Buckybowl Structure of Sumanenes and Distortions of Thiophenes Induced by the Pseudo Jahn-Teller Effect

N N Gorinchoy¹, I Arsene¹², I B Bersuker¹³

¹Department of Quantum Chemistry, Catalysis and Physics Methods, Institute of Chemistry, Kishinev, Republic of Moldova
²Biology and Chemistry Faculty, Tiraspol State University, Kishinev, Republic of Moldova
³Institute for Theoretical Chemistry, The University of Texas at Austin, Austin TX 78712, USA

ngorinchoy@yahoo.com

Abstract. We extended the procedure of pseudo Jahn-Teller effect (PJTE) analysis of the origin of instability of molecular high-symmetry configuration to relatively large organic compounds containing several ring-structures by exploring two types of possible distortions: the buckyball non-planarity of sumanenes and its derivatives, and the torsional rotations in two-ring and four-ring thiophenes. We performed electronic structure calculations of the ground and several excited states of these systems and revealed their main excited states that contribute to their instability in the ground state as well as the numerical values of the parameters of the PJTE. The findings describe in detail the interim mechanism that controls the main structural properties of these compounds, opening the possibility to manipulate them by targeting the PJTE features that are vulnerable to external influence. Among other details, the analysis of the PJTE shows how tri-atomic substitutions in sumanenes influence their buckling instability, especially the intriguing origin of the difference between tri-oxygen and tri-sulfur substitutions, the former being much stronger than the latter. The worked out procedures of application of the PJTE theory to such relatively large organic compounds can be used for studies of other systems and other kind of distortions.

1. Introduction

A series of bowl shaped molecular systems containing five, six, or more contiguously linked carbon rings may serve as structural elements of fullerenes and nanotubes, with possible applications in molecular electronics (see, e.g., review [1] and references therein). Similarly, polythiophenes are used in organic electronics [2]. In the usual methods of electronic structure calculations [2-4] the main properties of these compounds are revealed, but their origin is not explained. Meanwhile, from the general theory [5, 6] it follows that the deviation from the high-symmetry planar configuration of these compounds is induced by the pseudo Jahn-Teller effect (PJTE). Encouraged by this understanding, we performed electronic structure calculations of the ground and several excited states for a series of sumanene and its derivatives, as well as several many-ring thiophenes, and revealed the main excited states that contribute to the instability of the ground state, and the numerical values of the parameters of the underlying PJTE.
Sumanene is a typical representative of the class of compounds known as molecular bowls, or buckybowls [1, 3]. Heterosumanenes with benzylic positions substituted by heteroatoms have been reported as well [3, 4, 7, 8]; the replacement of skeletal carbon atoms by isoelectronic substituents was shown to be most effective in modulating the curvature, bowl-to-bowl inversion barrier, and the consequent physicochemical properties [3, 4] (see also adsorption of small molecules [9, 10]). With regard to torsional distortions in thiophenes, the PJTE explains the origin of their main structural features and provide us with a key to manipulate their planarity by means of external influence that change the parameters of the PJTE. For this purpose we used two thiophene-based systems, bithiophene, C₈H₆S₂, and model oligothiophene 2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]-thiophene (BTTT). This kind of conformational flexible molecules is studied extensively because they constitute the units of polythiophenes, which are used in organic electronics (see, for example, [2] and references herein), making the problem of reducing the conformational flexibility and planarization of such systems very topical. The specific information obtained by the PJTE analysis, including numerical estimates of the parameter values, is important also in view of applications that may require manipulation of their structure by means of external (targeted) influence of the PJTE parameters, as described recently [11-13].

For all the considered molecules the geometry optimization and vibrational frequency analysis in the planar high-symmetry and equilibrium nuclear configurations were carried out at the B3LYP level of DFT method [14]. All the calculations were performed with the GAUSSIAN09 package [15]. The Pople’s 6-31+G(d,p) split basis sets [16] were utilized in all steps of the calculations. The potential energy profiles along the normal distortion coordinates were calculated with the CISD method. The numerical values of the vibronic coupling constants were estimated by means of fitting the solutions of the secular equations to the ab initio calculated energy profiles (described in detail, for example in [17, 18] for three- and four-levels PJTE problems).

