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Study of the Terminal Interactions between Molecules of (4-*n*-Butoxyphenyl)-*N*-(*p*-tolyl)methanimine

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Abstract—The energy of interaction between (4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules has been estimated and decomposed by Morokuma method. It has been shown that the intermolecular interaction energy is a function of both intermolecular distance and relative orientation. Terminal interactions have been found to be very weak.

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One of the topical issues in the research on thermotropic liquid crystals is the theoretical investigation of their mesomorphism basing on the information of the molecules structure, their conformational behavior [1–3], most probable mutual configurations, and the nature and the role of intermolecular interactions. It is known that stacking, planar, and terminal intermolecular interactions influence the phase transitions and type of the physicochemical processes in liquid crystals [4, 5].

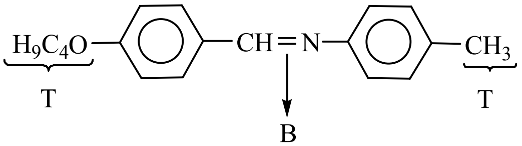
Physical and physicochemical experiments as well as computer simulation by means of quantum chemistry and molecular dynamics methods are sources of knowledge on the intermolecular interactions. Such computations have revealed relations between microscopic properties and macroscopic behavior that are important in studies of nematic liquid crystals.

This work was aimed at the study of terminal interactions between molecules of 1-(4-butoxyphenyl)-*N*-(*p*-tolyl)methanimine, and the estimation of intermolecular interaction energy and its constituting parts.

Preliminary calculations of 1-(4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules and models of various types of terminal interaction of two molecules were performed using the HF/AM1 method (HyperChem [6]). The geometry optimization was performed without any restrictions on the symmetry type. The proof of the belonging of the stationary point type to the true potential energy surface minimum was obtained if no imaginary frequencies were found.

Major quantum-chemical calculations of the studied molecular systems and the decomposition of the energy of terminal intermolecular interactions were performed by the Morokuma method [4, 5] (HF/6-31G++**, GAMESS [7]).

The studied mesogenic molecule consists of a rigid scaffold formed by aromatic rings connected via a bridging (B) fragment and containing terminal (T) substituents: methyl and butoxy groups.

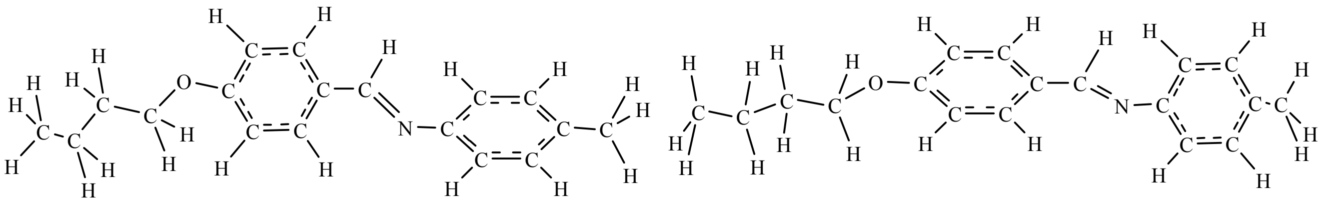


To study the terminal intermolecular interactions, three models were constructed, differing in the mutual orientation of the (4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules.

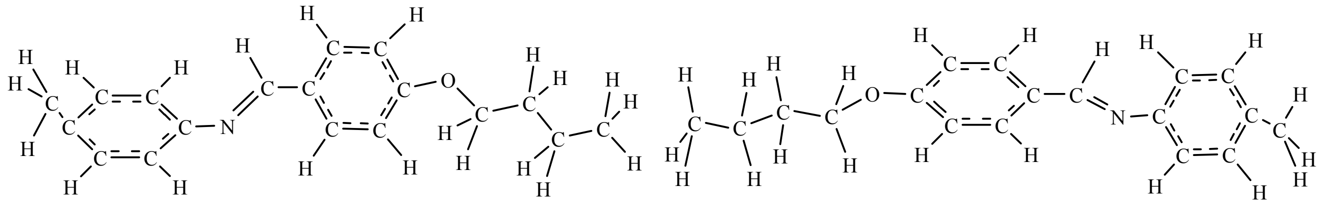
For all models discussed here, the initial distance between closest carbon atoms of the two molecules (r) was 10 Å [8–11] before geometry optimization was run; after optimization, r decreased for A and B molecules to 8.57 and 7.90 Å, respectively, for the model C the final distance (10.27 Å) was close to the initial one.

