T-shaped dimer of coronene

O. I. Obolensky, V. V. Semenikhina, A. V. Solov’yov, and W. Greiner

Frankfurt Institute for Advanced Studies,
Johann Wolfgang Goethe-University, Max von Laue str. 1,
D-60438 Frankfurt am Main, Germany

An evidence of importance of the T-shaped configuration of coronene dimer is presented. That is, the dimer’s lowest energy configuration is not necessarily a stack, as it might had been expected a priori. This is a surprising result for dimer of such a large polycyclic aromatic hydrocarbon (PAH) as coronene (C_{24}H_{12}). The energy of the T-shaped configuration at all considered levels of density functional theory (B3LYP,PBE/6-31+G(d),D95,cc-pVDZ,cc-pVTZ) was systematically lower than the energies of three plausible stack configurations. In order to get a better description of the van der Waals interaction, the density functional theory (DFT) results were adjusted by adding a phenomenological Lennard-Jones-type term into the total energy of the system. However, the van der Waals correction is somewhat arbitrary and its magnitude can not be rigorously justified. Depending on the choice of the parameters in the phenomenological term both the T-shaped and the parallel-displaced (PD) stack configurations can be the global energy minimum of the system. A simple model is proposed which is useful for qualitative understanding of possible geometries of the coronene dimer and larger coronene clusters. The model represents coronene dimer as two sets of charged rings interacting via Coulomb and Lennard-Jones potentials. The model provides an intuitively clear explanation why the T-shaped dimers can be of importance even for some of moderately large PAHs such as coronene and, may be, for circumcoronene. The unexpectedly strong binding of the coronene dimer in the T-shaped configuration is connected to the round shape of the coronene molecules. Indeed, rotation or parallel-displacement of the non-round monomers results in significantly smaller Coulomb repulsion as compared to the "face to face" sandwich configuration. On the other hand, rotation and/or displacement are much less effective for the stacked round molecules. Therefore, the round shape of the coronenes leads to an increased role of the electrostatic repulsion
in the stack configurations and the T-shaped configuration can become competitive. The proposed model can be easily generalized to other polycyclic aromatic hydrocarbons, DNA bases, etc.

PACS numbers:

I. INTRODUCTION

Molecules of polycyclic aromatic hydrocarbons and their ions are of current interest as they are believed to be one of the most probable species in the interstellar space responsible for converting the UV radiation of stars into the intensive IR radiation, known as unidentified infrared bands [1, 2, 3, 4, 5, 6, 7]. The physical mechanisms and effectiveness of energy transfer from the UV to the IR radiation occurring via transient heating [8] are currently being studied, see, e.g., [1, 3, 10, 11].

Astrophysical observations suggest that the interstellar medium contains a variety of small carbonaceous particles with the sizes ranging from dust grains down to single molecules [12]. The most abundant particles contain between 100 and 1000 carbon atoms [13] in the forms of collections (clusters) of PAH-like molecules [10] of various degrees of hydrogenation [2]. Hence, studying properties of PAH clusters presents a necessary step in further research of interstellar medium.

The current knowledge of structure and ways of formation of PAH clusters is very limited. Laboratory studies have just started to appear and only anthracene [14, 15], naphthalene [14] and coronene [16, 17] clusters have been produced so far, so that the array of available experimental data is sparse. Theoretical investigations of oligomers of the larger PAHs are also scarce and, furthermore, their results are very sensitive to a subtle interplay between the van der Waals polarization forces (also sometimes called dispersive interaction) and the electrostatic interaction. Even for benzene, the simplest aromatic hydrocarbon, an
unequivocal choice between the T-shaped and the parallel-displaced stack configurations can not be made since the calculated binding energies for these configurations strongly depend on the choice of the method of calculation and on the basis set and they do not seem to be converging even at the most advanced levels of theory \cite{18, 19, 20}. Alternative approaches based on mixing of the \textit{ab initio} and the phenomenological treatments have been suggested which allow a more flexible tuning of interactions (see, e.g., \cite{21, 22, 23, 24, 25}), but their universality and predictive power are not quite clear yet.

We have performed density functional theory calculations of energies for four plausible configurations \cite{22} of the coronene dimer. These included three stack configurations (superimposed stack - ”sandwich” (SS), twisted stack (TS) and parallel-displaced (PD) stack) and the T-shaped configuration. To our knowledge, this is the first comparative study of the configurations of the coronene dimer within the \textit{ab initio} approach. The only other \textit{ab initio} calculation of coronene dimer parameters was done for the PD stack configuration \cite{21}.