2. The PJTE origin of buckyball structure of sumanenes

2.1. Planar and Non-Planar Equilibrium Configurations

As usually in the study of the PJTE, we start with the nuclear configuration of the highest possible symmetry, in our case, the planar configuration of D₃h symmetry. Calculations of all the compounds under consideration in the planar nuclear configuration of D₃h symmetry show the presence of only one imaginary frequency corresponding to the out-of-plane distortions of a₂ symmetry, which transforms the planar D₃h nuclear configurations into the equilibrium buckyball structures of C₃v symmetry (figure 1).

![Figure 1. Puckering normal mode a₂ in heterosumanenes C₁₈X₃H₆ (X=BH, CH₂, NH, O and S) in the planar D₃h configurations. The numbers 1-6 denote carbon atoms C₁-C₆ of the inner cycle (hub ring), numbers 7-12 denote the carbon atoms C₇-C₁₂ connected with heteroatoms, and numbers 13-18 denote the carbon atoms C₁₃-C₁₈ of external cycles (rim six-membered ring).](image-url)
The most important calculated parameters characterizing the degree of distortion (bowl depth (BD), and rigidity of the systems (bowl-to-bowl inversion barrier (IB), values of imaginary frequencies (IF) and the curvature of the APES along the \( a_2'' \) distortion in the planar \( D_{3h} \) configuration) are given in the table 1. It is seen that both the bowl structure and rigidity of the systems vary considerably depending on the heteroatoms. All the parameters increase with increasing electronegativity of the atoms of the second row of the Periodic Table of elements, from triborasumanene to trioxosumanene, and decrease substantially in trithiasumanene.

**Table 1.** Bowl Depth, BD (Å), Bowl-to-Bowl Inversion Barrier, IB (kcal/mol), Curvature \( K \) (eV/Å\(^2\)) of the APES along the \( a_2'' \) distortion, calculated by a point-by-point procedure, and corresponding Imaginary Frequency, IF (cm\(^{-1}\)) for the series of heterosumanenes \( C_{18}X_3H_6 \) (\( X=\text{BH, CH}_2, \text{NH, O and S} \)) obtained at the B3LYP/6-31 level of theory.

| Parameters | Molecule | X  | TP a) | BH | CH\(_2\) | NH | O  | S  |
|------------|----------|----|-----|----|--------|----|----|----|
| BD         |          | 0  | 0.825 | 1.089 | 1.258 | 1.423 | 0.321 |
| IB         |          | 0  | 5.17  | 18.26 | 42.63 | 64.67 | 0.13  |
| \( K \)    |          | -  | -1.31 | -2.74 | -4.81 | -7.86 | -0.27 |
| IF         |          | -  | 88.60i | 129.25i | 168.47i | 184.24i | 34.20i |
| Normal modes in Cartesian coordinates z | | C1-C6 | - | +0.0888 | +0.0903 | +0.0920 | +0.0922 | +0.0926 |
|            | C7-C12   | - | +0.0034 | +0.0012 | +0.0002 | +0.0006 | +0.0129 |
|            | C13-     | - | -0.0587 | -0.0589 | -0.0552 | -0.0567 | -0.0491 |
|            | C18      | - | -0.0407 | -0.0348 | -0.0401 | -0.0397 | -0.0353 |
|            | X        | - | -0.1251 | -0.1247 | -0.1139 | -0.1159 | -0.1128 |
|            | H        | - | -0.1033 | ±0.0300 | -0.0945 |

\( a_2'' \) distortion in the planar \( D_{3h} \) configuration.

\(^{a)}\) TP denotes triphenylene molecule, \( C_{18}H_{12} \).