According to results of the HF/AM1 calculations, the system energy minimum was achieved at r equal to 3.4 Å. Upon further geometry optimization (HF/6-31G++**), the distance increased to 4.64 Å (A), 4.79 Å (B), and 4.88 Å (C).

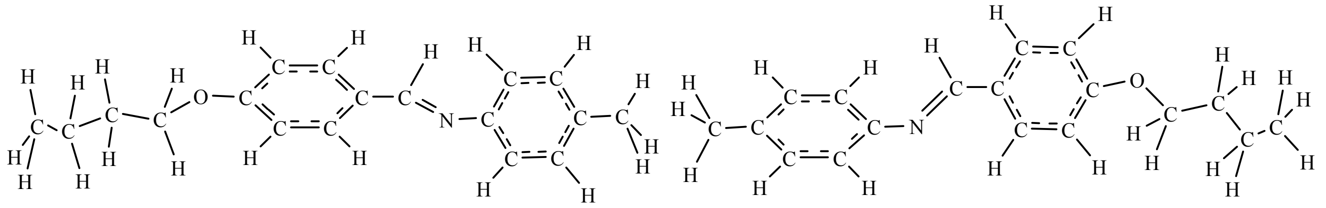
A



B



C



Following the Morokuma method, the effect of intermolecular distance and the molecules mutual orientation on the terminal interaction energy and its constituents was analyzed for each model (see the table).

In the case of model B, weak intermolecular interactions at $r = 8–10$ Å were by an order of magnitude larger than those in the other two models. The molecules interaction energy (ΔE) was mainly due to electrostatic energy (E_{es}); the positive ΔE meant that the interaction was repulsive.

At $r = 4.6–4.9$ Å, weak intermolecular interactions were observed in all the studied models, and constituents other than E_{es} contributed to the full energy. The charge transfer energy (E_{ct}) was dominative in ΔE: the absolute value of E_{ct} was 4 times greater than E_{es} in model A, 1.9 times greater than E_{es} in model B, 1.7 times greater than E_{es} in model C. It was the charge transfer energy that led to weak attraction of the molecules

The electrostatic energy of repulsion between (4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules was larger at $r = 4.6–4.9$ Å than at $r = 8–10$ Å (see the table). The repulsive character of the interaction between the molecules followed also from the values of the exchange energy (E_{ex}), which was positive as well; in model A it was comparable to E_{es}. For models B and C E_{ex} was almost three times lower than E_{es}. Thus, as two (4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules came closer, both the value of ΔE and the interaction type changed.

From the tabulated data, it may be noted that the highest interaction energy between the (4-*n*-but-

Constituents of the interaction energy of the 1-(4-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules

r, Å	Constituents of the interaction energy, 10^5 Hartree					
	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{mix}	ΔE
	Model A					
8.57	0.6	0.0	0.0	0.0	0.0	0.6
4.64	2.0	2.2	–0.1	–8.1	0.2	–3.8
	Model B					
7.90	1.3	0.0	0.0	0.0	0.0	1.3
4.79	2.8	1.0	–0.1	–5.4	0.1	–1.7
	Model C					
10.27	0.5	0.0	0.0	0.0	0.0	0.5
4.88	3.2	0.9	–0.2	–5.3	0.1	–1.3

oxyphenyl)-*N*-(*p*-tolyl)methanimine molecules was achieved in model A (r = 4.64 Å), that is, when the terminal interaction occurred between terminal groups of different type. This likely resulted from the orientation of the dipole moments of the interacting molecules.

The orientation of the electrical dipole moment (μ) is defined as the direction of the radius-vector from the negative charge center of gravity to the positive charge center of gravity [12].

Thus, the orientation of the dipole moments of the molecules was opposite in the molecules B and C, and the repulsive interactions should dominate; this was confirmed by the results of the calculations. The highest energy of the electrostatic interaction was observed when the dipole moments of the molecules were in reversed orientation. When the dipole moments orientation was identical (model A), the charge transfer energy increased (E_{ct} was twice as high as the sum of E_{es} and E_{ex}). Basing on the obtained values of the intermolecular interaction energy, it was concluded that the terminal interactions did not significantly affect the self-organization of the (4-*n*-butoxyphenyl)-*N*-(*p*-tolyl)methanimine molecules and their mesomorphic properties. The results obtained are well consistent with the data of X-ray analysis [8] and of computer simulation [13, 14] of nematic liquid crystals, both having revealed the dominating role of stacking and planar interactions between the molecules.

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