

Electronic structures of the electron donor-acceptor complexes of fullerenes C₆₀ and C₇₀ with azulene and some of its derivatives employing *ab initio* and DFT methods

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Received 20 August 2010; revised and accepted 29 October 2010

Quantum mechanical calculations have been carried out to determine the structural and electronic properties of the electron donor-acceptor complexes of C₆₀ and C₇₀ with azulene and some of its derivative, viz, 1,3-dichloroazulene, 2-hydroxyazulene and 4,6,8-trimethyl azulene. The molecules studied are optimized first with semi-empirical molecular orbital theory at the third parametric level, and, then further optimized by Hartree Fock method. The optimized geometries, calculated energies, spatial distribution, HOMO and LUMO energies along with the electrostatic potential maps of the individual molecules and the electron donor-acceptor complexes are obtained by *ab initio* and density functional theory methods. The results suggest that the LUMO state of these complexes is localized on the fullerene moiety whereas the HOMO state is positioned on the azulenes. The energy difference of localized LUMO levels strongly depend on the functional group attached to the azulene and the structure of the fullerene-azulene molecular complexes.

Keywords: Theoretical chemistry, *Ab initio* calculations, Density functional calculations, Azulenes, HOMO–LUMO energy, Molecular electrostatic potential maps

The non-alternant azulene and its derivatives have been of interest to the theoretical chemists because of their properties, such as a large permanent dipole moment (for a hydrocarbon),^{1,2} intense fluorescence from S₂ to S₁ state³ and large hyperpolarizability^{4,5}. The molecular dipole moment and electron densities of azulene have already been ascertained employing semiempirical quantum chemistry method^{1,2,6,7}. Morley suggested that the dipole moments of the azulenes can be tuned by a careful selection of substituents^{3,4}. Moreover, the results of various aromaticity theories⁸⁻¹⁰ indicated that azulene possesses much lower aromatic delocalization energy (e.g., 4.2 kcal/mol from Dewars result⁸) compared to benzene (20 kcal/mol), thiophene (16.1 kcal/mol) and naphthalene (30.5 kcal/mol). Thus, the physico-chemical properties of azulene-containing hydrocarbons are to a large extent controlled by the aromaticity of the tropylium cation cyclopentadienyl anion mesomeric form, which rationalizes facile electrophilic attack at C1 (to form vinyl tropylium cation) and nucleophilic attack at C4/C6 (to form 1,2-divinyl-cyclopentadienyl anion) positions. As a

result of this, azulene occupies a place of special importance in molecular spectroscopy. Strong emission from its S₂ state occurs in violation of Kasha's rule¹¹. It is observed that the S₁ state of azulene is found to be almost non-fluorescent¹² ($\phi_f(S_1) \sim 10^{-6}$) and very short-lived¹³ ($\tau(S_1) \sim 1$ ps), whereas relatively long-lived¹⁴ ($\tau(S_2) \sim 1-2$ ns) and strong fluorescence¹⁴ ($\phi_f(S_2) \sim 0.04$) are observed from its second excited state. Asato *et al.*¹⁵ reported several novel and thermally stable azulene-containing donor-acceptor chromophores with significant second-order non-linear optical properties.

On the other hand, C₆₀ and C₇₀ have attracted considerable attraction during the last decade¹⁶. Fullerenes have been used as a good electron acceptor, and can be chemically bonded with other organic molecules without changes to their electronic properties. In particular, the reorganization energy in electron transfer reactions for fullerene C₆₀ was found to be small due to their unique structure and symmetry^{17,18}. Thus, fullerenes are actively involved in the molecular design of photoactive donor-acceptor systems¹⁹⁻²². Very recently, Rahman *et al.*²³ have

reported that azulene and derivatized azulenes can undergo very strong binding with fullerenes C_{60} and C_{70} resulting in a very large value of association constant. However, an unified approach regarding theoretical interpretation on the nature of molecular interaction between fullerenes with azulene and derivatized azulenes is long overdue, and according to the best of our knowledge, there are no such theoretical reports on elucidation of electronic and structural properties of the fullerene-azulene systems.