The energy of the T-shaped configuration at all considered levels of theory (combinations of the B3LYP and PBE functionals with 6-31+G(d), D95, cc-pVDZ, and cc-pVTZ basis sets) was systematically lower than the energies of the stack configurations. In order to get a better description of the van der Waals interaction, the DFT results were adjusted by adding a phenomenological Lennard-Jones-type term into the total energy of the system. The problem of this approach is that the van der Waals correction is somewhat arbitrary and different authors choose different parameters even for the same systems (cf., e.g., \cite{21} and \cite{22}). Depending on magnitude of the van der Waals term, both the T-shaped and the stack configurations can be the global minimum configuration of the system. Even though the definitive conclusion can not be drawn at the moment, it is quite surprising on its own that the T-shaped configuration is energetically competitive for such a large system for which a graphite-like stacked structure was expected \cite{21}.

We propose a simple model useful for qualitative understanding of dimerization and clusterization of polycyclic aromatic hydrocarbons. The model represents a PAH molecule as a set of circular or deformed rings corresponding to the chains of carbon atoms surrounded by a chain of hydrogens. For example, the coronene molecule is represented as a set of four nested circular rings with the outer ring corresponding to the hydrogens. The electron density in PAHs is shifted from the hydrogens towards the interior of the molecules. In a crude approximation this charge distribution can be described as a polarized band (with a posi-
tively charged outer edge and a negatively charged inner edge) located along the perimeter of a molecule. This charge distribution can also be considered as a dipole distributed along the border of a molecule. Two PAH molecules interact electrostatically and via the van der Waals forces between the sets of the rings substituting the monomers.

The model provides a qualitative explanation why even for such a large PAH as coronene (C_{24}H_{12}) the T-shaped configuration is comparable in energy with the stack configuration. This happens due to the round shape of the coronene molecule which leads to an increased electrostatic repulsion in the stack configurations. For non-round molecules in the stack configurations, the electrostatic interaction can be made less repulsive (or even attractive) by rotating or by parallel displacing the molecules in the dimer, while for stacked round molecules the rotation or displacement are much less effective and the T-shaped configuration can become competitive.

II. DENSITY FUNCTIONAL THEORY TREATMENT OF CORONENE DIMER

We have performed density functional theory calculations of binding energies for four configurations of coronene dimer. The dimer binding energy is defined as follows:

\[ E_b = 2E_{\text{mono}} - E_{\text{dimer}}, \]  

where \( E_{\text{dimer}} \) is the total energy of the dimer and \( E_{\text{mono}} \) is the energy of the single molecule. Note that according to this definition the binding energies of the stable bound states of the dimer are positive.

The studied geometries are shown in Figure 1 and the binding energies are summarized in Table III. The calculations have been done with the B3LYP and PBE functionals by expanding the molecular orbitals into the standard 6-31+G(d), D95, cc-pVDZ, and cc-pVTZ basis sets as implemented in Gaussian03 package [26, 27].

The energy of the T-shaped configuration at all considered levels of theory was systematically lower than the energies of the three stack configurations. It is a quite surprising result for such a large PAH molecule. For the smallest aromatic hydrocarbon, benzene, the T-shaped configuration is almost isoenergetic with the parallel-displaced stack configuration [18, 19, 20]. It is commonly believed that increase in number of aromatic rings favors stack configurations over the T-shaped ones [22, 24, 28]. In accord with this assumption, the
TABLE I: The binding energies (in kcal/mol) calculated at various levels of theory. For notations and geometries of the dimer configurations see Figure 1.

| Method               | SS  | TS  | PD  | T   |
|----------------------|-----|-----|-----|-----|
| B3LYP/6-31+G(d)      | -12.55 | -9.16 | -9.41 | 0.33 |
| B3LYP/D95           | -2.99 | -2.64 | -1.91 | 0.43 |
| B3LYP/cc-pVDZ        | -4.49 | -2.72 | -2.55 | 0.43 |
| PBE/6-31+G(d)        | -5.34 | -0.91 | 1.7   | 1.98 |
| PBE/D95             | 0.88  | 1.39  | 2.32  | 2.83 |
| PBE/cc-pVDZ         | 0.12  | 0.66  | 1.72  | 1.79 |
| PBE/cc-pVTZ         | -0.51 | 0.76  | 1.22  | 1.48 |
| PBE/TZV(2d,2p) from Ref. [21] |       |       |       | -4.89 |
| BLYP/TZV(2d,2p) from Ref. [21] |       |       |       | -17.52 |

T-shaped (or, more generally, "edge to plane") dimers of pyridine, naphtalene, azulene and anthracene have been found less binding than the stacked configurations [15, 24, 25, 29]. In the only other ab initio calculation of a coronene dimer [21] a graphite-like (parallel-displaced) stacked structure was considered only.

