

Distorted allotropes of bi-benzene: vibronic interactions and electronic excitations

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Abstract. Bi-benzene - chemically bound two benzene molecules in stuck position is studied both analytically and numerically. There are several allotropes of bi-benzene having different geometry. The reason of the existence of sundry distorted structures is the pseudo-Jahn-Teller effect. The parameters of vibronic couplings causing distortions are found. For the calculation of these parameters both, the vibronic coupling of carbon atoms in different C_6 rings and the vibronic coupling in the rings are considered. The contribution of the distortion of C_6 -planes to the latter coupling is also found. The energies of all the electronic states of π -electrons in all bi-benzene allotropes are determined by using the calculated vibronic interaction parameters.

1. Introduction

Benzene is one of the basic petrochemicals with a simple molecular formula C_6H_6 . The carbon ring C_6 in this molecule is almost identical to those in graphene, graphite and carbon nanotubes. The properties of benzene, unlike saturated hydrocarbons, are essentially determined by the presence of the conjugated 6 π -electron cloud of D_{6h} symmetry [1], [2], [3], [4]. For example, this cloud makes the benzene molecule planar [5], although the planar structure is not very stiff; see e.g. numerical studies [6], [7], [8] of the stability of this structure with respect to several distortions. In usual conditions benzene is a liquid with predominantly weak van-der Waals forces acting between the molecules [9], [10], [11], [12], [13], [14]. However, recently in our theoretical study [7] it was found that at a short distance these molecules may interact chemically forming metastable compounds of benzene molecules stacked on each other at the distance ~ 0.16 nm in a hollow position, called as bi-benzene. Analogous bound states have been found for benzene and graphene [8], [15] and for two graphene sheets [16]. Moreover graphene nanoribbons (GNRs) and carbon nanotubes (CNTs) may also form chemically bound states [17]. In all these cases the bondings take place between adjoined C_6 rings. An examination shows that the reason of this chemical bonding is in 6 π -electrons: the inter-bonds of these electrons, connecting the adjoined C_6 rings, are of σ -type and they are stronger than the intra π -type bonds in C_6 rings. Therefore for a short distance it is energetically favorable to switch-off the intra- π bonds and to form stronger inter- σ bonds.

An important property of the adjoined C_6 rings discovered in Refs. [7], [15], [17] is that not all intra- π bonds can be switched off to inter- σ bonds. As a consequence the C_6 rings may be strongly distorted. This rearrangement of the bonds followed by distortions of adjoined C_6 rings opens new possibilities for various applications of these structures including the opportunity to fabricate All-Carbon-Devices.



In Ref. [7] we have shown that distortions of the adjoined C_6 rings in bi-benzene may be considered as the result of the pseudo-Jahn-Teller effect (PJTE) caused by the length-dependence of the inter-bonds of carbon atoms in adjacent C_6 rings. This effect works in bi-benzene because the HOMO-LUMO energy difference in this system is rather small ($\sim 2\text{eV}$ Ref. [7]) - much smaller than in benzene ($\sim 5\text{eV}$). We have also found that PJTE is responsible for distortions of adjoined C_6 rings in conjoined structures of benzene, GNRs and CNTs [17], [7], [15]. PJTE in adjoined C_6 rings has some analogy with considered in Refs. [18], [19], [20], [21], [22] PJTE in benzene. It may also be compared with the Berry softening of the in-plane b_{2u} vibration (1306 cm^{-1} mode) which connects the symmetric D_{6h} structure of the benzene molecule with a Kekulé-like structure of D_{3h} symmetry: the observed reduction of the mode frequency by $\sim 300\text{cm}^{-1}$ is a result of the vibronic interaction stemming from the dependence of the π -type bond of $2p_z$ -electrons on its length [20], [23]. This interaction is insufficient for making D_{3h} symmetry of a single benzene molecule to be energetically favorable. However it still shows-up as a remarkable decrease of the frequency of the b_{2u} mode. Note also that the account of PJTE appeared to be essential in a number of cation and anion radicals of benzene [20].

