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DFT-BASED MOLECULAR CONFORMATIONAL ANALYSIS OF A DIARYLETHYLENE CYANO-DERIVATIVE

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Structural stability and conformational behavior of *trans*-4,4′-methoxycyanostilbene are studied theoretically within the method of density functional theory using the B3LYP functional and 6-31G(*d*) and cc-pVDZ split-valence basis sets. According to quantum chemical calculations performed for the molecule in its ground state, two possible conformations of the molecule differ in energies so that the configuration with triple conjugation (*p*,π-, π,π-, and direct polar conjugation of substituents) is energetically preferable. First- and second-order saddle points are found by scanning the three-dimensional potential energy surface. Vibrational analysis is used to find stationary points.

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INTRODUCTION

Correlation between the structure and the mesomorphism of liquid crystals (LCs) has been subject to extensive experimental and theoretical studies (e.g., [1-17]). It has been studied how geometric anisotropy of the molecules, the nature, topology, and the internal rotation of their structural fragments affect physicochemical properties of LCs. It was found that physical properties of compounds are closely related to their preferred conformations; therefore, studying energy preferable conformers is interesting in terms of both theory and practice. However, molecular conformations are statistically distributed in the bulk substance due to thermal fluctuations, so that molecules at a given temperature may appear in different conformations rather than in the low-energy conformation only [18]. Therefore, physical characteristics of compounds are averaged over this statistical distribution. As an example, *trans*-isomer (symmetry group C_{2h}) is the most stable conformation of dichloroethane. Theoretically, centrosymmetric molecules should have zero dipole moments, but the experimental dipole moment of 1,2-dichloroethane is 1.12 D at 25 °C and 1.54 D at 270 °C due to the contribution of other conformations [19]. Thus, it is necessary to know the potential energy surface of the molecules to predict physical properties, including mesomorphic properties, of the substances which depend on internal rotation and rotational isomerism.

The choice of the objects of study was due to the following facts. Cyano-derivatives of various chemical classes are the most widely used components to develop liquid crystal materials. Weakly polar liquid crystal compounds are another group of practically important components. We previously considered [20] internal rotation of *trans*-4,4′-methoxypropylstilbene, stilbene with donor substituents of various strengths. According to experimental data, thermal

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stability of the mesophase and the temperature of phase transitions increase in the row from stilbene alkyl- and alkoxy-derivatives to its cyano-derivatives [2, 17]. Therefore, it is interesting to study cyano-derivatives and compare them with weakly polar compounds. This paper presents the results of a quantum chemical conformational analysis of cyano-substituted stilbene using the example of the *trans*-4,4′-methoxycyanostilbene molecule whose conjugate fragment (containing ethylene bonding and phenyl rings) exhibits mesomerism affected also by the terminal alkoxy radical and highly polar group.

CALCULATION DETAILS

Full geometry optimization was performed and vibrational frequencies of 4,4′-methoxycyanostilbene conformers were calculated within the quantum chemical method of density functional using the B3LYP correlation functional, the 6-31G(*d*) split-valence basis set with polarization functions on heavy atoms, and Dunning's correlation consistent medium-sized basis set cc-pVDZ with polarization functions. Transition states were calculated within the B3LYP/6-31G(*d*) method using the Gaussian 03 package [22]. Stationary points were searched using vibrational analysis. Rotational energies were calculated with and without taking into account zero frequencies. Vibrational frequencies were calculated with a scaling factor of 0.9613 using the B3LYP/6-31G(*d*) method [23].

RESULTS AND DISCUSSION

This work concerns substituted stilbenes with the general formula $RC_6H_4CHCHC_6H_4X$. These stilbenes are uniaxial two-ring mesogenic compounds. The bridging fragment in their molecules is the HC=CH group, terminal substituents R and X are alkyl and alkoxy radicals and/or strong polar groups, respectively.