To our knowledge, this paper is the first comparative study of the possible configurations of the coronene dimer performed within the ab initio approach. There were also studies of the coronene dimer which used phenomenological approaches [22, 30, 31]. In the most recent study of this type [22], the dimers and clusters of PAH molecules were modeled within a rigid-body approximation with the use of explicit interatomic potentials (a sum of an electrostatic and a van der Waals terms). None of these semiempirical studies found the T-shaped form of the coronene dimer to be energetically preferable.

It is well known that the pure DFT methods does not reproduce the attractive polarization interactions well enough, for a discussion see, e.g., Ref. [21] and references therein. This may present a serious problem in such intricate cases as determining the binding energy for loosely bound dimers of PAH molecules. In order to estimate the influence of the polarization van der Waals interaction on the preferred dimer geometry, we have included a phenomenological Lennard-Jones-type term into the total energy of the system, similar to
FIG. 1: (Color online) Geometries of four configurations of the coronene dimer. In the sandwich (SS) configuration the distance $R$ between the centers of mass of the monomers equals 4.27 Å. In the twisted sandwich (TS) configuration $R = 4.21$ Å and the rotation angle is $30^\circ$. In the parallel-displaced (PD) configuration $R = 3.95$ Å and the shift is 2.70 Å. In the T-shaped (T) configuration $R = 8.02$ Å. The binding energies, calculated at various levels of theory, can be found in Table I.

the procedure developed in [21]:

$$E = E_{\text{DFT}} + \sum_{i,j} \left( \frac{C_{ij}^{12}}{r_{ij}^{12}} - \frac{C_{ij}^6}{r_{ij}^6} \right).$$

(2)

Here $E_{\text{DFT}}$ is the total energy of the system calculated within the frame of the DFT. Index $i$ enumerates atoms in one monomer, index $j$ enumerates atoms in the other monomer; correspondingly, $r_{ij}$ is the distance between atom “$i$” in the first monomer and atom “$j$” in the second monomer. The coefficients $C_{ij}^6$ and $C_{ij}^{12}$ can be tabulated directly (as is in Ref. [32]) or found with the help of a combining rule (as is in Ref. [21])

$$C_{ij}^M = 2 \frac{C_{iM}^i C_{jM}^j}{C_{iM}^i + C_{jM}^j}, \quad M = 6, 12.$$

(3)

Unfortunately, there are no fixed values for the coefficients $C_6$ and $C_{12}$ which would be universally applicable in a wide scope of situations. Even for the same systems different
authors choose different parameters (cf., e.g., [21] and [22]). The arbitrariness of the van der Waals correction seems to be a general problem of all such hybrid approaches.

In order to illustrate how sensitive the overall conclusions may be with respect to the values of the phenomenological parameters we present in Table II the binding energies for each of the considered dimer configurations for various reasonable choices of the parameters \(C_6^C\), \(C_6^H\), \(C_{12}^C\), and \(C_{12}^H\). Depending on magnitude of the van der Waals term, both the T-shaped and the stack configurations can be the global minimum configuration of the system. Thus, we suppose that a definitive conclusion can not be drawn at the moment. An experimental measurement of certain characteristics (such as frequencies of transitions between rotational levels) would be useful for determining the global energy minimum configuration of the dimer. To facilitate identification of the dimer configurations, in Table III the rotational constants for each configuration are given. The rotational constants \(B_{\eta}\), connected to the principal values of the inertia tensor \(I\) as \(B_{\eta} = \hbar / (4\pi I_{\eta\eta})\) (\(\eta = x, y, z\)), define the rotational levels \(E_\eta = B_{\eta} J(J + 1)\) corresponding to different rotational quantum numbers \(J\).