In the present communication we investigate the vibronic interactions causing distortions of bi-benzene bound states. We consider that only π -electrons of conjoined C_6 rings remarkably contribute to the vibronic interactions responsible for the formation of different conjoined structures of these molecules. In our work the combined analytical and numerical (density functional theory, DFT) description of the problem is given. To this end we use simple tight binding model allowing one to treat the vibronic interactions analytically. To take these interactions into account we consider that the parameters of the model depend on the lengths of the bonds and on the distortions of C_6 planes. A comparison of the theoretical results with the DFT calculations of the ground state for properly chosen configurations allows us to determine the numerical values of vibronic interaction parameters. The knowledge of these parameters makes possible to analytically consider all states of the π -electrons for any configuration of the system. Here we have found these states for the allotropes of bi-benzene.

2. Allotropes of bi-benzene

The different rearrangements of the bonds of π -electrons, which are followed by subsequent different distortions of benzene rings, lead to different allotropes of bi-benzene. Four valence electrons of carbon atoms occupying almost degenerate $2S$ and $2P$ states, form in a benzene molecule three sp^2 hybrid orbitals. One of these orbitals makes a bond with hydrogen and two residuary orbitals establish the σ -bonds with the nearest carbon atoms. The residual $2S^1$ electron is promoted to the empty $2p_z$ state, making possible the formation of π -type bonds with the nearest carbon atoms. As a result, twelve $2p_z$ states of both spins in benzene remain half-occupied. The σ -bonds are stronger than π -bonds. Therefore, if to place two benzene molecules on a short distance in hollow position, then, as it was shown in Ref. [7] it will be energetically favorable to switch intra- π bonds to inter- σ bonds forming bi-benzene. At that different intra- π bonds may switch to the inter- σ bonds differently. As a result bi-benzene may form different allotropes. In Ref. [7] four possible allotropes were found. Schematically the shape of these allotropes is given in Fig. 1: the symmetric allotrope and three distorted allotropes. The differences in the geometry of all these allotropes are remarkable, they are caused by differences in the chemical bonds, which are reflected in the changes of electronic densities.

The calculations in Ref. [7] were made using CASTEP of *Material Studio* program module [24]. In these calculations the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional [25] was used. The cutoff energy of the plane waves, which determines the size of the basis set, was taken as 400 eV. The Monkhorst-Pack k -points grids were set as $2 \times 2 \times 4$ for the Brillouin zone integration.

In the symmetric structure (see Fig. 2A) six $2p_z$ -electrons of every C_6 ring are removed from

