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Model calculation of liquid crystal dimers

The potential surface of internal rotation in the pair interaction between molecules of nematic liquid crystal with the general formula XC_6H_4OR ($X = H, F, Cl, Br, CN, NO_2$ and $R = CH_2CCC_6H_5$) has been investigated by *ab initio* methods in the RHF/6-31G(d) approximation. It is shown that the shape of the potential surface is modified for phenylpropargyl ethers of phenols with electron-donating substituents and unsubstituted ether, passing from a single molecule to molecular pair. However, *ab initio* calculations predict the same stable conformation for all examined ethers.

Key words: potential surface, nematic liquid crystals, electron-donating substituents.

Substituted phenylpropargyl ethers of phenols (PPEP) with the general formula $n-XC_6H_4OR$ (X — polar substituent, $R = CH_2CCC_6H_5$) are nematic liquid crystal compounds. According to the nature and position of substituent X in the aryl ring of phenoxy fragment the melting point and thermal stability of these substances change [1]. These and other physical properties of liquid crystals (LC) are due to the interaction of mesogenic molecules. In turn, intermolecular interactions play an important role in determining the molecular conformations of liquid crystal.

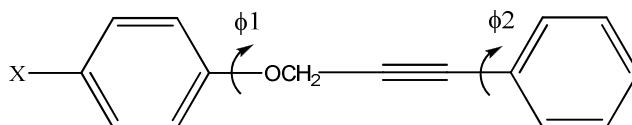
Using different models of semi-empirical (AM1, PM3) [2] and *ab initio* (HF) [3] quantum chemical calculations, we previously identified stable conformations of isolated molecules of PPEP and constructed the potential functions and surfaces of internal rotation [4–6].

This paper is concerned with the quantum chemical study of the potential surface of internal rotation in the pair interaction between PPEP molecules since it is well known from the literature [7, 8] that nematic liquid crystals can form paired associates (dimers).

Calculation

The quantum chemical calculations were performed in the single-determinant Hartree-Fock approximation using a split-valence basis 6-31G(d) with the polarization functions. We have simulated and studied PPEP with electron-donating (F, Cl, Br, basis set 6-31G(d) for iodine is absent), electron-withdrawing (CN, NO_2) substituents in the *para*-position of aryl ring of phenoxy fragment and reference unsubstituted PPEP.

A conformation of anisometric molecules of nematic LC is mainly determined by π -conjugated fragments belonging to the aromatic core of mesogenic molecules since internal rotation of these fragments significantly affects the polarizability, electronic and other properties of molecules. In the case of PPEP the scanning is carried out by two torsion angles about the C-O and C-C-bonds:



The scan is carried out for the geometry of the molecules optimized by PM3 method [4] and for fixed values of torsion angles ϕ_1 from 0° to 90° and ϕ_2 (122 – 212°) with increments of 30° .

Results and Discussion

We considered only typical for polar LC antiparallel and stacking-arrangement of molecules above each other (Fig.). For the dimers the angle between the long axes of the molecules is $\sim 0^\circ$, i.e. molecules in the short-range order are strictly parallel. One of two identical molecules taken at rest, and the center of gravity position and orientation of the second molecule were varied relative to the first one. The moved molecule was used as a rigid rotor model, as it is well known that the intermolecular forces have mainly an effect on the angles of internal rotation, almost without changing the bond lengths and bond angles.