**TABLE II**: The binding energies (in kcal/mol) for four configurations of the coronene dimer (see Figure 1) calculated according to expressions (1) and (2) for several sets of the coefficients \(C_6\) (in J/mol nm\(^6\)) and \(C_{12}\) (in mJ/mol nm\(^{12}\)). The energies of the van der Waals terms are given in parentheses. The optimization of the dimer geometries and calculations of the DFT binding energies have been done with the PBE/D95 method.

| \(C_6^C\) \(C_6^H\) \(C_{12}^C\) \(C_{12}^H\) | SS         | TS         | PD         | T          |
|---------------------------------------------|------------|------------|------------|------------|
| \(= 2.77\) \(= 0.14\) \(= 0.63\)         | 25.73 (24.85) | 19.07 (17.68) | 17.72 (15.40) | 7.54 (4.71) |
| \(= 4.87\) \(= 0.09\) \(= 0.68\)        |            |            |            |            |
| \(= 1.15\) \(= 0.11\) \(= 0.68\)        | 17.97 (17.09) | 10.12 (8.73) | 9.97 (7.65) | 5.52 (2.69) |
| \(= 0.88\) \(= 0.11\) \(= 0.68\)        | 2.34 (1.46) | 5.73 (4.34) | 6.00 (3.68) | 3.51 (0.68) |
| \(= 4.87\) \(= 0.09\) \(= 0.68\)        |            |            |            |            |
| \(= 0\) \(= 0\) \(= 0\)                 | 0.88 (0.00) | 1.39 (0.00) | 2.32 (0.00) | 2.83 (0.00) |

\(\text{\textsuperscript{a}}\)From Ref. 32.
\(\text{\textsuperscript{b}}\)From Ref. 21 \(C_6\) is adjusted by the factor 0.7 from one of the values (1.65) given in Ref. 33.
\(\text{\textsuperscript{c}}\)A dump function has been used instead of \(C_{12}\) [21].
\(\text{\textsuperscript{d}}\)Another possible value (1.26) of the coefficient \(C_6^C\) from Ref. 33 multiplied by 0.7 as in Ref. 21.
\(\text{\textsuperscript{e}}\)Coefficients \(C_{12}\) are from Ref. 32.

We note that the superimposed stack (sandwich) configuration probably is not a minimum on the potential energy surface. An analysis [22] done with the use of a phenomenological potential has identified it as a transitional state between the twisted stack and the parallel-
displaced stack configurations. This conclusion is indirectly supported by the results of the high-level *ab initio* calculations which demonstrated that in benzene the superimposed stack is also a saddle point rather than a true minimum [18].

TABLE III: Rotational constants (in GHz) for different configurations of the coronene dimer calculated for the geometries optimized at B3LYP/D95 and PBE/D95 levels of theory. For notations and geometries of the dimer configurations see Figure 1.

|         | SS   | TS   | PD   | T    |
|---------|------|------|------|------|
| B3LYP/D95 | 0.085 | 0.085 | 0.082 | 0.087 |
| PBE/D95   | 0.087 | 0.087 | 0.082 | 0.089 |

III. RINGS MODEL OF POLYCYCLIC AROMATIC HYDROCARBONS

The model approaches sometimes can be very useful in revealing the underlying physics of a process and in pointing to the directions of search. In some situations, when the *ab initio* calculations are not feasible, the model calculations are the only approach one has to resort to. We present here a model which elucidates the role of the shapes of PAH molecules in the process of dimerization and in formation of bigger PAH clusters.

The model represents PAH molecules as a set of circular or deformed rings which correspond to the chains of carbon atoms surrounded by a chain of hydrogens. For example, the coronene molecule can be described as consisting of four concentric circular rings representing three chains of carbon atoms and one chain of hydrogens, see Figure 2.

The electron density in PAHs is shifted from the hydrogens towards the interior of the molecules. Therefore, the outer ring (corresponding to the hydrogens) is always charged positively. The inner rings can, in principle, bear any charge, but their net charge, in the case of a neutral molecule, must be negative and compensate the positive charge of the outermost ring.