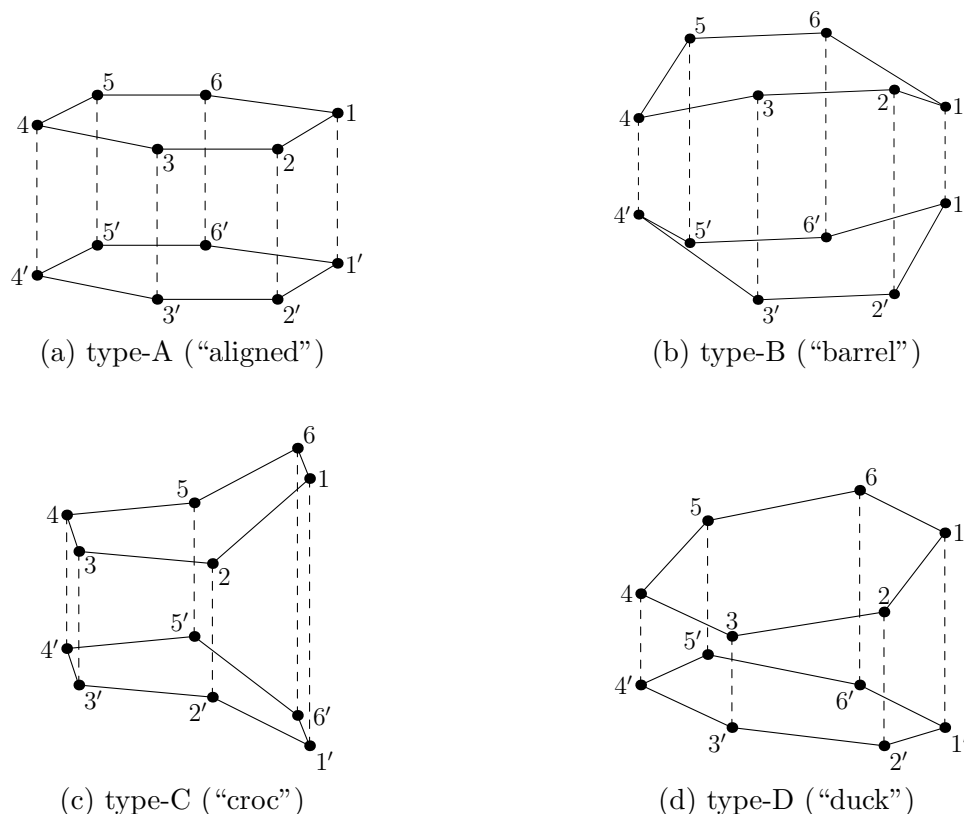


Figure 1. Schematic structures of bi-benzene

the $\sigma - \pi$ bonds in C_6 rings and these are used to form six σ -bonds between the C_6 rings. As a result, all nearest carbon atoms in the symmetric bi-benzene become chemically bound by the σ -bonds of practically the same length 1.55 Å (see Table 1). In the distorted structures (Fig. 2 B, C and D) a redistribution of the inter- and intra-bonds of $2p_z$ electrons takes place, resulting in the weakening of some inter- σ bonds and the formation of double $\pi - \sigma$ intra-bonds in C_6 rings. For example, in the structure B four inter-bonds are elongated from 1.55 Å to 2.69 Å. Simultaneously, two opposing each other intra-bonds in every C_6 ring are shortened due to the forming double bonds of the length 1.33 Å. In the C structure two inter- σ bonds are weakened and elongated from 1.55 pm to 3.50 Å. This is followed by the formation of one $\sigma - \pi$ bond of the length 1.33 Å in each C_6 ring. All other bonds change only slightly. In the third, most stable D structure only two adjoining inter-bonds remain practically unchanged. Two nearby inter-bonds are weakening moderately, while the remaining two inter-bonds are weakening strongly. Correspondingly, two opposing each other intra- σ bonds in every C_6 ring remain practically unchanged, two intra- σ bonds are increased due to formation of $\sigma - \pi$ intra-bonds with the length 1.34 Å and two remaining intra-bonds are gaining strength only slightly by forming σ -bond with the partial π -bond of the length 1.48 Å.

3. Vibronic Hamiltonian of bi-benzene

Here we consider the vibronic interactions of $2p_z$ electrons of conjoined C_6 rings contributing to different allotropes of bi-benzene. We take into account that electron-electron correlation and spin-orbital interaction of these electrons in benzene are relatively weak and may be excluded from consideration of vibronic interaction. The Hamiltonian of $2p_z$ electrons in bi-benzene can be taken as the sum of the Hamiltonians of two benzene molecules and to include there

Table 1. Characteristic lengths of *in-plane* bonds ($C_n - C_{n+1}$), z -shifts (transverse components of $C_n - C_{n+1}$), *out-of-plane* bonds ($C_n - C'_n$) and intra/inter-plane coupling parameters (β, β') for different structures of bi-benzene. Lengths are given in Å, coupling parameters β, β' in eV.

