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Pseudo Jahn–Teller effect in stacked benzene molecules

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ABSTRACT

Chemically bound structures of several benzene molecules are studied both analytically and numerically. The bonds in these structures are established by replacing the intra π-bonds of C_6 rings by the inter σ-bonds. The rearrangements of different π-bonds may take place differently which causes distortions of C_6 rings. The reason of the distortions is the pseudo-Jahn–Teller effect (PJTE). In the case of two chemically bound benzene molecules in a hollow position (with direct on-top stacking), called as bi-benzene, three different distorted states in addition to the undistorted one are found to exist. PJTE leads also to a chemical bonding of three and more benzene molecules stacked directly on-top of each other. These bound structures do not exist for undistorted molecules. All bound states, although being metastable are separated from the unbound ones by energy barriers $\gtrsim 2$ eV. It is found that the height of the barrier for symmetric bi-benzene is essentially affected by the Jahn–Teller effect.

1. Introduction

The hexagonal C_6 "rings" are the basic structural elements of many organic molecules and novel compounds, including fullerenes, carbon nanotubes and graphene. Considering the rapidly growing number of applications, it may be interesting to study the conjoined structures of such compounds, especially when the mechanism behind their cooperation is the pseudo Jahn–Teller effect (PJTE). Such conjoined structures are numerically found to exist for two graphene sheets [1] and for benzene molecule and graphene [2]. Moreover, as it follows from calculations [3], graphene nanoribbons and carbon nanotubes may also form chemically bound states. In all these cases chemical bonds are established between the adjoined carbon atoms in parallel C_6 rings in a hollow position (here i.e. in a configuration with carbon atoms located at the atop positions, stacked directly on the top of each other – direct on-top stacking) by switching off the intra π-bonds to inter σ-bonds.

In Ref. [3] it was found that not all intra-π-bonds of conjoined C_6 rings are switched off to inter-σ-bonds in the same way: the rearrangement of different bonds takes place differently. Some bonds are rearranged changing sp^2 to sp^3 hybridized orbitals, others not. As a consequence the conjoined C_6 rings in the bound carbon nanotubes and graphene nanoribbons are strongly distorted. It is natural to suppose that the different rearrangement of the bonds of π-electrons followed by subsequent different distortions must be common for the compounds with C_6 and analogous rings

In this communication we present an analytical and numerical study of adjoined benzene molecules. A detailed investigation of the simplest relevant system, two benzene chemically bound molecules in a hollow position with direct on-top stacking, is performed. Unlike the known benzene dimers with T-shaped (edge-to-face) and displaced-stacked (face-to-face) structures, where interaction between two benzene molecule is non-covalent (see, e.g. [4–9]), it is found that these molecules may also make a chemically bound state (we call this state a bi-benzene). We have also found that, in addition to a symmetric bi-benzene, three distorted allotropes of this compound molecule may exist. The minimum energy is the one having the shape analogous to thymine dimer [10] (the latter dimers are produced by UV light in DNA [11,12]). The mechanism of appearance of the distorted states is the pseudo-Jahn–Teller effect (PJTE). All bound states are separated from unbound ones by rather high ($\gtrsim 2$ eV) energy barriers. To the best of authors' knowledge, it has been found for the first time that the barrier between the bound and unbound states may be essentially affected by the Jahn–Teller effect (this has happened for two undistorted benzene molecules). It is also shown that PJTE can lead to a chemical bonding of an arbitrary number of benzene molecules stacked in a hollow position. The stack may form a column of C_6 rings of arbitrary length. However three or more benzene molecules with undistorted C_6 rings do not form chemically bound states.

The PJTE in adjoined C_6 rings have close analogy with PJTE in excited state of benzene considered in Refs. [13–16] and with JTE

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and PJTE in benzenoid cations discussed in [17]. PJTE is also responsible for the Berry softening of the in-plane b_{2u} vibration (~1310 cm^{-1} mode) in benzene: the observed reduction of the mode frequency by ~300 cm^{-1} (260 cm^{-1} from [15]) is a result of the vibronic coupling stemming from the dependence of the π-type bond of $2p_z$ electrons on its length [15,18,19].

