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Conformational Space of 4,4'-Methoxypropylstilbene Molecule

L. K. Abulyaissova*, S. O. Kenzhetaeva, and M. S. Kasymova

Buketov Karaganda State University, ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan
**e-mail: abu.lyazzat@gmail.com*

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Abstract—Quantum-chemical simulation of the ground state [the density function B3LYP/6-31G, B3LYP/6-31G(d), and B3LYP/6-31+G(d,p) and the perturbation theory MP2/6-31G(d) methods] and the transition states [the B3LYP/6-31G(d) method] of 4,4'-methoxypropylstilbene molecule has been performed. Using the Ellinger MM2 force field method, the potentials of internal rotation have been obtained for each rotational degree of freedom of the molecule. The B3LYP simulation has revealed the planarity of the conjugated system and the orthogonal position of the alkyl substituent, whereas the benzene rings have deviated by about 20° with respect to the double bond plane according to the MP2 data. Three transition states of the molecule corresponding to the saddle points of the first and the second orders have been revealed. The stationary points have been identified by means of vibrational analysis.

Keywords: stilbene, conformational analysis, molecular mechanics, density functional theory

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Many optical decolorants, synthetic drugs, intermediate products of dyes synthesis, and liquid crystalline compounds are derivatives of stilbene hydrocarbon [1, 2]. Conformational flexibility of such compounds is among the major factors determining their physical properties including mesomorphism [3, 4].

The structure of the ground state and the internal rotation barriers of *trans*-stilbene (the simplest diarylethylene) have been studied over four recent decades by means of experimental (electron and X-ray diffraction, etc.) and theoretical (molecular mechanics and quantum chemistry) methods [5–13]. However, the obtained data have been contradictory, revealing either planar or nonplanar structure of the molecule. Theoretically, the bridging group (ethylene bond) and the benzene rings of stilbene should form a common conjugated system requiring the coplanarity of the molecule, i.e. the π-system of the benzene rings and the double ethylene bong should be in the same plane. This is only possible for the *trans*-isomer, whereas in the *cis*-isomer of stilbene this is hindered by the spatial interaction of the benzene rings. However, the experimental data [14] have revealed the nonplanar structure of the *trans*-stilbene as well (at elevated temperatures in the gas phase), resulting from the steric hindrance between the hydrogen atoms of the ethylene bond and the *ortho*-hydrogens of the phenyl fragments.

In contrast to *trans*-stilbene, the structure of the ground state of the *para*-substituted diarylethylenes is also affected by the terminal alkyl and alkoxy groups or by highly polar substituents. In this work, we discuss the results of conformational analysis of the 4,4'-methoxypropylstilbene molecule performed using the force field and quantum mechanics methods.

Rotational Hamiltonian of the molecule with internal rotation could be expressed as follows (1).

$$H = H_{\mathrm{rot}} + H_{\mathrm{int.rot}} + H_{\mathrm{interact}}, \qquad (1)$$

with H_{rot}, the Hamiltonian (energy) of the rigid rotator; $H_{\mathrm{int.rot}}$, the Hamiltonian of the internal rotation; H_{interact}, the Hamiltonian of the interaction of those rotations.

The rotation of the molecule as a whole (for instance, that occurring in the liquid-crystalline phase around the director) was neglected at that stage. In the considered molecule, the internal rotations around the carbon–carbon and the carbon–oxygen ordinary bonds were operative, both rotations being one-dimensional periodical process.

Potential energy of the one-dimensional internal rotation could be expressed as the Fourier series (2) [15].

$$V(\varphi) = V_0/2 + \sum_{n=1}^{\infty} V_n\cos nw\varphi + \sum_{n=1}^{\infty} V_n'\sin nw\varphi. \qquad (2)$$

In Eq. (2), n is an integer, V_n and V_n' are the series coefficients, $w = 2\pi/T$ (T, rotation period), and φ is the rotation angle. If $V(\varphi)$ is an even function, expression (2) should contain only cosine terms. However, the studied compound revealed more complex internal rotation, having several conformational degrees of freedom. Therefore, the potential function of its rotation should be written in the form (3).

$$V(\varphi_1,\varphi_2,\ldots,\varphi_n) = V_0/2 + \sum_{n=1}^{8} V_n\cos nw(\varphi_1,\varphi_2\ldots)$$
$$+ \sum_{n=1}^{8} V_n'\sin nw(\varphi_1,\varphi_2\ldots). \qquad (3)$$