Fig. 1 shows the structures of the *trans*-4,4′-methoxycyanostilbene molecule optimized with respect to all independent coordinates to find the minimum energy configuration in its ground state; Fig. 2 shows theoretical vibrational spectra of these structures; Fig. 3 shows charge density distribution over the atoms of *a* and *b* conformers; Figs. 4 and 5 image the three-dimensional potential energy surface (PES) plotted with respect to internal rotation and molecular conformations at the PES saddle points, respectively. The effect of basis sets on the geometry of the *trans*-4,4′-methoxycyanostilbene molecule can be seen in Table 1. Internal rotation barriers are summarized in Table 2.

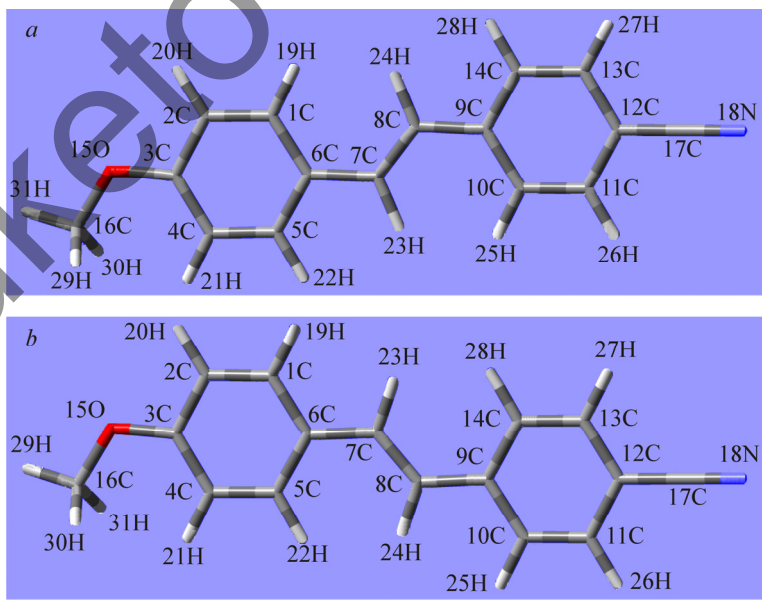

Fig. 1. Ground-state conformations of the 4,4′-methoxycyanostilbene molecule.

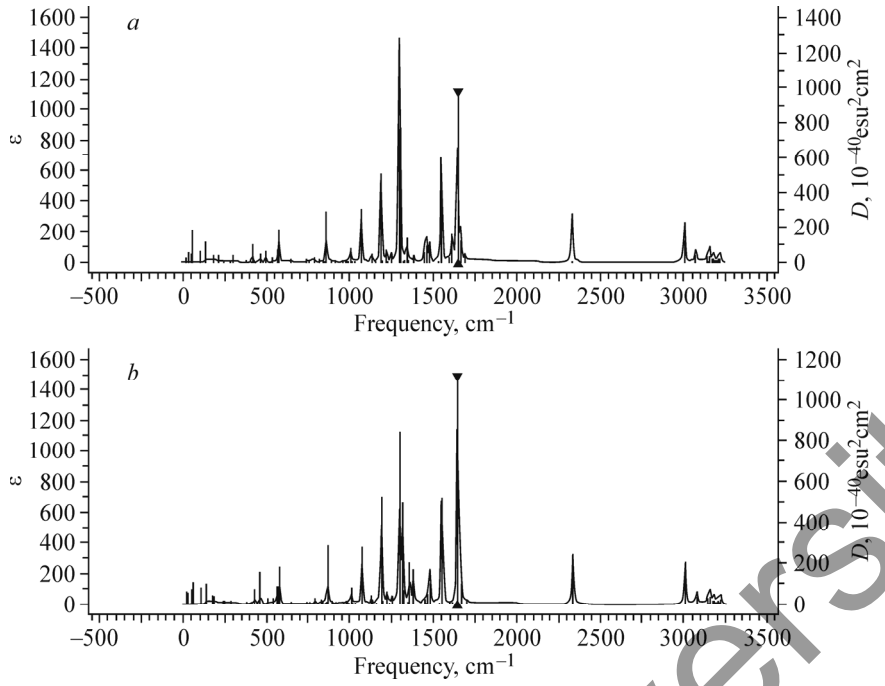

Fig. 2. Vibrational spectra of conformations *a* and *b* of the *trans*-4,4′-methoxycyanostilbene molecule as predicted by the B3LYP/cc-pVDZ method (plotted against the coordinates *absorption coefficient* (ε) – *frequency*).