The magnitude of charge for each ring is defined on the basis of the results of the DFT calculations as the sum of the partial charges of the atoms belonging to the corresponding chain. Various methods can be used for assigning the partial charges to the atoms. For example, Mulliken suggested to calculate partial charges as the integral over the electron density contained within a sphere of a given radius, specific to the corresponding type of atoms [34]. Alternatively, one can expand the electron density into a set of "natural bond
FIG. 2: (Color online) The round-shaped coronene molecule represented as a set of four nested circular rings. The radii of the rings are 1.438, 2.876, 3.595, and 4.691 Å ($R_{C-C}=1.438$ Å, $R_{C-H}=1.096$ Å). The outermost ring corresponds to the hydrogens and is positively charged ($Q=1.8e$). In the simplest case, this charge is compensated by the negative charge of the next ring, corresponding to the chain of outer carbon atoms. Two inner rings, then, are neutral.

“Natural orbitals” (NBO) chosen in such a way that each orbital is occupied by, ideally, two electrons \cite{35, 36, 37}. We use the so-called Electrostatic potential scheme (ESP), in which the partial charges are determined from the best fit of the actual electrostatic potential of the molecule \cite{27}. This method is not only better justified physically for our purposes, but it is also less dependent on the choice of basis set used in the calculations, see Table \ref{tab:charges}.

In the simplest approximation, the electron density, shifted from the hydrogens, is assigned to the outer carbons, covalently bonded to the hydrogens. Then the ring corresponding to the chain of the outermost carbons is charged negatively. The inner rings remain neutral. The charge distribution in such approximation can be crudely described as a polarized band (with a positively charged outer edge and a negatively charged inner edge) located along the perimeter of the molecule. This charge distribution can also be considered as a dipole continuously distributed along the outer border of the molecule. In fact, within this approximation one can assign a typical value of the partial charge (say, 0.15$e$) to all the hydrogen atoms and then one immediately obtains the charges of the two outer rings. The DFT analysis of the electron density in this case is not necessary. This approximation
TABLE IV: Partial charges in coronene assigned to carbon and hydrogen atoms according to the Mulliken [34], natural bond orbitals (NBO) [36] and best fit electrostatic potential (ESP) [27] schemes (in units of elementary charge). C\textsubscript{1} are carbons from the innermost chain (there are 6 of them), C\textsubscript{2} are carbons from the intermediate carbon chain (6), C\textsubscript{3} are carbons from the outer carbon chain (12).

| Method          | C\textsubscript{1} | C\textsubscript{2} | C\textsubscript{3} | H   | C\textsubscript{1} | C\textsubscript{2} | C\textsubscript{3} | H   |
|-----------------|--------------------|--------------------|--------------------|-----|--------------------|--------------------|--------------------|-----|
| B3LYP/6-31+G(d) | -0.346             | 0.741              | -0.384             | 0.185| 0.158              | -0.138             | -0.213             | 0.241| -0.002            | 0.129             | -0.207             | 0.148|
| B3LYP/D95       | -0.008             | 0.463              | -0.46              | 0.232| -0.016             | -0.041             | -0.19              | 0.218| 0.002             | 0.13              | -0.237             | 0.168|
| B3LYP/cc-pVDZ   | 0.064              | -0.02              | 0.026              | -0.049| -0.008             | 0.053              | -0.199             | 0.229| -0.004            | 0.095             | -0.171             | 0.129|
| PBE/6-31+G(d)   | -0.362             | 0.807              | -0.42              | 0.197| 0.115              | -0.136             | -0.22              | 0.251| -0.003            | 0.121             | -0.223             | 0.148|
| PBE/D95         | 0.033              | 0.454              | -0.482             | 0.238| -0.016             | 0.044              | -0.196             | 0.225| -0.003            | 0.133             | -0.236             | 0.16|
| PBE/cc-pVDZ     | 0.076              | -0.014             | 0.009              | -0.04| -0.008             | 0.055              | 0.207              | 0.239| -0.0023           | 0.086             | -0.18              | 0.13|
| PBE/cc-pVTZ     | 0.371              | -0.029             | -0.335             | 0.164| -0.009             | 0.054              | -0.187             | 0.218| 0.002             | 0.114             | -0.205             | 0.149|

provides a tool for studying interactions of large PAHs which cannot be treated with \textit{ab initio} methods.

The interaction energy between two PAH molecules consists of a Coulomb and a van der Waals terms calculated for each pair of the rings:

\[ E = \sum_{\alpha,\beta} \left( E_{\alpha\beta}^{\text{Coul}} + E_{\alpha\beta}^{\text{vdW}} \right), \]  

where index \( \alpha \) enumerates the rings in one monomer, and index \( \beta \) enumerates the rings in the other monomer.