All the considered molecules in the planar nuclear configurations of \( D_{3h} \) symmetry have a non-degenerate ground electronic states, \( ^1A_1' \). According to the general theory, since the instability coordinate transforms as \( a_2'' \), only excited states of the \( A_2'' \) symmetry can contribute to the instability of the ground state, with \( F^{(0,1)} = \left\langle A_1' \right| \left( \partial H / \partial Q_{a_2''} \right) \bigg| A_2'' \rangle \neq 0 \). To clarify which one-electron excitations \( i \rightarrow \alpha \) can yield such excited states, consider the MO energy levels schemes of the systems (figure 2). It is seen that in all the compounds, the 12 \( p_\pi \)-electrons occupy the highest-lying MOs, they are denoted as \( i''\)-MOs in figure 2. The lowest unoccupied MOs are also formed by \( p_\pi \)-AOs of the atoms (\( a''\)-MOs in figure 2). The occupied \( \sigma \)-MOs of \( i'\)-symmetry are located lower than \( \pi \)-MOs, and, respectively, the unoccupied \( \sigma \)-orbitals (\( \alpha'\)-symmetry) lie above the unoccupied \( \pi \)-MOs. From this scheme we can see that the excited electronic states of \( A_2'' \) symmetry can be formed by one-electron excitations \( e'' \rightarrow e', \) and \( e' \rightarrow e'' \).
Figure 2. MO energy levels schemes of heterosumanenes in the D_{3h} ground $^1A_1'$ electronic state with indication of the one-electron excitations $i \rightarrow \alpha$ to $^1A_2''$ excited states.

Such an arrangement of the molecular energy levels shows that the low-energy band consists of $A_1'$, $A_2''$, and $E'$ energy terms. The excited states of $A_2''$ symmetry lie rather high in energy (figure 3). We note also that the substitution of CH$_2$ groups in benzylic positions of the sumanene molecule by heteroatoms significantly changes the relative energies of the $A_2''$ excited states.

Figure 3. Ab initio calculated relative energies of the ground $A_1'$ and excited $A_2''$ states in the series of heterosumanenes.
2.2. PJTE in sumanene C$_{21}$H$_{12}$

Consider the cross section of the APES of the sumanene molecule along the $a_{2}''$ distortion coordinate, showing the ground and four low-lying excited states of $A_{2}''$ symmetry, as illustrated in figure 4.

Figure 4. Ab initio calculated energy profiles for the ground $A_{1}'$ and for four excited $A_{2}''$ electronic terms of the sumanene molecule along the $a_{2}''$ out-of-plane displacements. As $Q_{a_{2}''}$ coordinate values, we used the bowl depths at each point.

In order to estimate which of these excited states contribute essentially to the instability of the ground state, we have carried out some additional calculations. In our previous works [12, 14, 19-22] it was shown how the change in the occupancies of certain molecular orbitals affects the PJTE resulting in either additional buckling of two-dimensional (2D) molecular system or in the restoration of its planar nuclear configuration. If the orbital is not involved in the formation of the PJTE-active excited state, change of its population has no significant influence on the PJTE. Thus, analysis of the change of the PJTE in the charged states of the molecule allows us to make indirect conclusions about the activity of the excited state in the PJTE.

In the sumanene molecule the first excited state of $A_{2}''$ symmetry is mainly formed by one-electron excitation from the HOMO of $e''$ symmetry to the LUMO+4 of $e'$ symmetry. Then the removal of two electrons from the HOMO should reduce approximately by half the negative PJTE contribution of this state to the curvature of the APES. Indeed, the vibronic contribution $K_{v1}$ is equal to $-8f^2/\Delta$ in the neutral molecule versus $-4f^2/\Delta$ in its radical dication, where $f$ is the orbital vibronic coupling constant (OVCC) $f = \langle e_x'' \mid (\partial H/ \partial Q_z)_0 \mid e_x' \rangle$, that mixes the occupied $e'$ and unoccupied $e''$ MOs. If this value $K_{v1}$ is sufficiently large, the absolute value of the curvature of the AP in the dication decreases, which, in turn, decreases the value of the imaginary frequency in the dication, compared with the neutral molecule. However, calculations show that the imaginary frequency remains practically unchanged (129.25$^i$ for the neutral molecule versus 124.19$^i$ for dication).