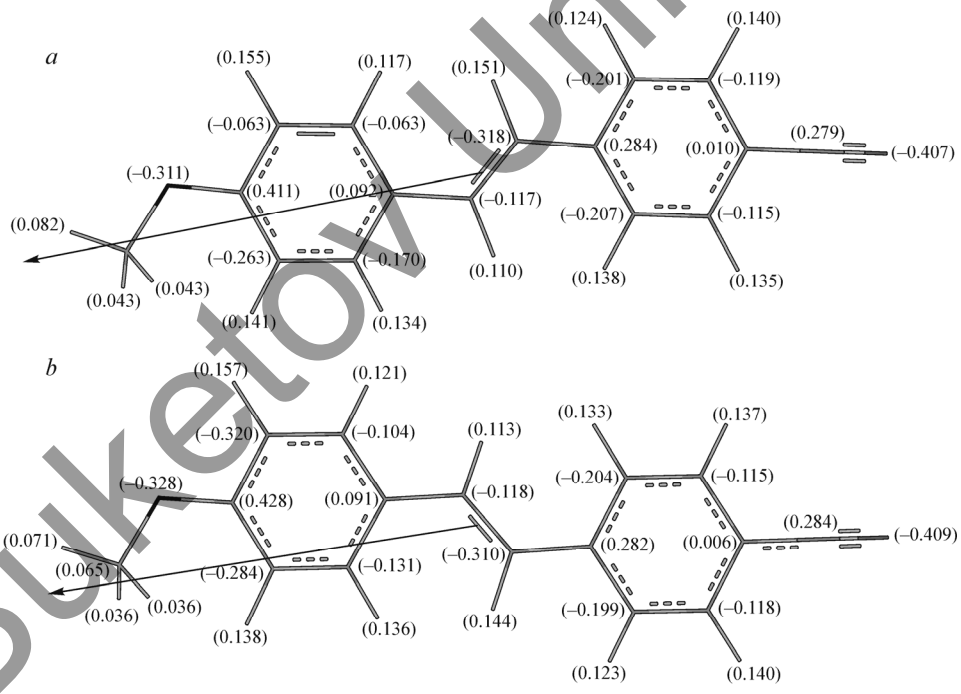

Fig. 3. Charge density distribution over atoms and directions of the dipole moment in the 4-methoxy-4′-cyanostilbene molecule in *a* and *b* ground-state conformers (B3LYP/cc-pVDZ method).

Conformations of anisometric liquid crystal molecules are mainly determined by π-conjugated fragments which are parts of the aromatic core of mesogenic molecules. Polarizability, electronic and other molecular properties are significantly affected by internal rotations of these fragments [17].

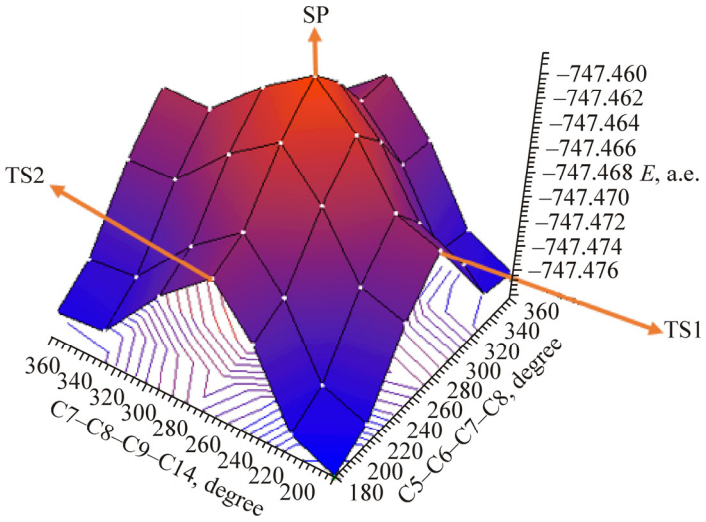

Fig. 4. Potential energy surface of 4,4′-methoxycyanostilbene obtained by rotating two molecular fragments (B3LYP/6-31G(*d*)).