The energy of Coulomb interaction of two charged rings \( E_{\alpha\beta}^{\text{Coul}} \) can be found by integrating the electrostatic potential created by one ring along the contour of the other ring:

\[ E_{\alpha\beta}^{\text{Coul}} = \frac{Q_{\beta}}{|\ell_{\beta}|} \oint \phi_{\alpha}^{\text{Coul}}(r) \, dl_{\beta}, \]  

where \( Q_{\beta} \) is the charge of the ring \( \beta \) equal to the sum of partial charges of all atoms belonging to the ring, \( |\ell_{\beta}| \) is the length of the ring. The electrostatic potential \( \phi_{\alpha}^{\text{Coul}}(r) \) created by a circular ring is expresses via the complete Elliptic function \( K \),

\[ \phi_{\alpha}^{\text{Coul}}(r) = \frac{2Q_{\alpha}}{\pi} \frac{1}{\sqrt{2rR_{\alpha}}} \frac{1}{\sqrt{x+1}} K\left( \frac{2}{x+1} \right), \]  

\[ x = \frac{r^2 + R_{\alpha}^2}{2rR_{\alpha} \sin \theta}. \]
Here $R_\alpha$ is the radius of the ring $\alpha$, $r$ is the modulus of $\mathbf{r}$, $\theta$ is the angle between $\mathbf{r}$ and the ring normal.

The van der Waal’s term $E_{\alpha\beta}^{\text{vdW}}$ can be calculated similarly,

$$E_{\alpha\beta}^{\text{vdW}} = \oint \left( \frac{Q^W_\beta}{|\ell_\beta|} \phi^W_\alpha(\mathbf{r}) + \frac{Q^X_\beta}{|\ell_\beta|} \phi^X_\alpha(\mathbf{r}) \right) d\ell_\beta. \quad (8)$$

The van der Waals charges $Q^W_\beta$ and $Q^X_\beta$ are defined as sums of the $C_6$ and $C_{12}$ coefficients, respectively, of all the atoms belonging to the ring. For a circular ring the van der Waals potentials $\phi^W_\alpha$ and $\phi^X_\alpha$ are expressed via elementary functions,

$$\phi^W_\alpha(\mathbf{r}) = \frac{Q^W_\alpha}{2} \frac{1}{(2rR_\alpha)^3} \frac{2x^2 + 1}{(x^2 - 1)^{5/2}}, \quad (9)$$

$$\phi^X_\alpha(\mathbf{r}) = \frac{Q^X_\alpha}{8} \frac{1}{(2rR_\alpha)^6} \frac{x(8x^4 + 40x^2 + 15)}{(x^2 - 1)^{11/2}}. \quad (10)$$

The model predicts the T-shaped and PD configurations to be stable, in accordance with the results of the DFT calculations. In addition to it, the model provides an intuitively obvious explanation why even for such a large PAH as coronene the T-shaped configuration is comparable in energy with the stack configuration. This happens due to the round shape of the coronene molecule, since only the ”edge to plane” configurations can be stable electrostatically. On the other hand, the dispersive interaction favors superimposed stacks for which the ”contact area” is largest. For the non-round molecules, e.g., anthracene, the interplay between these two factors results in parallel-displaced or rotated configurations [24], because a parallel displacement or a rotation can significantly decrease the electrostatic repulsion while not seriously affecting the van der Waals attraction. However, for the round molecules, such as coronene, the rotation or parallel displacement are much less effective in decreasing the Coulomb repulsion and the T-shaped configuration can become competitive.

Therefore, we conclude that in the dimerization process (and in formation of larger clusters of PAH molecules) the shapes of the molecules are very important. The proposed simple model can be useful in qualitative analysis of the possible configurations and in making the results of such analysis intuitively clear. The model can be applied to any polycyclic aromatic hydrocarbons, and it can be easily generalized on the DNA bases, etc. The model can also be used for predicting structures of larger coronene clusters and clusters of other PAHs.
Acknowledgments

This work is partially supported by the European Commission within the Network of Excellence project EXCELL, by INTAS under the grant 03-51-6170 and by the Russian Foundation for Basic Research under the grant 06-02-17227-a. We are grateful to Dr. A. Korol for fruitful discussions and Dipl. Phys. I. A. Solov’yov for providing us with a useful graphical software for drawing molecular images. We acknowledge access to the computer cluster at the Center for Scientific Computing of the Johann Wolfgang Goethe-University where the computations have been performed.