The second $A_{2}''$ excited state is formed mainly by the one-electron excitation from the HOMO-4 of $e'$ symmetry to the LUMO of $e''$ symmetry. In this case the addition of two electrons to the LUMO
also reduces the PJTE negative contribution $K_{32}$ to the curvature of the APES approximately by half. Again, if the value of $K_{32}$ is big enough, then the value of the imaginary frequency should decrease. However, in this case, too, the imaginary frequency varies insignificantly (133.87).

All this allows us to conclude that the first and the second excited states give insignificant contributions to the curvature of the ground state APES. This can be explained by the fact that both the HOMO $e''$ and the LUMO $e''$, which participate in the formation of the first and the second excited $A_2''$ states, do not contain AOs of benzylic carbon atoms. Therefore, the vibronic interaction of the ground state with the $1A_2''$ and $2A_2''$ excited states does not change the interaction of carbon atoms and heteroatoms in benzylic positions with near-neighbour carbon atoms $C_7$-$C_{12}$. These MOs are almost the same as in a triphenylene molecule, where excited states formed with participation of these MOs do not provide instability of the ground state, so the triphenylene molecule is planar.

The contribution of the higher excited states not taken into account in PJTE analysis was discussed in the literature (see, e. g., [23, 24]). It can be taken into account by means of an additional second order perturbation correction, which slightly changes the revealed vibronic coupling parameters, provided the main active excited states are included in the PJTE secular equation. These active excited states can be determined without second order corrections, just from the estimate of the force constants of the ground state, which should become negative when the correct excited state are included in the calculations.

Hence we can assume that the instability of the planar nuclear configuration of the sumanene molecule is provided by the PJT coupling of the ground state with the third and fourth excited $A_2''$ electronic states, that is, in this case we have a three-level PJTE problem ($A_{1'} + 3A_2'' + 4A_2'$$/\theta a_{1''}$). Using the well-known procedure of fitting the secular equation to the calculated energy profiles [17, 18], we can estimate the parameters of the PJTE coupling, as presented in Table 2.

| Molecule                      | $K_0$ | $\Delta_{03}$ | $F_{03}$ | $K_{33}$ | $\Delta_{04}$ | $F_{04}$ | $K_{34}$ | $K_0 + K_{33}$ | $K_0 + K_{34}$ | $K_0 + K_{33} + K_{34}$ |
|-------------------------------|-------|---------------|----------|----------|---------------|----------|----------|----------------|----------------|------------------------|
| Sumanene, $C_{21}H_{12}$      | 8.60  | 13.91         | 6.03     | -5.23    | 14.32         | 6.51     | -5.90    | -11.13         | -11.13         | -2.53                  |
| Trioxasumanene, $C_{18}O_3H_6$| 7.8   | 12.1          | 7.21     | -8.59    | 13.8          | 6.95     | -7.00    | -15.59         | -15.59         | -7.79                  |
| Trithiasumanene, $C_{18}S_3H_6$| 8.8   | 11.1          | 5.05     | -4.60    | 12.2          | 5.24     | -4.50    | -9.10          | -9.10          | -0.30                  |

At small values of the displacements $Q$ the curvature of the APES for the ground state can be estimated approximately as $K \approx K_{00} + K_{03} + K_{33}$, where $K_{03} = -2F_{03}/\Delta_{03}$, and $K_{33} = -2F_{03}/\Delta_{03}$. With the parameters from Table 2 we get $K_{03} = -5.23 \text{ eV}/\text{Å}^2$, $K_{33} = -5.90 \text{ eV}/\text{Å}^2$, so the resulting value of the curvature $K$ is negative, equal to $-2.53 \text{ eV}/\text{Å}^2$. Thus, we conclude that the instability of planar $D_{3h}$ nuclear configuration of the sumanene molecule and its bowl structure is due to the PJT coupling of the ground $A_{1'}$ state to the two excited $A_2''$ states, which thus can be targeted for external manipulation. Obviously, the estimated parameter values are approximate, but they are approximately correct, and they confirm the PJTE mechanism of the configuration distortions.