	type-B						type-C						type-D					
atom, n	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
<i>in-plane</i>	1.52	1.33	1.52	1.52	1.33	1.52	1.49	1.56	1.55	1.56	1.49	1.34	1.34	1.49	1.57	1.49	1.34	1.46
z -shift	-0.55	0	0.55	-0.55	0	-0.55	0.69	0.03	0	-0.03	-0.69	0	0.59	0.70	0	-0.70	-0.59	0
<i>out-of-plane</i>	1.64	2.73	2.73	1.64	2.73	2.73	2.98	1.61	1.56	1.56	1.61	2.98	4.07	2.96	1.58	1.58	2.95	4.06
β	1.5	2.5	1.5	1.5	2.5	1.5	1.7	1.35	1.4	1.35	1.7	2.5	2.5	1.7	1.3	1.7	2.5	1.8
β'	3.5	2.5	2.5	3.5	2.5	2.5	0.88	2.83	2.95	2.95	2.83	0.88	0.30	0.9	3.63	3.63	0.9	0.3

additionally the interaction between the adjoined carbon atoms of C_6 rings. In the tight-binding approximation this Hamiltonian gets the form:

$$H = \sum_{n=1}^6 \left[\alpha a_n^\dagger a_n + \alpha a_n'^\dagger a_n' + \left(\beta_{n,n+1} a_{n+1}^\dagger a_n + \beta_{n,n+1} a_{n+1}'^\dagger a_n' + \beta_n' a_n^\dagger a_n' + Hc \right) \right] \quad (1)$$

Here a_n^\dagger and a_n are the creation and destruction operators of electrons on atom n , a_n' and $a_n'^\dagger$ are the destruction and creation operators of the valence electrons in the second benzene molecule, α is the one-site energy, $\beta_{n,n+1}$ are the transfer (overlapping) integrals of the π -bond of nearest atoms in the C_6 rings which depend on the lengths and on the orientation of the corresponding bonds with respect to the symmetry plane (their signs are not important here, we chose them to be positive), Hc is the Hermitian conjugated term. For benzene the $\pi - \pi$ exchange interaction equals $\beta = 2.5$ eV. In Ref. [7] it was found that the length of the σ -bonds in symmetric bi-benzene is practically the same as the length of the intra- σ bonds in benzene (0.16 nm). Therefore, we can take for exchange interaction of the adjacent carbon atoms in different C_6 rings (the $\sigma - \sigma$ interaction) at this distance $\beta' \approx 3.7$ eV which is the strength of the σ -bonds in a benzene molecule. Consequently, in symmetric state of bi-benzene $\beta' \approx 1.5\beta$. Note that β' is remarkably larger than β . Due to this ratio it is energetically more favorable to switch at short distance the intra- π bonds into the inter- σ bonds and to form bi-benzene. This fact is of primary importance for the formation of bi-benzene [7].

The Hamiltonian (1) includes into consideration the dependence of the exchange interactions on the distance between the carbon atoms in the C_6 rings and on the relative shift of them in normal direction. This allows us to take into account the difference in the lengths of intra-bonds in the C_6 rings of the bi-benzene allotropes and the distortion of the plane symmetry of these rings, not considered in previous analytical treatment of bi-benzene allotropes. These factors are essential to be taken into account for the description of the energies of the excited states of the distorted allotropes of bi-benzene.

In symmetric bi-benzene the stationary states of π -electrons are very simple: they have the form $|\Psi_k\rangle = 6^{-1/2} \sum_{n=1}^6 e^{i\pi kn/3} |\Phi_n\rangle$, where $|\Phi_n\rangle$ are two-component states of two adjoining carbon atoms. In the k -basis the Hamiltonian H_2 of bi-benzene reads $H_{2,kk'} = (E_{1k} \cdot I + \beta \sigma_x) \delta_{kk'}$, where σ_x is the Pauli matrix. The eigenvalues of this matrix equal ± 1 .

Therefore the energies of the levels of the undisturbed bi-benzene in the used approximation are $E_k = 2\alpha + 2\beta_0 \cos(\pi k/3) \pm \beta'$.

The energy difference of LUMO and HOMO in symmetric bi-benzene is $\Delta E_{LH}^{bibz} = 2(\beta' - \beta) \approx 2$ eV, i.e. essentially smaller than the energy difference of LUMO and HOMO in benzene $\Delta E_{LH}^{bz} \approx 5.2$ eV. This causes the change of the order of the HOMO and LUMO when decreasing the distance between the adjoined C_6 rings, which is precondition of the existence of the chemically bound state of two benzene molecules [7].

