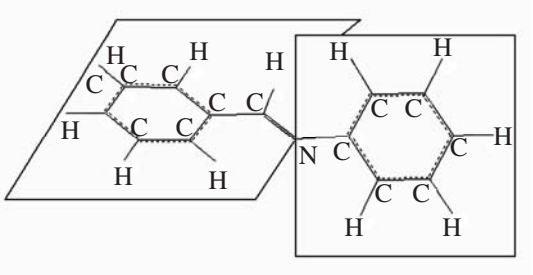

Fig. 1. Mutual arrangement of benzene rings in the central part of azomethine molecules.

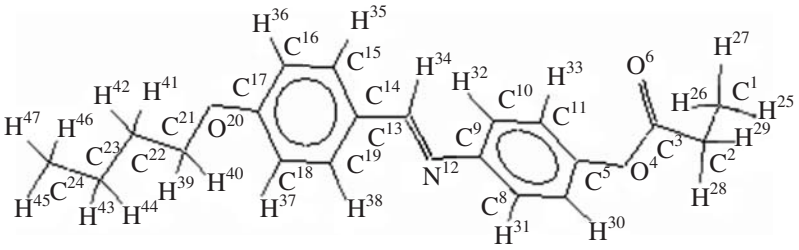

Fig. 2. Atom numbering in the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule.

The synthesis and mesomorphic properties of *p*-methoxybenzylidene-*p*'-toluidine were reported in [9]. The scheme of phase transitions of the compound under consideration is as follows:

$$C \xrightarrow{t_1} N \xrightarrow{t_2} I,$$

t_1 85°C, t_2 119°C.

By the conformational analysis we determined the molecular structure of *p*-butoxybenzylidene-*p*'-propionyloxyaniline in the crystalline state and at temperatures of the crystal → nematic and nematic → isotropic liquid phase transitions (see scheme). In the crystalline phase (25°C), this molecule has 42 conformations; at the temperature of the first phase transition (*t* 85°C), 45 conformations; and at the temperature of the second phase transition (*t* 119°C), 61 conformations. For the analysis we chose the conformations with the lowest total energy. The total energies and dihedral angles are given in Table 1.

Table 1. Total energies (E_t, kcal mol^{-1}) and dihedral angles (deg) in the *p*-butoxybenzylidene-*p*'-propionyloxy-aniline molecule in the crystalline state and at temperatures of the crystal → nematic and nematic → isotropic liquid phase transitions

Angle[a]	*C*, E_t –93279.31	$C \rightarrow N$, E_t –93279.31	$N \rightarrow I$, E_t –93279.56
$C^{17}O^{20}C^{21}H^{39}$	–60.4[б]	–60.4	49.6
$C^{18}C^{17}O^{20}C^{21}$	0.4	0.4	175.0
$H^{27}C^{1}C^{2}H^{28}$	175.3	175.3	175.4
$H^{29}C^{2}C^{3}O^{6}$	79.2	79.2	77.0
$H^{34}C^{13}C^{14}C^{15}$	–4.1	–4.1	–155.1
$C^{3}C^{4}C^{5}C^{11}$	47.4	47.4	–50.8
$H^{40}C^{21}C^{22}H^{42}$	177.4	177.4	174.5
$H^{41}C^{22}C^{23}H^{43}$	–179.56	–179.56	–179.19
$H^{44}C^{23}C^{24}H^{45}$	–58.68	–58.68	–58.55
$O^{6}C^{3}C^{4}C^{5}$	–1.54	–1.54	–0.15
$C^{8}C^{9}N^{12}C^{13}$	–148.4	–148.4	–122.14
$C^{9}N^{12}C^{13}H^{34}$	–1.52	–1.52	–178.44

[a] Negative values of torsion angles correspond to counterclockwise rotation. The atom numbering is shown in Fig. 2; the same for Tables 2 and 3.

The conformational analysis shows that, in the crystalline phase and at the temperature of the $C \rightarrow N$ phase transition, the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule exists in the form of structure a shown in Fig. 3. The molecule is acoplanar with the $C^{8}C^{9}N^{12}C^{13}$ dihedral angle equal to 31.6°.

Table 1 shows that there are no differences in the conformation of the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule in the crystalline phase and at the $C \rightarrow N$ phase transition. They have the same structure and are characterized by the same values of the energy, atomic charges, and bond lengths.

For the conformation corresponding to the $N \rightarrow I$ phase transition, the total energy is the same (Table 1) but the dihedral angles differ essentially from those in the crystalline phase and at the C → N phase transition (Fig. 3, structure b). The bond lengths in the two conformations of *p*-butoxybenzylidene-*p*'-propionyloxyaniline are essentially similar (Table 2). The largest difference, 0.012 Å, is observed for the N^{12}–C^{13} bond. The conformations differ from each other in electronic properties also. As compared to structure a (Fig. 3), in the conformation corresponding to the $N \rightarrow I$ phase transition the electron density is redistributed: The charges on the carbon atoms decrease, and those on the hydrogen and nitrogen atoms increase (Table 3), which is reflected on the dipole moments. The

calculated dipole moments for the conformations shown in Figs. 3a and 3b are 1.05 and 2.98 D, respectively.

Thus, our calculations show that the $N \rightarrow I$ phase transition is accompanied by a change in the conformation of the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule as a result of changes in the dihedral angles involving the azomethine group.