The purpose of the present work is to investigate the genesis of the complexation phenomena between fullerenes and various azulenes, namely, azulene (**1**), 1,3-dichloroazulene (**2**), 2-hydroxyazulene (**3**) and 4,6,8-trimethylazulene (**4**) by *ab initio* and density functional theory (DFT) quantum chemistry methods. The existence of the electrostatic interactions between fullerenes and azulenes has been discussed from the results obtained on frontier molecular orbital and electrostatic potential maps (MESP) calculations.

Methodology

The geometries of the molecules were optimized first using the molecular mechanics force field calculations from which the lowest energy conformations were obtained. The final optimized geometries of the complexes were obtained by performing the semi-empirical molecular orbital calculations at the PM3 level of theory followed by *ab initio* calculations using STO 3-21G basis set. All the structural variables have been obtained using the self-consistent Hartree-Fock (HF) and density functional theory (DFT) methods. Calculations were done using the SPARTAN'06 Windows version software²⁴. Localization of the frontier orbitals were investigated by a single point energy calculation using 3-21G basis set for *ab initio*, 6-31G* and 6-311G* basis sets for DFT levels of theory. The spatial distribution of frontier orbital (highest occupied molecular orbital and lowest unoccupied molecular orbital) provided a strategy from which the electronic structures were predicted.

Results and Discussion

Preliminary theoretical studies on azulene and substituted azulene

To understand the electronic nature of the azulene molecules, we first focused our attention on the

optimized geometries of a number of azulene and their derivatives with donor and acceptor ligands, employing HF/3-21G, DFT/B3LYP/6-31G* and DFT/B3LYP/6-311G* levels of theory^{25,26}. The results of the *ab initio* and DFT calculations for the HOMO and LUMO energy values of various uncomplexed azulenes are listed in Tables S1 and S2 and Table 1. For our present investigations, good descriptions of the LUMO states are very important, as the incoming electrons are assumed to pass through it. These data demonstrate a comparison of the HOMO-LUMO energies of different azulenes with electron donation and electron-withdrawing groups. It is clear from the above tables that when electron-donating group, such as -OH is attached to the five membered ring of azulene, the HOMO and LUMO energy levels increase. The converse is true when electron-withdrawing groups like -Cl is attached to the five membered ring of the azulene. This effect is due to the increase in electron density in the aromatic ring by the introduction of electron-donating groups. Therefore, one can imagine that the substitution in the five- and six-membered ring of azulene by an electron-withdrawing group can make the azulene to behave like a p-type molecular device while presence of electron-donating group results in an n-type molecular device. It should be mentioned at this point that for better understanding of the HOMO and LUMO energies, we have done extensive DFT calculations for all the fullerenes and azulenes independently employing 6-311G* basis set for B3LYP model. HOMO-LUMO energy gaps (HLG) for C_{60} and C_{70} corroborate fairly well with the reported HLG of C_{60} and C_{70} , i.e., 1.6-1.7 eV, determined by photoemission measurements²⁷.

The energy difference between the LUMO energies of individual n-type and p-type molecules ($E_{LUMO(\infty)}$)

Table 1 – Comparison of the five highest occupied and five lowest unoccupied orbital levels (eV) of azulene and functionalized azulenes obtained by DFT/B3LYP/6-311G* calculations

State	1	2	3	4
HOMO – 4	-9.2371	-8.6618	-9.2187	-8.9120
HOMO – 3	-9.1610	-8.5312	-8.6952	-8.6247
HOMO – 2	-8.3695	-8.5206	-8.2900	-7.6272
HOMO – 1	-6.5132	-6.8953	-5.9228	-6.1168
HOMO	-5.3762	-5.4289	-5.4865	-5.2244
LUMO	-2.1168	-2.5708	-1.8326	-1.8724
LUMO + 1	-1.1904	-1.6353	-1.1339	-1.0642
LUMO + 2	0.8811	0.6917	0.7838	1.1229
LUMO + 3	1.5260	1.1170	0.9804	1.5608
LUMO + 4	1.8655	1.3060	1.5691	1.6192