There are 18 bonds between the nearest carbon atoms in bi-benzene: 12 intra-bonds and 6 inter-bonds, which all may have different lengths and adjoined angles. However we are interested here only in the structures with mirror symmetry, i.e. with identical C_6 rings. These structures have twelve different lengths of bonds and six different angles of intra-bonds. In this case the vibronic Hamiltonian of bi-benzene can be taken in the form:

$$H = \left(2E_0 + 2 \sum_{n=1}^6 u_0(Q_n) + \sum_{n=1}^6 u'_0(q_n) \right) \cdot I + 2V, \quad (2)$$

where $u_0(q)$ and $u'_0(q)$ are the potential energy of the single intra- and inter- σ bonds, respectively,

$$V = \begin{pmatrix} m_1 & m_2 \\ m_2 & m_1 \end{pmatrix} \quad (3)$$

is the vibronic energy, m_1 and m_2 are following matrices:

$$m_1 = \begin{pmatrix} 0 & \beta_1 & 0 & 0 & 0 & \beta_6 \\ \beta_1 & 0 & \beta_2 & 0 & 0 & 0 \\ 0 & \beta_2 & 0 & \beta_3 & 0 & 0 \\ 0 & 0 & \beta_3 & 0 & \beta_4 & 0 \\ 0 & 0 & 0 & \beta_4 & 0 & \beta_5 \\ \beta_6 & 0 & 0 & 0 & \beta_5 & 0 \end{pmatrix}, \quad m_2 = \begin{pmatrix} \beta'_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta'_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta'_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta'_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta'_5 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta'_6 \end{pmatrix}, \quad (4)$$

the factors two in Eq. 2 stands for two spin values. For a weakly distorted structure

$$\beta_n = \beta - kQ_n - \kappa z_n^2, \quad \beta'_n = \beta' - k'q_n,$$

k , κ and k' are the positive constants of vibronic interactions inside the C_6 rings and between the C_6 rings, respectively, Q_n and the differences of the in-plane lengths of carbon bonds from their equilibrium value in the C_6 rings, z_n are the difference of the z -coordinates (perpendicular to symmetry plane) of atoms n and $n+1$; q_n are the differences of the lengths of the inter-bonds from their equilibrium value in the C_6 rings of symmetric bi-benzene. The minus signs in the equations for β_n and β'_n account for the fact that the strength of bonds decreases with the increasing of the distance between the carbon atoms. The same holds for the distortion terms of the plane.

Here we take into account that the small distortions of C_6 planes can be considered in terms of the appearance of small additional non-orthogonality of the basic states of the planar structure. This non-orthogonality results in the appearance of the additional matrix of overlapping integrals (see, e.g. [26]). In our concrete case these terms take into account the reduction of the overlapping integrals of the nearest π -functions when they move apart in z -direction. We include these terms into consideration by adding the $\propto \kappa$ terms to the exchange interaction parameters β_n . In the case of large Q_n , or z_n or q_n we apply the exponential reduction of the inter- and intra-bonds taking

$$\beta_n = \beta e^{-kq_n - \kappa z_n^2}, \quad \beta'_n = \beta' e^{-k'Q_n}.$$

Note that the ground state corresponds to the double occupancy of the six lowest levels. Therefore the vibronic energy of this state for any values of q_n , Q_n and z_n is determined by a double sum of six lowest eigenvalues of the Hamiltonian for the given Q_n , q_n and z_n . This energy considered as a function of the coordinates determines the shape of the multi-dimensional potential surface of the ground state.