2.3. **PJTE in trioxasumanene** $C_{18}O_3H_6$ and **trithiasumanene** $C_{18}S_3H_6$

Consider now how the PJTE changes in trioxasumanene and trithiasumanene molecules in which three benzylic CH$_2$ groups in the sumanene molecule are substituted by oxygen and sulfur atoms, respectively. Just as in the case of sumanene, in the trioxasumanene molecule, the first and second $A_2''$
excited states are mainly formed by one-electron excitations HOMO (\(e''\))→LUMO+4 (\(e'\)) and HOMO-4(e'→LUMO (e''), respectively (figure 5).

![Figure 5. Ab initio calculated energy profiles for the ground A_1' and four excited A_2'' electronic terms of trioxasumanene and trithiasumanene molecules along the a_2'' coordinate.](image)

Again, the removal of two electrons from the HOMO and the addition of two electrons to the LUMO reduce the PJTE negative contributions \(K_{v1}\) and \(K_{v2}\) to the curvature of the APES approximately by half, thereby reducing the absolute value of the curvature of the APES, which in turn should lead to a decrease in the values of the imaginary vibrational frequencies in the corresponding dication and dianion. However, the analysis of the frequencies in the oxidative and reduced forms of the trioxosumanene molecule shows that these values change insignificantly: 184.24\(i\) for the neutral molecule versus 185.81\(i\) for the dication and 186.57\(i\) for the dianion. Therefore, in this case, similar to the sumanene molecule, we conclude that the first and the second A_2'' excited states do not contribute to the instability of the ground state, thus dealing with the similar three-level PJTE problem (\(A_1'+3A_2''+4A_3'\))\(\otimes a_2''\). The values of the PJTE parameters estimated by the fitting procedure for this system are listed in table 2.

Note that the energy gaps between the ground and the corresponding excited states of A_2'' symmetry in this case are smaller compared with the sumanene molecule. On the other hand, the values of the vibronic coupling constants increase, because the contributions of the oxygen 2p-AOs in the mixing molecular orbitals are larger than those of the benzylic carbon atoms in the sumanene molecule. Both these factors, decrease of the energy gaps and increase of the vibronic coupling constants, lead to enhancement of the PJTE in the trioxosumanene molecule, which results in a stronger distortion.

In the trithiasumanene molecule, substitution of oxygen atoms by sulfur atoms leads to two opposite effects. Firstly, the energy gaps in this case are somewhat smaller compared to the trioxosumanene molecule, which enhances the PJTE. However, the main effect of this substitution is the significant decrease in the values of the vibronic coupling constants (see table 2) that leads to the
suppression of the PJTE. This decrease can be explained by taking into account that the orbital vibronic coupling constant is proportional to the derivative of the overlap integral of atomic orbitals of neighboring atoms, which characterizes the rate of change of interatomic coupling under distortion [5, p. 544]. In the case under consideration the changes in overlap of the more diffuse 3p-orbitals of the sulfur atoms with the 2p-AOs of near-neighbor carbon atoms are significantly slower than that between the 2p-AOs of the oxygen and carbon atoms. The same effect of planarization of the frameworks is expected to takes place in trisilasumanenes [7] and trigarmasumanenes [8].

To summarize, tri-atomic substitutions in sumanenes influence their buckling instability; more electronegative oxygen atoms enhances the PJTE due to the donation of additional electronic charge to the \( \pi \)-system of the sumanene molecule resulting in a stronger distortion, whereas in trithiasumanene \( \text{C}_{18}\text{S}_3\text{H}_6 \), the OVCC decrease and the PJTE is suppressed, resulting in a smaller distortion.