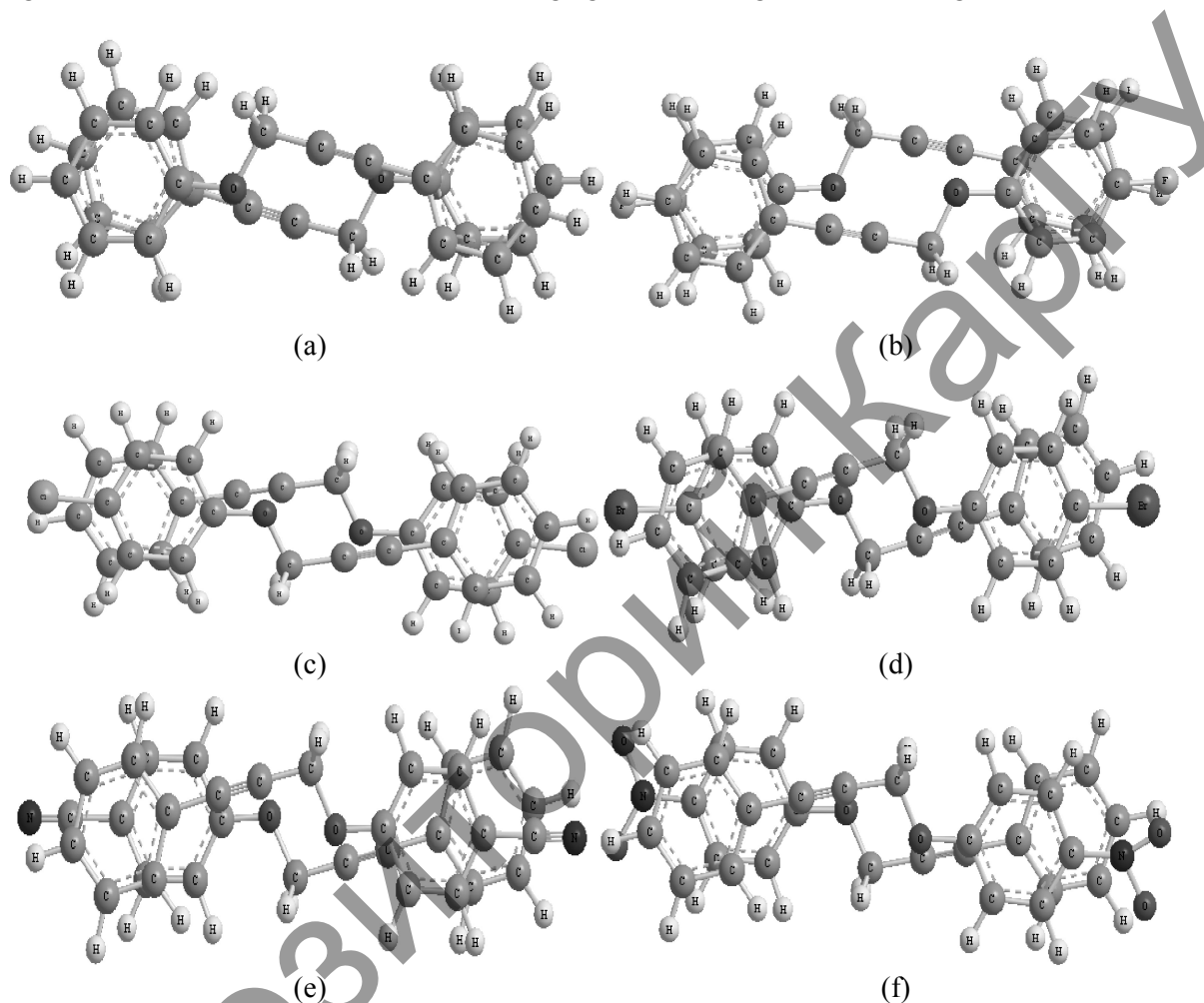


Figure. The stable forms ($\varphi_1=0^\circ$) of the molecular pairs of X-PPEP with X=H (a), F (b), Cl (c), Br (d), CN (e), NO₂ (f) as determined by ab initio calculations with the 6-31G(d) basis set

The rotation of the aryl ring of phenoxy fragment is accompanied by an increase in energy of the dimers (Table) which can be explained by a decrease in delocalization energy. The most stable conformations are observed for $\varphi_1 = 0^\circ$ and $\varphi_2 = 212^\circ$. It is interesting to note the following fact: every time you turn on the local 30° with the lowest energy conformations occur when the angle φ_2 changes in the opposite direction:

φ_1	0°	30°	60°	90°
φ_2	212°	182°	152°	122°

i.e. for all the considered substituents the phenyl ring rotation of the conjugated fragment causes violation of the coupling, and therefore electronic redistribution in the molecule, which in turn affects the spatial structure of the rest of the molecule. In other words, the second phenyl ring is sensitive to the rotation of the ring of conjugated fragment. In contrast, the rotation of the second phenyl ring does not affect the conjugated moiety and the energy of the molecule.

It should be noted that the rotation curves (basis sets from minimal to split-valence 6-31G, 6-31G (d)) and the potential energy surfaces (the basis 6-31+G(d)) of isolated molecules of *para*- H, F, Br-PPEP show

that a rotational energy was increased at the angle φ_1 from 0° to 20° (for $X = \text{Cl}$ $\varphi_1 = 30^\circ$), then it's decreased to 90° [5, 6] (semi-empirical calculations gave opposite results [4]). However, intermolecular forces didn't changed the most stable form of isolated molecules ($\varphi_1 = 0^\circ$). Nevertheless, an accounting of the molecular interaction in going from a single molecule to the molecular pair markedly changed the shape of the potential energy surface of rotation: the maximum at $\varphi_1 = 20^\circ$ (30°) and a local minimum at $\varphi_1 = 90^\circ$ from the previous ab initio calculations transform to the local minimum and maximum respectively in the present calculations. It is interesting to note that in the case of electron-withdrawing CN, NO_2 substituents (Fig. 1, (e), (f)) results of the previous study [5] and these calculations are the same: when you turn the aryl ring at 90° about the bond CO (φ_1) an energy of the system is continuously increased.