The energies of the electronic interactions $\beta \approx 2.5$ eV and $\beta' \simeq 3.7$ eV are known [7]. The parameter of the vibronic interaction k' determining the dependence of the vibronic interaction of the $\sigma - \sigma$ inter-bonds on their lengths (this interaction is responsible for the dimers formation) was found in Ref. [7] by combining the analytical and numerical (DFT) calculations of the vibronic contributions to the energy of the ground state of the system for its different configurations. This allows one to exclude the contribution of other interactions in numerical considerations. The calculated value of this parameter is $k' = 3.75$ eV/Å.

The remaining vibronic interaction parameters k and κ can be found by applying the same method. For example, to find k we compare the result of the calculations of the

- (1) totally symmetrically distorted C_6 rings with $Q_n = Q \neq 0$ (in this case $\beta_n = \beta - kQ$);
- (2) the rings elongated along the C_2 axis connecting the opposite corners with $Q_2 = Q_5 = Q\sqrt{3}$ and $Q_1 = Q_3 = Q_4 = Q_6 = 0$ (here $\beta_2 = \beta_5 = \beta - \sqrt{3}kQ$ and $\beta_1 = \beta_3 = \beta_4 = \beta_6 = \beta$).

In this case the difference of the energies of the elastic distortions for small Q comes solely from the vibronic interaction under consideration. Performing the analytical calculation of the vibronic energies of the ground state, we have found

$$E_{\text{symm}} - E_{\text{dist}} \approx 7(kQ)^2 e^{0.21k/\beta} / 9\beta. \quad (5)$$

Here the exponential factor $\exp(-0.21k/\beta)$ accounts for the reduction of the exchange energy β in C_6 rings on the increasing of the $C - C$ distance in symmetric bi-benzene by 0.21 Å. According to our DFT calculation $E_{\text{symm}} - E_{\text{dist}} \approx 30 Q^2$ eV (for Q in Å). This gives $k \approx 7.5$ eV/Å² which is almost 2 times larger than k' . This was to be expected: the longitudinal size of π -functions is smaller than their transversal size, which makes corresponding bond more strongly dependent on the length of the $\pi - \pi$ bond. Besides, in case of $\pi - \pi$ vibronic interaction both “petals” of the π -functions give a contribution to the vibronic coupling, while only one of them contributes to the inter- σ coupling.

To find the parameter κ , describing the vibronic effect of the transversal distortions of the C_6 rings, we consider two following structures:

- (1) the structure with two bent opposite angles (boatlike structure [6]); in this case $z_1 = z_4 \neq 0$ and $z_2 = z_3 = z_5 = z_6 = 0$;
- (2) the structure with all six alternatively bent angles with $z_1 = -z_2 = z_3 = -z_4 = z_5 = -z_6$.

If in both these cases the absolute value of the difference of z -coordinates of the nearest atoms is taken to be the same, then the non-vibronic elastic energy of the second distortion would be three times larger than that of the first distortion. The contribution of this energy to the energy of the distorted structures will be extractable, when the total elastic energy of the second structure from the triple distortion energy of the first structure. Our analytical calculations of the vibronic energies of the ground state of the C_6 ring with these distortions give $32\kappa z^2/3$ (first structure) and $8\kappa z^2$ (second structure). Therefore,

$$\kappa = (3E_{2,z} - E_{3,z})/24z^2. \quad (6)$$

According to our calculations $3E_{2,z} - E_{3,z} \approx 14.0 \cdot z^2$ eV (for z in Å) which gives $\kappa \approx 0.60$ eV/Å². Consequently, the vibronic interaction stemming from the distortion of the C_6 planes is rather weak. This agrees well with the known fact that the planar structure of benzene is not very stiff [6].

4. Energies of electronic states

The established values of the vibronic parameters k , k' and κ allows us to calculate the exchange integrals β_n and β'_n ($n = 1, 2, \dots, 6$) for any configuration of carbon atoms of bi-benzene. The knowledge of these parameters gives a possibility to find analytically all the 12 states of all valence (π) electrons for different configurations of bi-benzene without complete calculations of the excited states. To this end one should find the eigenstates and eigenvalues of the vibronic matrix V for the chosen coordinates of carbon atoms, which can be done analytically. Note that in our calculations of bi-benzene vibronic parameters we apply the DFT method only for ground state calculations. Therefore, our theory is free from the usual difficulties of the DFT with the calculations of excited states, e.g. when ensuring orthogonality in the ground-state wave function for the optimization of excited states [27].