Such function cannot be obtained using any experimental or theoretical methods. Even if the two-dimensional rotation can be simulated,

$$C_n^2 = \frac{n!}{2!(n-2)!}$$

combinations of the rotation angles should be probed for a molecule with n rotational degrees of freedom. For example, at $n = 7$, C_7^2 equals 21, leading to unreasonably resource-demanding computations. We propose different approaches to solve the conformational problem of finding the extremum of a multiparameter function: neglecting certain degrees of freedom (for example, these of the alkyl groups) or separate study of each of the degrees of freedom. In this work, we used the molecular mechanics method MM2 with the modified force field (developed by Ellinger [16]) for preliminary estimation of the potential energy as a function of the internal rotation angles; the obtained results were further refined using the non-empirical quantum-chemical methods.

Figure 1 displays the 3D models of the optimized conformations of 4,4'-methoxypropylstilbene molecule in the minimum and the saddle points of the potential energy surface (PES). Figure 2 shows the potential energy as a function of different internal rotation angle of the molecule obtained by means of molecular mechanics. The effects of the choice of the simulation method and the basis set on the molecule geometry is shown in the table.

Internal rotation in 4,4'-methoxypropylstilbene molecule is a result of rotations about the bonds of several types: the C–C bonds adjacent to the double bond and the benzene ring, the C–O bonds, and the bonds of the methyl and ethyl groups. The dihedral angles formed by the $C^1C^6C^7$ and $C^6C^7C^8$ planes (the $C^1C^6C^7C^8$ angle), the $C^7C^8C^9$ and $C^8C^9C^{10}$ planes ($C^7C^8C^9C^{10}$), the $C^{11}C^{12}C^{17}$ and $C^{12}C^{17}C^{18}$ planes ($C^{11}C^{12}C^{17}C^{18}$), the $C^2C^3O^{15}$ and $C^3O^{15}C^{16}$ planes ($C^2C^3O^{15}C^{16}$), the $C^3O^{15}C^{16}$ and $C^{15}C^{16}O^{32}$ planes ($C^3O^{15}C^{16}C^{32}$), the $C^{17}C^{18}C^{19}$ and $C^{18}C^{19}C^{39}$ planes ($C^{17}C^{18}C^{19}C^{39}$), and the $C^{12}C^{17}C^{18}$ and $C^{17}C^{18}C^{19}$ planes ($C^{12}C^{17}C^{18}C^{19}$) were considered as the rotation angles (Fig. 2). To compute the energy of the molecule conformations using the MM2 method, the dihedral angles were forced to change with a step of 5°. The full rotation about a bond was started at –180°, i.e. at the conformation with the marked four atoms were in the *trans*-configuration.

The rotation potentials of the fragments in the 4,4'-methoxypropylstilbene molecule could be expressed as Eq. (4) or (neglecting the constant) Eq. (5).

$$V = (V_n/2)(1 + \cos n\varphi), \qquad (4)$$

with n, an integer index; V_n, a series coefficient.

$$V(\varphi) = (V_1/2)(1 + \cos\varphi) + (V_2/2)(1 + \cos 2\varphi)$$
$$+ (V_3/2)(1 + \cos 3\varphi). \qquad (5)$$

Calculation of the sections of the internal rotation PES revealed that the second term of Eq. (5) was dominant for the cases (a), (c–f) (Fig. 2), since the molecular fragments close to planarity corresponded to the energy minimums, and the third term of Eq. (5) was dominant in the case (b).

From a physical viewpoint, the molecule energy E is a sum of four contributions (6) [17]: U_{nn}, repulsion of the nuclei; U_{ee}, repulsion of the electrons; T, kinetic energy of the electrons; U_{ne}, attraction of the nuclei and the electrons. The difference of the repulsion energy ($U_{nn} + U_{ee} + T$) and the attraction energy U_{ne} is the observable (conformational) energy.