[1] S. R. Langhoff, J. Phys. Chem. 100, 2819 (1996).
[2] W. W. Duley, S. Lazarev, ApJ 612, L33 (2004).
[3] M. P. Bernshtein, M. H. Moore, J. E. Elsila, S. A. Sandford, L. J. Allamandola, R. N. Zare, ApJ 582, L25 (2003).
[4] L. J. Allamandola, J. P. Barker, ApJ 290, L25 (1985).
[5] C. W. Bauschlicher, D. M. Hudgins, L. J. Allamandola, Theor Chem Acc 103, 154 (1999).
[6] W. W. Duley, S. Lazarev, ApJ 612, L33 (1981).
[7] A. Leger, J. Puget, L A&A 137, L5 (1984).
[8] K. Sellgren, ApJ 277, 623 (1984).
[9] A. L. Mattioda, L. J. Allamandola, D. M. Hudgins, ApJ 629, 1183 (2005).
[10] M. Rapicioli, C. Joblin, P. Boissel, A&A 429, 193 (2005).
[11] A. Li, ASP Conference series 309, 417 (2004).
[12] J. L. Puget, A. Leger, An. Rev. Astr. Ap. 27, 161 (1989). (and references therein)
[13] F. Boulanger, A. Abergel, C.,esarsky. BernardJP,D J. L. Puget, W. T. Reach, C. Ryter, ASP Conference series 132, 15 (1998).
[14] M. Mitsui, Sh. Kokubo, N. Ando, Y. Matsumoto, A. Nakajima, K. Kaya, J. Chem. Phys. 16, 121 (2004).
[15] F. Piuzzi, I. Dimicoli, M. Mons, P. Millie, V. Brenner, Q. Zhao, B. Soep, A. Tramer, Chem. Phys. 275, 123 (2002).
[16] Ph. Brechignac, M. Schmidt, A. Masson, T. Pino, P. Parneix, C. Brechignac, A&A 442, 239
(2005).

[17] M. A. Duncan, A. M. Khiight, Y. Negishi, S. Nagao, A. Kato, A. Nakajima, K. Kaya, Chem. Phys. Lett. 309, 49 (1999).

[18] P. Hobza, H. L. Selzle, E. W. Schlag, J. Phys. Chem. 100, 18790 (1996).

[19] R. Jaffe, L. G. Smith, D. J. Chem. Phys. 105(7), 2780 (1996).

[20] M. O. Sinnokrot, E. F. Valeev, J. Am. Chem. Soc. 124, 10887 (2002).

[21] S. Grimme, J. Comput. Chem. 25, 1463 (2004).

[22] M. Rapicioli, F. Calvo, F. Spiegelman, C. Joblin, D. J. Wales, J. Phys. Chem. A 109, 2487 (2005).

[23] O. A. Zhikov, O. V. Shishkin, K. A. Lyssenko, J. Leszczynski, J. Chem. Phys. 122, 144104 (2005).

[24] C. Gonzalez, E. C. Lim, J. Phys. Chem. 107, 10105 (2003).

[25] S. Grimme, M. Piacenza, ChemPhysChem 6, 1554 (2005).

[26] M. J. Frisch, et al., Computer code GAUSSIAN 03, Rev. C.02 (Gaussian, Inc., Wallingford CT, 2004).

[27] J. B. Foresman and A. Frisch, Exploring Chemistry with Electronic Structure Methods (Gaussian Inc., Pittsburgh PA, 1996).

[28] W. L. Jorgensen, D. L. Severance, J. Am. Chem. Soc. 112, 4768 (1990).

[29] M. Piacenza, S. Grimme, J. Am. Chem. Soc. 127, 14841 (2005).

[30] A. Marzec, Carbon 38, 1863 (2000).

[31] J. H. Miller, W. G. Mallard, K. C. Smyth, J. Phys. Chem. 88, 4963 (1984).

[32] B. W. van de Waal, J. Chem. Phys. 79, 3948 (1983).

[33] Q. Wu, W. Yang, J. Chem. Phys. 116, 515 (2002).

[34] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).

[35] P. O. Lowdin, Phys. Rev. 97, 1474 (1955).

[36] J. E. Carpenter, F. Weinhold, Theor Chem Acc 169, 141 (1988).

[37] F. Weinhold, C. R. Landis, Chem. Ed.: Research and Practice in Europe 2, 91 (2001).