The possibility to find analytically all states of valence electrons for any configuration of bi-benzene is an advantage of our method. For example, it gives one a possibility in the frame of unified approach to explore in detail the multi-configurational potential surfaces of all electronic states of bi-benzene and to find relaxation passes and conical intersections important for different processes (see in this connection Ref. [15] where we have found several conical intersections in the excited states of benzene bonded to graphene).

Table 2. Vibronic energies of bi-benzene allotropes (in eV).

	← Occupied energy levels						Unoccupied energy levels →					
Level nr.	1	2	3	4	5	6 (HOMO)	7 (LUMO)	8	9	10	11	12
Type-A	-8.70	-6.20	-6.20	-1.30	-1.20	-1.20	1.20	1.20	1.30	6.20	6.20	8.70
Type-B	-6.36	-5.09	-4.23	-1.89	-0.62	-0.45	0.45	0.62	1.89	4.23	5.09	6.36
Type-C	-6.94	-5.04	-3.48	-3.22	-1.21	0.08	0.43	1.72	3.73	3.99	5.55	7.45
Type-D	-5.46	-3.40	-3.40	-2.86	-1.18	-0.93	0.93	1.18	2.86	3.40	3.40	5.46

In the Table 1 the values of exchange integrals β and β'_n ($n = 1, 2, \dots, 6$) for configurations corresponding to the distorted allotropes B, C and D are presented (the values of these parameters for undistorted allotrope A are known [7]: $\beta = 2.6$ eV, $\beta' = 3.7$ eV). Using these values we calculated energies of electronic states for all four allotropes of bi-benzene. These energies are given in Table 2. From this table one can easily find the energies of all 36 electronic transitions of π -electrons in every structure. Note that according to this table the A structure should absorb light from 2.4 eV (green) to far ultraviolet (UV, 17 eV) and should not absorb in red and infrared, while the structures B, C and D should absorb light starting from near infrared till far ultraviolet (UV, 12-14 eV).

5. Conclusion

In the present study we investigated the vibronic interactions of valence (π) electrons in bi-benzene. These interactions plays crucial role in this system causing the appearance of four different allotropes: the symmetric allotrope A and three distorted allotropes B, C and D (see Fig. 1). The micro-mechanism of distortions in this system is the pseudo-Jahn-Teller effect – the lowering of symmetry due to the vibronic mixing of ground and excited states. In bi-benzene this mixing has a strong effect due to rather small value of the LUMO-HOMO energy difference. Here we have found the energies of the occupied and unoccupied state of π -electrons of all four allotropes.

In the appearing structures both, the different inter-bonds and the different intra-bonds of π -electrons have different lengths. Besides, the C_6 planes of B and C allotropes have out-of-plane distortions. To take these effects into account we considered the vibronic interactions stemming from the length dependence of the exchange interactions of both inter- and intra-bonds. We also take into account the dependence of these interactions on the C_6 plane distortions. To find the parameters of these interactions, we applied our method of combined analytical and numerical (DFT) considerations. In the analytical study we used for π -electrons the tight binding model. We compared the theoretical results with the DFT calculations of the ground state (to avoid the DFT difficulties with the calculations of excited states) for the properly chosen configurations that enabled us to determine the numerical values of the vibronic interaction parameters. The knowledge of these parameters gives a possibility to find analytically all 12 states of π -electrons for any configuration of the system.

Finally we note that the possibility to have analytical description of all electronic states for any configuration of the system is an advantage of the used method. Among other tasks, which may be solved by using this method, one can mention a possibility to explore within the framework of unified approach the multi-configurational potential surfaces of all electronic states of bi-benzene and to find relaxation passes and conical intersections important for different processes.

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