$$E = U_{nn} + U_{ee} + T - U_{ne}. \qquad (6)$$

The energy profiles of the bonds adjacent to the double bond (i.e. the C^6–C^7 and C^8–C^9 bonds) determined by the MM2 force field method were similar, and only one of them is given in Fig. 2a. In both cases, the conformations of the fragments corresponding to the energy minimum were almost transoid: the $C^1C^6C^7C^8$ and $C^7C^8C^9C^{10}$ dihedral angles equaled –160° and –165°, respectively. The energy of the conformations at the angles –35° and 35° (Fig. 2a)

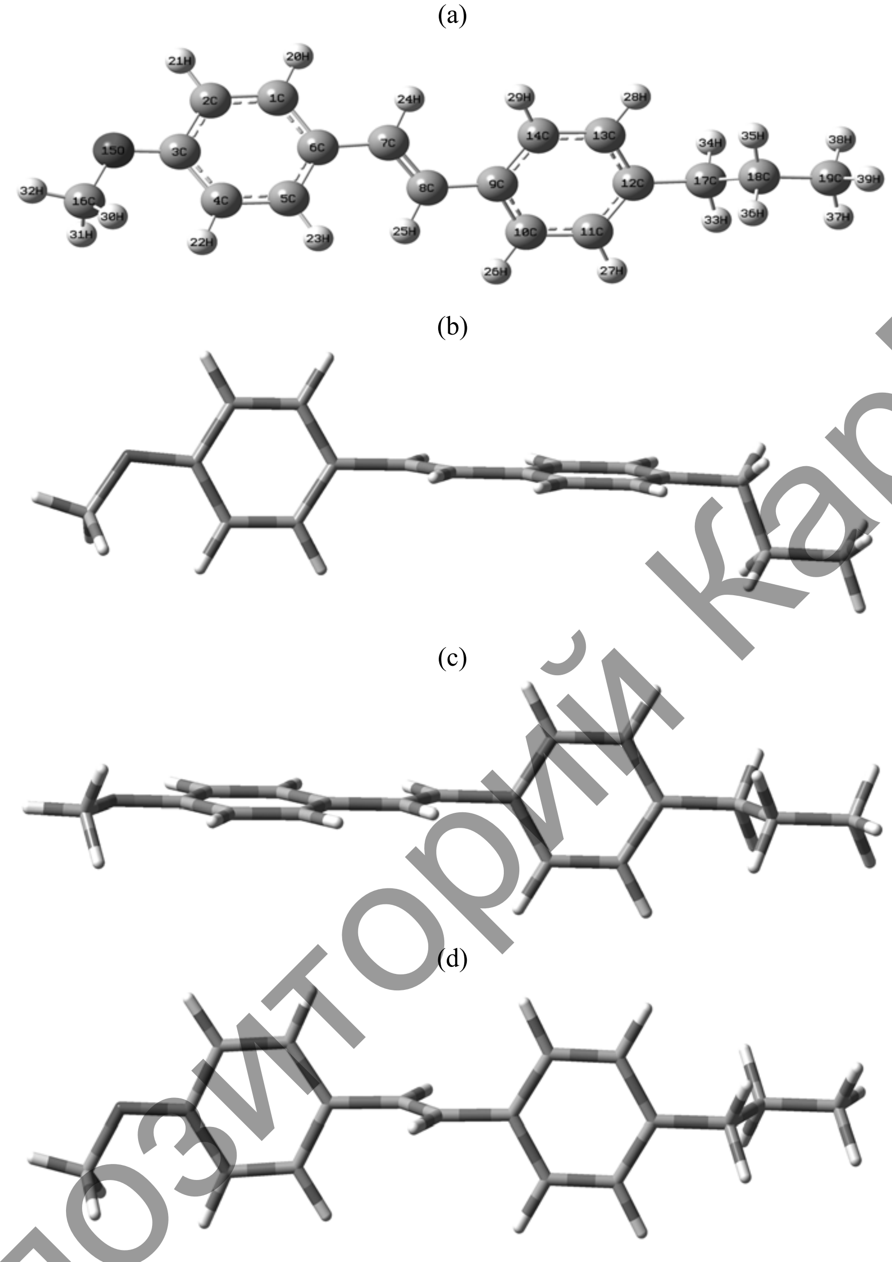

Fig. 1. Conformation of the 4,4'-methoxypropylstilbene molecule in the minimum (a) and the saddle points TS1 (b), TS2 (c), and TS3 (d) of the potential energy surface [B3LYP/6-31G(d) method].