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Table 2. Bond lengths (Å) in the *p*-butoxybenzyl-idene-*p*'-propionyloxyaniline molecule

Bond	$C, C \rightarrow N$	$N \rightarrow I$
C^1–C^2	1.505	1.507
C^2–C^3	1.500	1.499
C^3–O^4	1.377	1.377
O^4–C^5	1.392	1.394
C^3–O^6	1.230	1.229
C^9–N^{12}	1.411	1.411
N^{12}–C^{13}	1.293	1.281
C^{13}–C^{14}	1.467	1.467
C^{17}–O^{20}	1.378	1.378
O^{20}–C^{21}	1.434	1.429
C^{21}–C^{22}	1.519	1.517

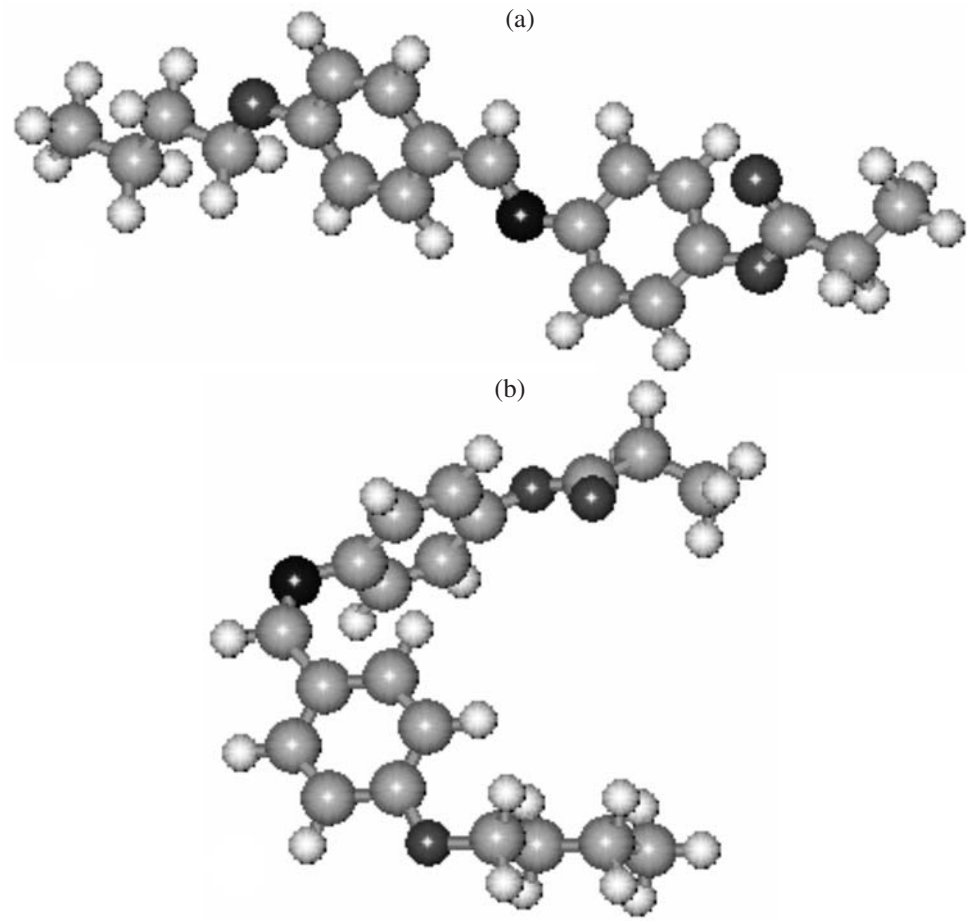

Fig. 3. Structure of the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule: (a) conformation corresponding to the crystalline state and to the temperature of the $C \rightarrow N$ phase transition; (b) conformation corresponding to the temperature of the $N \rightarrow I$ phase transition.

Table 3. Atomic charges in the *p*-butoxybenzylidene-*p*'-propionyloxyaniline molecule

Atom no.	*C*, *C* → *N*	*N* → *I*	Atom no.	*C*, *C* → *N*	*N* → *I*	Atom no.	*C*, *C* → *N*	*N* → *I*	Atom no.	*C*, *C* → *N*	*N* → *I*
	charge, e			charge, e			charge, e			charge, e	
1	–0.213	–0.213	13	0	0.021	25	0.085	0.085	37	0.155	0.152
2	–0.156	–0.156	14	–0.111	–0.156	26	0.085	0.097	38	0.080	0.135
3	0.310	0.308	15	–0.076	–0.060	27	0.120	0.084	39	0.081	0.084
4	–0.234	–0.232	16	–0.168	–0.211	28	0.119	0.118	40	0.098	0.111
5	0.058	0.0419	17	0.104	0.103	29	0.148	0.119	41	0.097	0.098
6	–0.332	–0.335	18	–0.220	–0.168	30	0.149	0.153	42	0.080	0.094
7	–0.133	–0.122	19	–0.044	–0.071	31	0.136	0.144	43	0.080	0.079
8	–0.094	–0.134	20	–0.212	–0.210	32	0.156	0.143	44	0.075	0.079
9	–0.019	–0.005	21	–0.022	–0.023	33	0.104	0.147	45	0.075	0.075
10	–0.140	–0.132	22	–0.165	–0.195	34	0.135	0.147	46	0.075	0.075
11	–0.129	–0.118	23	–0.158	–0.156	35	0.152	0.149	47	0.098	0.076
12	–0.159	–0.158	24	–0.211	–0.211	36	0.141	0.147			

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