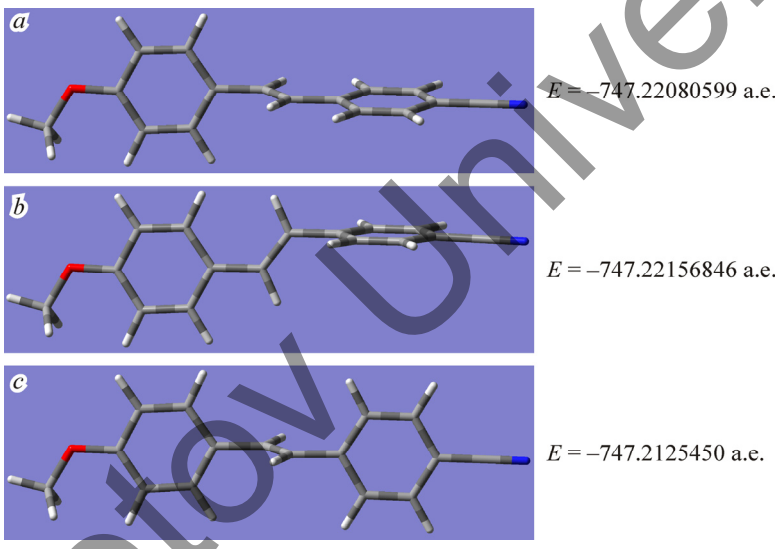

Fig. 5. Conformations of 4,4′-methoxycyanostilbene at saddle points TS1 (*a*), TS2 (*b*), and SP (*c*) (B3LYP/6-31G(*d*); the energies are calculated with the account of zero frequencies).

The ground energy state of the *trans*-4,4′-methoxycyanostilbene molecule can be represented by two conformations (Fig. 1*a*, *b*) with different positions of the C^7=C^8 ethene bond: coplanar with the C^1–C^6 bond (*a*) or the C^5–C^6 bond (*b*) of the methoxybenzene ring. In both cases, the bridging group and the benzene core form a single conjugated system. However, according to B3LYP calculations, these conformers possess different structural stabilities.

Conjugated fragments of the methoxybenzene ring and the ethylene bond or those of the cyanophenyl group and the C=C bond of the molecule may exhibit the effects associated with the interaction between substituents and double bonds on the one side and benzene rings (p,π, π,π) on the other side, as well as direct polar conjugation between donor and acceptor substituents and nonpolar resonance of benzene rings through the HC=CH bridging group. This is true for the case (*a*); the second case (*b*) exhibits no conjugation between lone pairs of the oxygen atom and π-orbitals of ethene bond, and this is apparently a factor to destabilize the conjugated form. According to B3LYP/cc-pVDZ calculations, the repulsion energy 1062.87079796 a.u. is lower for the more stable conformer *a* as compared to its value 1063.28216582 a.u. for the

TABLE 1. Optimized Geometry Parameters of 4-Methoxy-4′-Cyanostilbene in the Ground State

Parameter	Bond length, Å		Parameter	Bond angle, deg.	
	B3LYP/6-31G(*d*)	B3LYP/cc-pVDZ		B3LYP/6-31G(*d*)	B3LYP/cc-pVDZ
C^1–C^6	1.413	1.415	C^1–C^2–C^3	120.43	120.54
C^5–C^6	1.404	1.406	C^1–C^6–C^7	123.83	123.77
C^6–C^7	1.461	1.462	C^2–C^3–O^{15}	115.66	115.67
C^3–O^{15}	1.361	1.360	C^3–O^{15}–C^{16}	118.38	118.39
O^{15}–C^{16}	1.420	1.421	C^4–C^3–C^{15}	124.96	125.09
C^7=C^8	1.351	1.353	C^6–C^7=C^8	127.43	127.39
C^8–C^9	1.462	1.464	C^6–C^7–H^{23}	114.02	114.07
C^9–C^{10}	1.412	1.413	C^7=C^8–C^9	126.77	126.70
C^9–C^{14}	1.410	1.412	C^7–C^8–H^{24}	118.91	118.92
C^{11}–C^{12}	1.408	1.410	C^8–C^9–C^{10}	123.75	123.69
C^{12}–C^{17}	1.431	1.434	C^9–C^8–H^{24}	114.32	114.38
C^{17}–N^{19}	1.164	1.165	C^{10}–C^{11}–C^{12}	120.32	120.37
H^{23}…H^{25}	2.122	2.116	C^{11}–C^{12}–C^{17}	120.33	120.37