for the rotation about the C^6–C^7 bond (for the C^8–C^9 bond, those angles were –35 and 30°) was increased due to the "skewed" interaction of the hydrogen atoms. The statistical factor for the skewed conformations equaled 2. Conformational equilibrium between the forms should be temperature-dependent: the almost transoid conformation should dominate at low temperature, and the fraction of the skewed forms should increase on heating. Hence, the low-energy (and exhibiting the smallest volume) transoid conformation likely exist in the crystal, and the skewed forms will appear upon melting. The conformational energy was more than twice lower than the barrier separating the conformations. For example, the potential barrier of the rotation about the C^6–C^7 and C^8–C^9 bonds was of 17–18 kJ/mol. The energy maximums corresponded to the perpendicular location of the planes of the ethylene bond and benzene rings. The rotation about the C^{12}–C^{17} bond (adjacent to the benzene ring) exhibited the double-well potential. The minimums at the PES

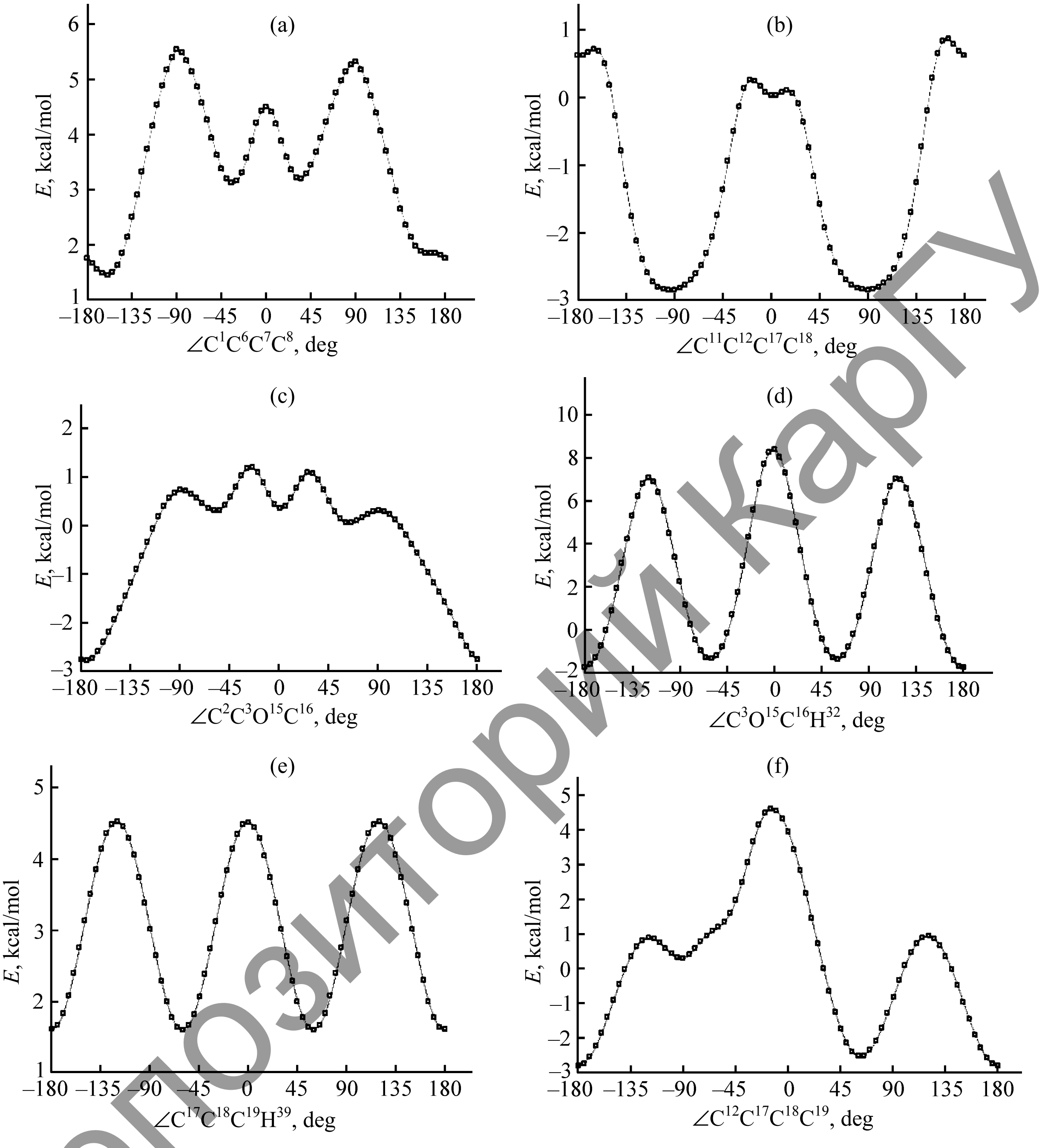

Fig. 2. (a–f) Sections of potential energy surface of the internal rotation of 4,4'-methoxypropylstilbene (force field method).

corresponded the almost degenerate conformations with the $C^{11}C^{12}C^{17}C^{18}$ angle –95° and 90° (Fig. 2b). The highest energy was found for the rotation angles –165° and 165°, corresponding to the closest proximity of the hydrogen atoms of the benzene ring and the methylene group. The barrier of the internal rotation was of almost 16 kJ/mol. The transoid and the skewed conformations were also possible for the C^3–O^{15} bond adjacent to the benzene ring (Fig. 2c). The conformational energy was of 10 kJ/mol, and the rotation barrier was about 16 kJ/mol. The rotation of the terminal methyl groups, like that in ethane, showed three minimums at φ ±60° and 180° corresponding to the staggered forms and three maximums at φ 0° and ±120° of the eclipsed forms (Figs. 2d, 2e) in the potential curve. The *trans*- and *gauche*-conformers were stable. The barriers were of 13–42 kJ/mol, the cosine height in the case (e) being 12.18 kJ/mol, Geometry of the ground state of 4-methoxy-4'-propylstilbene molecule (*d*, Å; φ, deg)