2. Ab initio calculations of bi-benzene allotropes

To calculate the possible structures of conjoined benzene molecules we have used the DFT (Density Functional Theory) based methods as implemented in CASTEP module of Materials Studio program [20]. Application of the DFT-based techniques to our systems is justified by fact that they work enough accurately for the systems with covalent interaction between constituent atoms [1]. Both the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional (PBE) [21] and local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger functional (CA–PZ) [22,23] were used (since, in general, GGA functionals tend to overestimate, while LDA functionals underestimate the experimental lengths of the chemical bonds). In order to treat non-covalent interactions [24], the calculations were also performed with the dispersion corrections of Tkatchenko and Scheffler (TS) [25] for GGA–GGA (TS) and Ortmann, Bechstedt, and Schmidt (OBS) [26] for LDA–LDA (OBS). The cutoff energy of plane waves, which determines the size of the basis set, was taken to be 800 eV and the Monkhorst–Pack k-point grid was set as $3 \times 3 \times 2$ for the Brillouin zone integration. The calculations were not spin-polarized. The convergence parameters for the geometry optimization were as follows: for the energy $1.0 \times 10 - 5$ eV/atom, for the maximum force 0.03 eV/Å, and for the maximum displacement 0.001 Å. The all calculations were made with the same accuracy.

According to our calculations four different chemically bound allotropic structures of bi-benzene are possible (see Fig. 1): the symmetric structure A (with the same D_{6h} symmetry) and three distorted structures and three distorted structures: B, C and D.

In the symmetric structure (see Fig. 1, Type-A) six $2p_z$-electrons of every C_6 ring are removed from the $\sigma - \pi$ bonds (σ-bonds along with π-bonds) in the C_6 rings and are used to form six σ bonds between the C_6 rings. As a result all nearest carbon atoms in the symmetric bi-benzene became chemically bound by the σ-bonds of practically the same length 1.56 Å.

As demonstrated by our calculations (see Table 1) the distortions result in the energy gain of the bi-benzene. The corresponding energies calculated by different methods, but with the same cut-off energy (800 eV) and k-points ($3 \times 3 \times 2$), are given in Table 1.

According to the presented results the energy gains due to the distortions lie between 1.6 eV and 2.6 eV. At that, all methods give that the lowest energy has the D structure, having the same shape as the thymine dimer created by the UV light in DNA [11,12]. The next low energy has the C structure and the smallest gain due to distortion corresponds to the B structure. In all the distorted structures the redistribution of the inter- and intra-bonds take place, resulting in the weakening and elongating of some intra-bonds and the strengthening and shortening of others (Table 2).

E.g. in the structure B four inter-bonds are elongated from 1.56 Å of the structure A to 2.73 (according to GGA calculations) due to the bending. Simultaneously, two opposing each other intra-bonds in every C_6 ring were shortened due to the formation of σ–π bonds of the length 1.33 Å.

In the structure C two inter-σ-bonds weakened and elongated from 1.56 Å of the structure A to 2.98 Å (according to GGA calculations). This elongation was followed by the formation of one σ–π bond of the length 1.34 Å in every C_6 ring. All other bonds change only slightly. In the most stable D structure only two adjoining inter-bonds remained practically unchanged. Two nearby inter-bonds were weakening moderately while the remaining two inter-bonds were weakening strongly. Correspondingly, two

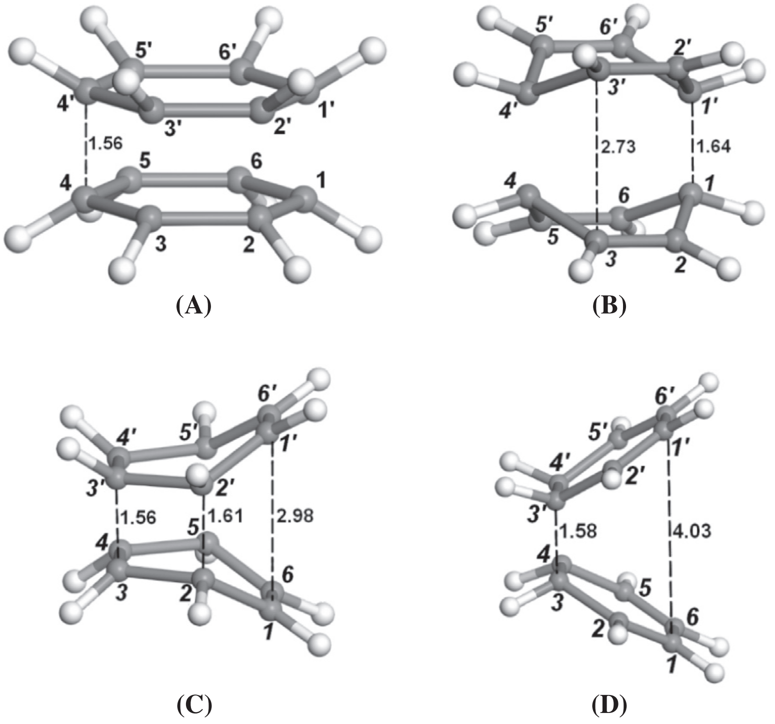

Fig. 1. Symmetric and distorted allotropes of bi-benzene (distances are given in Å). The distances were taken from GGA results for all types (gray small balls C, white small balls H).