3. The PJTE origin of torsion barriers to rotation in thiophene-based heterodimers. Two models of oligothiophene systems.

Somewhat complementing the buckyball distortions in sumanenes, we investigated another kind of distortions of multi-ring systems induced by the PJTE, the mutual ring rotations multi-ring thiophenes. For this reason, we considered two thiophene-based systems, 2,2′-bithiophene, \( \text{C}_8\text{H}_6\text{S}_2 \), and model oligothiophene 2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]-thiophene (BTTT), with the goal to rationalize the origin of their torsional instability, to reveal the excited states that are responsible for the PJTE leading to the instability, and with estimated energy gaps and vibronic coupling constants, to predict the possibility of planarization of these molecules. Although both twisted cis- and trans-conformations are discussed in the literature, here we have studied only 2,2′-bithiophene (\textit{syn} structure) and BT TT molecule in \textit{syn-syn} conformation [2].

Starting with the planar reference configurations, ab initio calculations of the electronic structure and vibrational frequencies of the systems in their high-symmetry nuclear configurations were carried out. The reference nuclear configuration of \textit{syn-C}_8\text{H}_6\text{S}_2 molecule is a planar structure of \( \text{C}_{2v} \) symmetry. Calculations for this configuration show the presence of one imaginary frequency corresponding to the out-of-plane distortions of \( a_2 \) symmetry, which corresponds to rotation of the two heterocycles around the central \( \text{C}_1-\text{C}_2 \) bond, which transforms the planar \( \text{C}_{2v} \) nuclear configuration into the twisted structure of \( \text{C}_2 \) symmetry at equilibrium (figure 6).

![Figure 6](image-url)  
Figure 6. Twisting \( a_2 \) normal mode of the \( \text{C}_8\text{H}_6\text{S}_2 \) molecule in the planar \( \text{C}_{2v} \) configuration (\textit{syn} structure).

In the planar \( \text{C}_{2v} \) nuclear configuration the system has a nondegenerate ground electronic state \( ^1\text{A}_1 \). Therefore, only the excited states of \( ^1\text{A}_2 \) symmetry can produce the instability of the ground state. In figure 7(b) the MO energy levels and the calculated energy profiles along the instability coordinate \( a_2 \) for the ground \( ^1\text{A}_1 \) and the low-lying excited \( ^1\text{A}_2 \) states of \( \text{C}_8\text{H}_6\text{S}_2 \) molecule are presented. The first excited \( ^1\text{A}_2 \) state is formed by the one-electron excitation from the HOMO of \( a_2 \) symmetry to the LUMO+3 of \( a_1 \) symmetry (figure 7(a)), the \( ^2\text{A}_2 \) state corresponds to the excitation \( a_2(\text{HOMO}-1)\rightarrow a_1(\text{LUMO}+3) \), while the \( ^3\text{A}_2 \) state is formed by the one-electron excitation \( b_{11}(\text{HOMO}-2)\rightarrow b_2(\text{LUMO}+2) \).
In order to identify which of these excited states are most strongly mixed with the ground state, leading to the symmetry breaking and distortion of the system, the following considerations can be useful. At small Q values, the curvature $K$ of the APES of the ground state can be written as $K=K_0+K_1+K_2+K_3$, where $K_3=2F_0^2/\Delta_3=4f_{22}^2/\Delta_3$ is the vibronic contribution to the $K$ provided by the $i$-th excited state, $F_0$ is the vibronic coupling constant between the ground and this state, $\Delta_i$ is the relative energy of the $i$-th excited state, and $f_i$ are the OVCCs between the mixing molecular orbitals, $f_1=\langle 2a_2 | (\partial H / \partial Q_{x})_0 | 1a_1 \rangle$, $f_2=\langle 1a_2 | (\partial H / \partial Q_{x})_0 | 1a_1 \rangle$, and $f_3=\langle 1b_2 | (\partial H / \partial Q_{x})_0 | 3b_1 \rangle$. Then, the removal of one electron from the HOMO reduces approximately by half the value of the $K_1$ provided by the first $1A_2$ excited state ($4f_{12}^2/\Delta_1$ in the neutral molecule versus $2f_{12}^2/\Delta_1$ in its radical cation), and therefore reduces the absolute value of $K$. The analysis of the vibrational frequencies in the planar C_{2v} configuration of the cation (C_8H_6S_2)^+ shows the absence of any imaginary frequency, that is, the planar geometry of the cation is at equilibrium. It means that the first excited $1A_2$ state contribute essentially to the instability of the ground state of the C_8H_6S_2 molecule.