Bond, angle	MP2/6-31G(d)	B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d,p)
C^1–C^6	1.410	1.416	1.413	1.414
C^5–C^6	1.402	1.408	1.404	1.404
C^6–C^7	1.463	1.465	1.463	1.465
C^3–O^{15}	1.370	1.391	1.364	1.366
O^{15}–C^{16}	1.425	1.451	1.419	1.422
C^7=C^8	1.352	1.353	1.350	1.351
C^8–C^9	1.464	1.466	1.465	1.467
C^9–C^{10}	1.406	1.411	1.407	1.408
C^9–C^{14}	1.407	1.413	1.409	1.410
C^{11}–C^{12}	1.403	1.408	1.404	1.405
C^{12}–C^{17}	1.505	1.515	1.512	1.513
C^{17}–C^{18}	1.534	1.549	1.543	1.543
C^{18}–C^{19}	1.526	1.536	1.532	1.532
$H^{23}\cdots H^{25}$	2.204	2.147	2.150	2.155
$C^1C^2C^3$	120.39	120.19	120.46	120.41
$C^1C^6C^7$	123.03	123.69	123.89	123.89
$C^2C^3O^{15}$	115.22	115.55	115.72	115.78
$C^3O^{15}C^{16}$	116.72	118.75	118.20	118.51
$C^6C^7C^8$	125.76	127.21	127.36	127.32
$C^7C^8C^9$	125.28	127.10	127.18	127.14
$C^8C^9C^{10}$	122.75	123.77	123.91	123.94
$C^{10}C^{11}C^{12}$	121.28	121.43	121.54	121.59
$C^{11}C^{12}C^{17}$	120.88	121.03	121.10	121.14
$C^{12}C^{17}C^{18}$	112.07	113.18	113.17	113.41
$C^{17}C^{18}C^{19}$	112.57	112.72	112.88	112.87
$C^1C^6C^7C^8$	–160.194	–179.996	–179.913	–179.871
$C^2C^3O^{15}C^{16}$	179.642	–179.880	–179.939	–179.828
$C^3O^{15}C^{16}C^{32}$	179.938	179.792	179.873	179.816
$C^7C^8C^9C^{10}$	156.310	–179.655	–179.394	–178.926
$C^{11}C^{12}C^{17}C^{18}$	–87.531	–87.508	–87.302	–87.303
$C^{12}C^{17}C^{18}C^{19}$	179.996	–179.936	–179.944	–179.946
$C^{17}C^{18}C^{19}C^{39}$	179.995	–179.867	–179.856	–179.955

almost equal to the experimental barrier of the internal rotation in ethane (12.20±0.20 kJ/mol [3]). The potential of the ethyl group rotation about the C^{17}–C^{18} bond was noticeably different, being asymmetrical.