TABLE 2. Rotation Barriers (kJ/mol) for Strongly Polar and Weakly Polar Stilbenes (B3LYP/6-31G(*d*) method)

Compound	TS1	TS2	TS1	TS2
	Without zero oscillations		With zero oscillations	
trans-4- Methoxy-4′-cyanostilbene	29.33	27.38	28.12	26.11
trans-4- Methoxy-4′-propylstilbene*	23.04	22.01	21.87	20.82

* According to [20].

b conformer. Although the energy difference ($E_b - E_a$) between the conformers is only 0.00193 a.u., which corresponds to 1.211 kcal/mol (6-31G(*d*) basis set) and 0.9 kcal/mol (CC-pVDZ basis set), the vibrational spectrum of the molecule demonstrates structural changes as far as the position of the central bond (Fig. 2).

The vibrational spectrum of a 31-atom 4-methoxy-4′-cyanostilbene molecule contains 87 normal vibrations. The most intense bands in the *a* and *b* spectra are due to C=C and C–O stretchings. It is well known that calculated harmonic frequencies are usually larger than the corresponding experimental values, so that vibrational frequencies are to be recalculated. Therefore, the scaling factor was used to correct the calculated data.

Vibrations of ethylene bonds and carbon-carbon bonds of the rings occur at ν_{calc} equal to 1581.57 cm^{-1} (Fig. 2*a*) and 1580.08 cm^{-1} (Fig. 2*b*), respectively. The spectra of these vibrations clearly demonstrate differences as far as the intensities and frequencies in the "fingerprint region" (below 1500 cm^{-1}). The absorption in the region 1240-1340 cm^{-1} contains a band with a maximum at 1246.73 cm^{-1} (*a*) (1242.79 cm^{-1} in the *b* case) corresponding to C–O stretchings. More intense C=C vibrations in the *b* spectrum (compared to the *a* spectrum) occur in the absence of direct polar conjugation of methoxyl and ethylene groups (Fig. 1*b*); on the contrary, valence modes of carbon–oxygen bonds in the *a* spectrum form a high intensity band due to this conjugation (Fig. 1*a*).

The substantial change in the intensity of vibrational frequencies is apparently due to the electron density redistribution on the atoms of the molecule containing electron-donating hydroxymethyl and electron-accepting nitrile groups. Since we used medium-sized split-valence basic sets and a correlation consistent basis set, we used chemically relevant electrostatic charges calculated from the electrostatic potential rather than the Mulliken population analysis [21]. The obtained data suggest that the conformers in the ground state possess different charge density distributions (Fig. 3*a*, *b*): charge transfer from methoxyl to nitrile is much stronger in the *a* conformer than in the *b* conformer. Nevertheless, the

nitrogen atom of the electron-accepting group CN has the largest negative charge in both cases. The observed charge redistribution over remaining atoms also indicates delocalization of the effect caused by the interaction between the methoxyl radical and the HC=CH group. The oxygen charge state is determined by the conditions of the above conjugation, which are different in *a* and *b* conformers. Therefore, the greatest differences between charges *a* and *b* are exhibited by methoxy group atoms and carbon atoms of the phenyl ring next to the OCH_3 group. The calculations suggest that the negative charge on the oxygen atom increases by –0.017 *e* in the row from *a* to *b*. This indicates that the methoxy substituent acts as an *ortho-, para*-director in *a*, whereas its inductive effect prevails over the mesomeric effect in *b*. On the contrary, the CN group virtually does not affect the electron density in the benzene ring in the row from *a* to *b*. As the group of atoms rotates and the charge gets redistributed, the dipole moment vector shifts and decreases in magnitude from 7.387 D to 7.279 D.