Similarly, the addition of one electron to the LUMO reduces approximately by half the PJTE negative contribution $K_3$ to the curvature of the APES provided by the third $1A_2$ excited state ($4f_{32}^2/\Delta_3$ in the neutral molecule versus $2f_{32}^2/\Delta_3$ in its radical anion). Calculations of the anion (C_8H_6S_2^-) indicate that this species too is planar (no imaginary frequencies). Therefore, the vibronic coupling of the ground and the $3^1A_2$ excited states, too, gives the essential negative contribution to the curvature of the APES of the ground states of bithiophene molecule. As for the second $2^1A_2$ excited state, it can be assumed that its vibronic mixing with the ground state is less significant in comparison with the first and the third states. The rationale in this assumption is that, although the curvature $K_2$ of the APES of this state is positive, its value is several times smaller than those for the $1^1A_2$ and $3^1A_2$ states. Therefore, we can assume that in this case the three-level PJTE problem ($A_1+1A_2+3A_2$)⊗$a_2$ is
approximately valid for describing the instability of the ground state, provided that the vibronic contribution to the curvature from the \(2^1\text{A}_2\) excited state is included in the primary force constant \(K_0\). Fitting the secular equation to the calculated energy profiles yields the following values of PJTE parameters: \(K_0=2.52\) eV/Å\(^2\), \(F_{01}= 2.41\) eV/Å, \(F_{03}= 2.32\) eV/Å. Calculated energy gaps are: \(\Delta_1= 7.10\) eV and \(\Delta_1= 9.50\) eV. Then, at small displacements \(Q\), \(K \approx K_0+K_v1+K_v3\), where \(K_v1= -1.63\) eV/Å\(^2\), and \(K_v3= -1.15\) eV/Å\(^2\). The value of the curvature of the APES becomes negative, \(K= -0.26\) eV/Å\(^2\). With the obtained parameter values, we can also estimate the curvature in the cation and the anion state of the molecule: \(K_{\text{cat}}= +0.54\) eV/Å\(^2\), and \(K_{\text{an}}= +0.32\) eV/Å\(^2\), indicating that corresponding radicals are planar.

The reference nuclear configuration of \(\text{syn-syn-BTTT}\) molecule is its planar structure of \(C_{2h}\) symmetry. Calculations show that this configuration is unstable (one imaginary frequency) with respect to the twisting distortions of \(b_g\) symmetry, which corresponds to the rotation of two heterocycles around the \(C_1-C_2\) and \(C_3-C_4\) bonds. This distortion transforms the planar \(C_{2h}\) nuclear configuration into the equilibrium twisted structure of \(C_i\) symmetry (figure 8).

Figure 8. The twisting \(b_{1g}\) normal mode in the \(C_{14}H_8S_4\) molecule in the planar \(C_{2h}\) configuration (\(\text{syn-syn}\) conformer).