To refine the molecular mechanics results and to evaluate the effect of the choice of the basis set and the simulation method on the geometry and physicochemical properties of 4,4'-methoxypropylstilbene, we performed the quantum-chemical simulations by means of the perturbation theory and density functional theory methods in the split-valence basis sets including polarization and diffuse functions, aiming to optimize the geometry and find the transition states of the molecule.

The B3LYP simulation has revealed the almost full coplanarity of the conjugated system (the benzene rings and the ethylene bond) and orthogonal location of the alkyl substituent in the low-energy conformation (Fig. 1a), qualitatively confirming the MM2 results. The introduction of polarization and diffuse functions shortened the bonds in the molecule (by 0.010–0.032 Å), but they were still longer in comparison with the MP2 values, evidencing the more accurate account for the electronic correlation in the B3LYP method. The difference in the bond angles determined using the perturbation and density functional theories was 0. 1°–2.4°, the MP2 method giving the lower values (see the table). The values of dihedral angles obtained using those methods were close, except for the angles of the

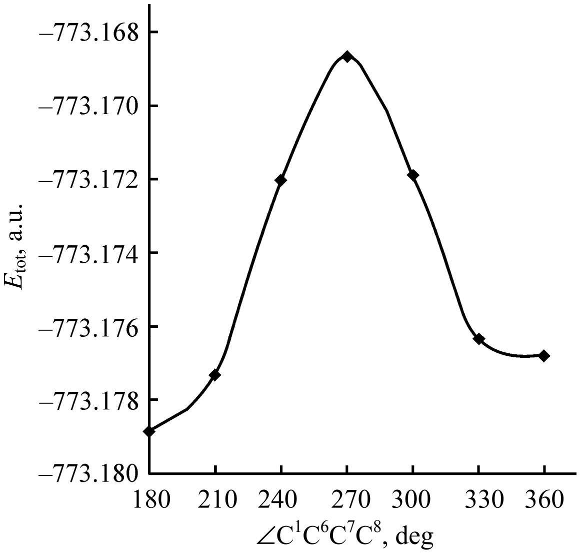

Fig. 3. Change in the total electron energy of 4,4'-methoxypropylstilbene during rotation of one of the benzene rings [B3LYP/6-31G(d) method].

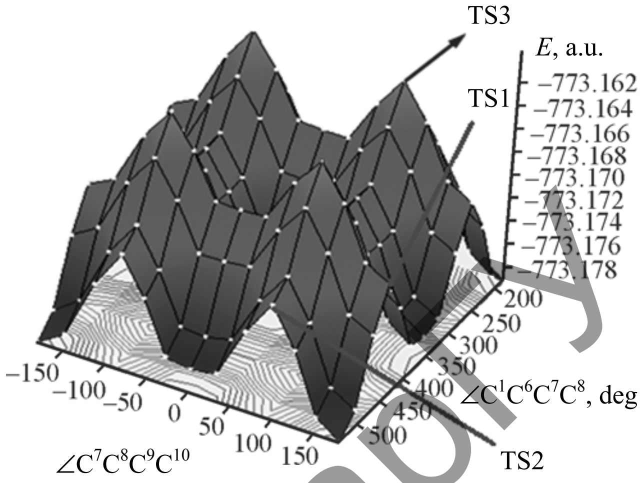

Fig. 4. Potential energy surface of 4,4'-methoxypropylstilbene at simultaneous rotation of two benzene rings [B3LYP/6-31G(d)].

benzene rings rotation: the B3LYP method revealed that the benzene rings deviated from the double bond plane by about 20°. The simulations revealed the expected decrease in the dipole moment μ {1.608 D (B3LYP/6-31G), 1.476 D [B3LYP/6-31+ G(d,p)]}, energy gap $E_{\text{LUMO–HOMO}}$ {0.14743 a.u. (4.012 eV) (B3LYP/6-31G); 0.14326 a.u. (3.898 eV) [B3LYP/6-31+G(d,p)]}, and full electronic energy E {–772.991983 a.u. (B3LYP/6-31G); –773.233636 a.u. [B3LYP/6-31+G(d,p)]} of the molecule with the increase in the simulation level. The corresponding MP2 values of the $E_{\text{LUMO–HOMO}}$ [0.35390 a. u. (9.630 eV)] were much higher, and the E (–768.120118 a. u.) and μ (1.450 D) were lower.