As far as the influence that a chosen basis set has on the calculation results, it was found that bond lengths and bond angles are slightly smaller in the case of the medium-sized basis set, which confirms the fact that correlation effects are more correctly described by the correlation consistent cc-pVDZ basis set, which was specially developed for this purpose. The only exception concerns the parameters of the bonds which act as transmitters of conjugation (Table 1).

The most stable ground-state conformer *a* was used as the starting point when scanning the potential energy surface with the B3LYP/6-31G(*d*) method. When doing this, molecular fragments were subject to joint internal rotation around single bonds C_{Ar}–C=. The calculations were carried out for fixed torsion angles varying from 180° to 360° at step size of 30°, and remaining intramolecular geometrical parameters were optimized at each step. The chosen torsion angles were the angles most important for this molecule, namely, the angles associated with the rotation around – C_{Ar}–C= bonds acting as transmitters of conjugation.

According to the calculation results, the potential energy function includes two parameters for each rotation angle: the potential barrier and the energy difference between the conformers. The above conformations *a* and *b* (Fig. 1) correspond to the global and local minima at the PES of rotation, respectively (Fig. 4).

Transition states TS1 and TS2 of the 4,4′-methoxycyanostilbene molecule (Fig. 5*a* and *b*, respectively) were redetermined as a result of full optimization of PES saddle points and calculation of vibrational frequencies; it was found that these states correspond to real transition states. TS1 and TS2 structures were obtained by rotating molecular fragments around the C^6–C^7 bond (angle C^1–C^6–C^7=C^8 = 89.961°) and the C^8–C^9 bond (angle C^7=C^8–C^9–C^{10} = 89.939°), respectively. The TS2 structure has lower energy than the TS1 structure, which is explained by the fact that its fragment preserves coplanarity with π,π- and *p*,π-conjugations, which is partially violated in TS1. Rigid parameters such as bond lengths and bond angles remain almost constant when the molecule transforms into the TS1 and TS2 states. Table 2 shows rotation barriers calculated with and without zero frequencies and compared with the barriers of weakly polar stilbene.

Simultaneous rotation of two stilbene rings, methoxybenzene ring and cyanophenyl ring, reveals another PES stationary point. It is a saddle point (SP) (Fig. 4) corresponding to the conformation with the torsion angles between the benzene rings plane and the ethylene bond plane almost equal to 90° (Fig. 5*c*). According to the vibrational analysis, this point is a second-order saddle point, whose energy is 21.69 kJ/mol and 23.70 kJ/mol higher than the energies of TS1 and TS2, respectively (with the account of zero frequencies). This point corresponds to the conformation where π,π- and *p*,π-conjugations are completely violated.

Comparison of calculation data obtained for strongly polar 4-methoxy-4′-cyanostilbene and weakly polar 4-methoxy-4′-propylstilbene [20] suggests a similarity between the forms of their PESs, transition states, saddle points, and low barriers on the one hand, and a difference between their rotational barriers on the other hand (Table 2). The barrier heights indicate torsion flexibility of stilbene derivatives, in particular, weaker flexibility of the strongly polar stilbene. This can be explained by the fact that weakly polar stilbene has no conjugation in its alkylphenyl moiety and between terminal substituents; on the contrary, internal rotation in the strongly polar compound is subject to multiple conjugations which naturally require more energy.

CONCLUSIONS

Ground-state conformations, local conformers, and first- and second-order saddle points of the *trans*-4-methoxy-4′-cyanostilbene molecule were calculated within the B3LYP quantum chemical method. All stationary points were identified using the analysis of vibrational frequencies. A larger number of conjugate fragments is a factor that enhances the stability of the system by increasing rotation barriers, which in turn may be reflected in the properties of these compounds.

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