The ground electronic state of the \(C_{14}H_8S_4\) molecule in the planar \(C_{2h}\) configuration is the nondegenerate one \(^1\text{A}_g\). The distortion along the \(b_h\) coordinate is due to the PJTE mixing of the ground state with the excited one of \(^1\text{B}_g\) symmetry. The MO energy levels scheme and the calculated energy profiles along the instability coordinate \(b_g\) for the ground \(^1\text{A}_g\) and the low-lying excited \(^1\text{B}_g\) states of the \(C_{14}H_8S_4\) molecule are presented in figure 9.
Figure 9. (a) MO energy level scheme for the C_{14}H_{8}S_{4} molecule in the ground \(A_g\) state with indication of the one-electron excitations to \(B_g\) terms; (b) ab initio calculated energy profiles along the \(b_g\) twisting coordinate for the ground \(1A_g\) and three excited \(B_g\) electronic terms. As the \(Q_{bg}\), we used the values of the out-of-plan displacements of peripheral sulfur atoms.

The first (1\(B_g\)) and the second (2\(B_g\)) excited states are mainly formed by one-electron excitations \(a_d(\text{HOMO})\rightarrow b_u(\text{LUMO}+2)\) and \(a_d(\text{HOMO}-2)\rightarrow b_u(\text{LUMO}+2)\), respectively, and the 3\(B_g\) state corresponds to the excitation \(b_g(\text{HOMO}-1)\rightarrow a_d(\text{LUMO}+3)\). It is seen from figure 9 that the first \(B_g\) states have a negative curvature meaning that it is influenced by higher states with positive curvature (at least, the next one 2\(B_g\)). Notwithstanding, the 1\(B_g\) state gives a significant negative contribution to the curvature of the ground state. This follows from the fact that, as in the previous case, the removal of one electron from the HOMO leads to planarization of the cation (\(C_{14}H_{8}S_{4}\)^+). Therefore the approximate PJTE problem in this case should be at least \((A_g+1B_g+2B_g)\otimes b_g\). The argument that the second 2\(B_g\) state also contributes significantly to the curvature of the ground state is as follows. The analysis of the atomic orbital populations in both the planar and distorted configurations shows that under the distortion, the populations of \(p_{\pi}\)-AOs of the central sulfur atoms decrease, whilst populations of their \(p_{\sigma}\)-AOs increases. From figure 9 it is seen that the latter describes the redistribution of the electron density. The third \(B_g\) state lies rather high in energy and has a strong negative curvature. So we can assume that this state gives only insignificant contribution to the curvature of the ground state. Solving the three-level \((A_g+1B_g+2B_g)\otimes b_g\) PJTE problem with the use of the procedure of fitting [ ], we obtained the following values of the PJTE parameters: \(K_0= 5.40\text{ eV/Å}^2\), \(F_{01}= 3.76\text{ eV/Å}, F_{02}= 3.21\text{ eV/Å}\). Calculated energy gaps are: \(\Delta_1= 6.70\text{ eV}\) and \(\Delta_2= 8.15\text{ eV}\). Then, at small displacements \(Q\), \(K \approx K_0+K_{11}+K_{22}\), where \(K_{11}=-4.22\text{ eV/Å}^2\), and \(K_{22}=-2.54\text{ eV/Å}^2\). The resulting value of the curvature of the APES is negative, \(K \approx -1.35\text{ eV/Å}^2\). For the cation (\(C_{14}H_{8}S_{4}\)^+), the curvature \(K_{\text{cat}}\) is positive, \(K_{\text{cat}} \approx +0.75\text{ eV/Å}^2\), which means that this radical is flat.
4. Conclusions
The paper extends the applicability of the PJTE methodology in revealing the mechanism that controls the structural and related properties of molecular systems. Two kinds of distortions of high-symmetry configurations of relatively large organic compounds are explored: buckling of sumanenes and mutual (torsional) ring rotations in multi-ring thiophenes. The procedures worked out in this paper can be applied to other kind of distortions of high-symmetry configurations of large organic compounds, while the specific findings for the analysed systems can be employed directly in further research and applications. In particular, the revealed and numerical estimated PJTE parameters can be used for manipulation of their structure and properties by means of targeted external influence, including oxidation-reduction and chemical substitutions, as well as coordination to other species with donor-acceptor properties.

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