In the MM2 simulation, the energy maximums were observed at orthogonal location of the ethylene bond and benzene rings planes. Scanning of the PES (along certain coordinate) using the B3LYP method gave similar coinciding results for the $C^1C^6C^7C^8$ (Fig. 3) and $C^7C^8C^9C^{10}$ angles. The transition states TS1 and TS2 of the molecule (Figs. 1b, 1c) were refined via the full optimization and vibrational simulation: they corresponded to the first-order saddle points with a single imaginary frequency, i.e. true transition states. The TS1 structure [energy with account for the zero vibrations E –772.837411 a.u., B3LYP/6-31G(d)] appeared due to the rotation of the molecule fragment about the C^6–C^7 bond (the $C^1C^6C^7C^8$ angle 90.01°, Fig. 3), and the TS2 structure [E –772.837809 a.u., B3LYP/6-31G(d)] resulted from the rotation about the C^8–C^9 bond (the $C^7C^8C^9C^{10}$ angle –90.55°). The lower energy of the TS2 structure was probably due to the preserved coplanarity of the fragment with the π,π- and *p*,π-conjugation, whereas the coplanarity was partially broken in the TS1 structure. The bond lengths and angles (besides those of the central ethylene bond) were practically unchanged. The double C^7=C^8 bond was shortened by 0.007 Å in the TS1 and TS2 structures, whereas the ordinary C–C bond became longer by 0.027 (C^6–C^7) and 0.006 Å (C^8–C^9) for the TS1 structure; and by 0.006 (C^6–C^7) and 0.025 Å (C^8–C^9) for the TS2 structure. The noticeable lengthening of the bonds was evidently owing to the broken π,π-conjugation. The rotation barriers were as follows: without accounting for the zero vibrations 23.04 [TS1, B3LYP/6-31G(d)] and 22.01 kJ/mol [TS2, B3LYP/6-31G(d)]; with accounting for the zero vibrations 21.87 [TS1, B3LYP/6-31G(d)] and 20.82 kJ/mol [TS2, B3LYP/6-31G(d)]. The relatively low barriers evidenced the high torsion flexibility of the stilbene derivatives.

The simultaneous rotation of two benzene rings of 4,4'-methoxypropylstilbene molecule gave rise to a new transition state TS3 in the PES (Fig. 1d) corresponding to the conformation with torsion angles between the benzene ring and the ethylene bond planes equaling 90° (Fig. 4). The vibrational analysis showed that the TS3 structure was the second-order saddle point. The observed global minimums corresponded to the conformations with absolute coplanarity of the *p*,π- and π,π-conjugated fragments. The internal rotation barrier for the TS3 structure [49.89 kJ/mol without accounting for the zero vibrations, B3LYP/6-31G(d)] was almost twice higher than those for the TS1 and TS2 structures, due to the completely broken π,π-conjugation in the molecule. Therefore, the non-synchronous rotation of the phenyl rings in the molecule was likely favorable.

In summary, we estimated the potentials of rotations about each of the ordinary bonds in the 4,4'-methoxypropylstilbene molecule using molecular mechanics simulation. Final conclusion on the conformations, rotation potentials, and transition states of the molecule was drawn using the density functional theory simulation. First- and second-order saddle points were found in the PES of the stilbene.

EXPERIMENTAL

Potential energy as a function of the internal rotation angles was studied by means of molecular mechanics using the Ellinger MM2 extended force field method. Structure optimization and vibrational analysis of the stable conformer of 4,4'-methoxypropylstilbene were performed using the quantum-chemical methods [perturbation theory MP2 and density functional theory with correlation functional B3LYP in the split-valence basis sets 6-31G, 6-31G(d), and 6-31+G(d,p)] implemented in Gaussian software [18]; the transition states were simulated using the B3LYP/6-31G(d) method. Since the molecule was asymmetric, the local symmetry of methylene and methyl groups was not accounted for. The stationary points were identified by means of vibrational analysis. Energetics of the rotations was determined with and without accounting for the zero vibrations.

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