Table

The total energies of the molecular conformations of ether pairs with different substituents X (6-31G(d) basis)

φ_1 , degrees	E_{tot} a.u.					
	X=H	F	Cl	Br	CN	NO_2
0	-1299,5877	-1497,2814	-2217,1381	-6437,7291	-1483,0631	-1706,5287
30	-1299,5860	-1497,2799	-2217,1364	-6437,7273	-1483,0613	-1706,5265
60	-1299,5849	-1497,2792	-2217,1353	-6437,7261	-1483,0593	-1706,5243
90	-1299,5839	-1497,2784	-2217,1343	-6437,7250	-1483,0569	-1706,5225

This can mean that such a turn of p , π -conjugated fragment is disadvantageous either in terms of the intramolecular interactions, or in terms of intermolecular interactions. Also this is borne out by the magnitude of the internal rotation barriers:

X	F	H	Cl	Br	CN	NO_2
E_{rel} , kJ/mole	7,98	9,90	10,29	11,87	18,54	17,07
σ [9]	-0,073	0	0,114	0,150	0,659	0,790

The barrier value is in the range $\sim 2\text{--}5$ kcal/mol, and the barrier to internal rotation is affected by the volume of the substituent. It is self-evident that the barriers are increased by an increase in resonance σ -constants of substituents (barriers for $X = \text{CN}$, NO_2 are very close, so we can assume that the common law is not violated). We have observed a similar situation in semi-empirical calculations of isolated molecules previously, which agrees with the conclusion of other authors that the method PM3 correctly reproduces the general trends of the influence of substituent electronic nature on the barriers to internal rotation about the $\text{C}_{\text{Ar}}\text{--E}$ bonds, experimentally determined for number of related compounds [10–12].

Conclusion

Thus, the conformations of isolated molecules and molecular pairs of PPEP are determined by varying the angle of rotation of the aryl ring around the CO bond (φ_1) of the p , π -conjugated phenoxy fragment. The rotation is energetically disadvantageous, and the barrier value is influenced by the volume and nature of the substituent. The rotation of the phenyl ring does not affect the total energy of the system, i.e. it seems that phenyl group rotates almost freely.

Ab initio calculations predict the same stable conformation (with $\varphi_1 = 0^\circ$) for isolated molecules and molecular pairs of PPEP, confirming the assumption [13] that if the potential well depth is greater than 2–3 kcal/mol, the molecule will have a similar conformation in all three phases — vapor, liquid and crystal. It may well be in a liquid crystal.

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Сұйық кристалдар димерлерінің үлгілі есептеулері

Мақалада жалпы формуласы XC_6H_4OR ($X = H, F, Cl, Br, CN, NO_2$; $R = CH_2CCC_6H_5$) нематикалық сұйық кристалдардың екі молекуласының әрекеттесу кезіндегі ішкі айналуының потенциалдық беті зерттелген. *Ab initio* әдісімен HF/6–31G(d) жуықтауында электрондонорлы орынбасушылары бар эфирлер және орынбасылмаған эфир үшін жеке молекуладан молекулалық жұпка ауысқандағы потенциалдық бет пішінінің өзгергені көрсетілген. Бірақ осы эмпирикалық емес есептеулер бойынша барлық қарастырылған эфирлер үшін тұрақты конформациялар бірдей деген қорытынды шығарылды.

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Модельные расчеты димеров жидких кристаллов

Методом *ab initio* в приближении HF/6–31G(d) исследована потенциальная поверхность внутреннего вращения при парном взаимодействии молекул нематических жидких кристаллов с общей формулой XC_6H_4OR ($X = H, F, Cl, Br, CN, NO_2$; $R = CH_2CCC_6H_5$). Показано, что для эфиров фенолов с электронодонорными заместителями и незамещенного эфира при переходе от отдельной молекулы к молекулярной паре изменяется форма потенциальной поверхности. Однако для всех рассмотренных замещенных эфиров на основании неэмпирических расчетов предсказывается одна и та же устойчивая конформация.