can be used as an approximate measure of the potential drop across a molecule chemically bonded by n-type and p-type molecular subunits. These results show that the HOMO and LUMO energy levels of the molecule **4** (-CH₃ substitution), increase by 0.1326 and 0.2205 eV, respectively, as compared to the azulene molecule as revealed by HF calculation, and by 0.1591 and 0.2297 eV as estimated by DFT/B3LYP/6-31G* calculations. Expectedly, for the -Cl substituted molecule (**2**), the HOMO and LUMO energy levels are lowered by 0.1982 and 0.5574 eV, respectively, obtained at HF level of theory. Although, DFT (B3LYP/6-31G*) calculation predicts lower HLG, i.e., 0.0664 and 0.4566 eV, the effects of both electron withdrawing and electron donating groups are found to be dissimilar with respect to the HLG. In the case of **4**, it has been observed that there is a reduction of 0.0879 eV HLG as compared to the unsubstituted azulene estimated by HF calculations. However, DFT results predict much higher value, i.e., 0.0706 eV in terms of HLG for the same molecules under consideration. But, when an -Cl or OH group is substituted in azulene moiety, the HLG of the azulene molecule (originally 8.3886 eV) is increased to 8.0264 and 8.9755 eV, respectively as determined by HF calculation. DFT calculations at B3LYP/6-31G* level, however, give a much lower HLG in the case of unsubstituted azulene, i.e., 3.282 eV. Similarly, DFT calculations at B3LYP/6-31G* level estimated lower HLG in the case of **2** and **3** (2.8918 and 3.6698 eV, respectively). The accuracy of B3LYP calculations can be enhanced considerably applying 6-311G* basis set. Using this basis set, we have got very reliable HLG values for azulene and derivatized azulene. For example, DFT/B3LYP/6-311G* calculation predicts 0.0226 eV lower HLG for **1** (3.2594 eV) in comparison to DFT/B3LYP/6-31G* calculations. The most interesting feature of the present investigation is a similar sort of effect is reflected when both electron withdrawing and electron donating groups are added to the azulene. For example, HLG value for **2**, **3** and **4** are estimated to be 2.8581, 3.6539 and 3.3520 eV, respectively. The above results clearly demonstrated that DFT approach at B3LYP/6-311G* level of theory gives results of high accuracy comparable to those from sophisticated *ab initio* treatments justifying the validity of such calculations in our present investigations.

Geometric and electronic structure calculations on C₆₀ and C₇₀ complexes of **1**, **2**, **3** and **4** in ground state

Figure 1 shows some typical optimized ground state geometric structures of the fullerene (C₆₀ and C₇₀) complexes of azulene and derivatized azulenes obtained after DFT calculations using 6-311G* basis set at B3LYP level of theory. Optimized ground state structures of various fullerene-azulene molecular complexes using *ab initio* and DFT/B3LYP/6-31G* method are provided as Supplementary Data (Figs S1-S6). The perfectly planar structure of all the azulenes is retained even after complexation with fullerenes as revealed by both *ab initio* and DFT calculations. The distance between the nearest carbon atom of the fullerenes and azulene in the above complexes lies within the 3 – 3.25 Å. It has been envisaged that upon complexation with C₆₀, the bond distance of C-Cl and C-CH₃ for **2** and **4** molecules, respectively, undergo little change. Thus, for C₆₀-**3** complex, the C-Cl bond distance changes from 1.657 – 1.655 Å, whereas for the C₆₀-**4** complex, the C-CH₃ bond distance has negligible change from 1.497 Å – 1.496 Å in *ab initio* calculation. DFT calculations on the above two systems reproduce similar results. However, for C₆₀-**2** complex, DFT calculations failed to make any significant contribution regarding C-O distance in respect to uncomplexed azulene. The bond distance practically remains same, i.e., 1.354 Å. The above features strongly suggest that presence of different substituent groups of varying electron density may lead to a strong propensity in the perturbation of electronic charge for azulene and derivatized azulenes upon complexation with C₆₀ and C₇₀. From the above discussions, it is quite clear that orbital interaction energy arises mainly due to molecular interaction between occupied and unoccupied orbitals. To understand the electronic nature of the EDA complexes of azulenes with C₆₀ and C₇₀, we have investigated in detail the spatial distribution of the frontier orbitals of the optimized C₆₀, C₇₀ and azulenes, (**1**, **2**, **3** and **4**) independently, along with various fullerene-azulene molecular complexes. In our present investigations, the existence of the electrostatic interactions between azulene and fullerene moiety was evidenced by the results obtained on HOMO and LUMO using HF and DFT methods. Position of HOMO on the azulene and substituted azulenes certainly indicates that they act as donor molecule during formation of EDA complexes with fullerenes. Tables S3, S4 and 2 show

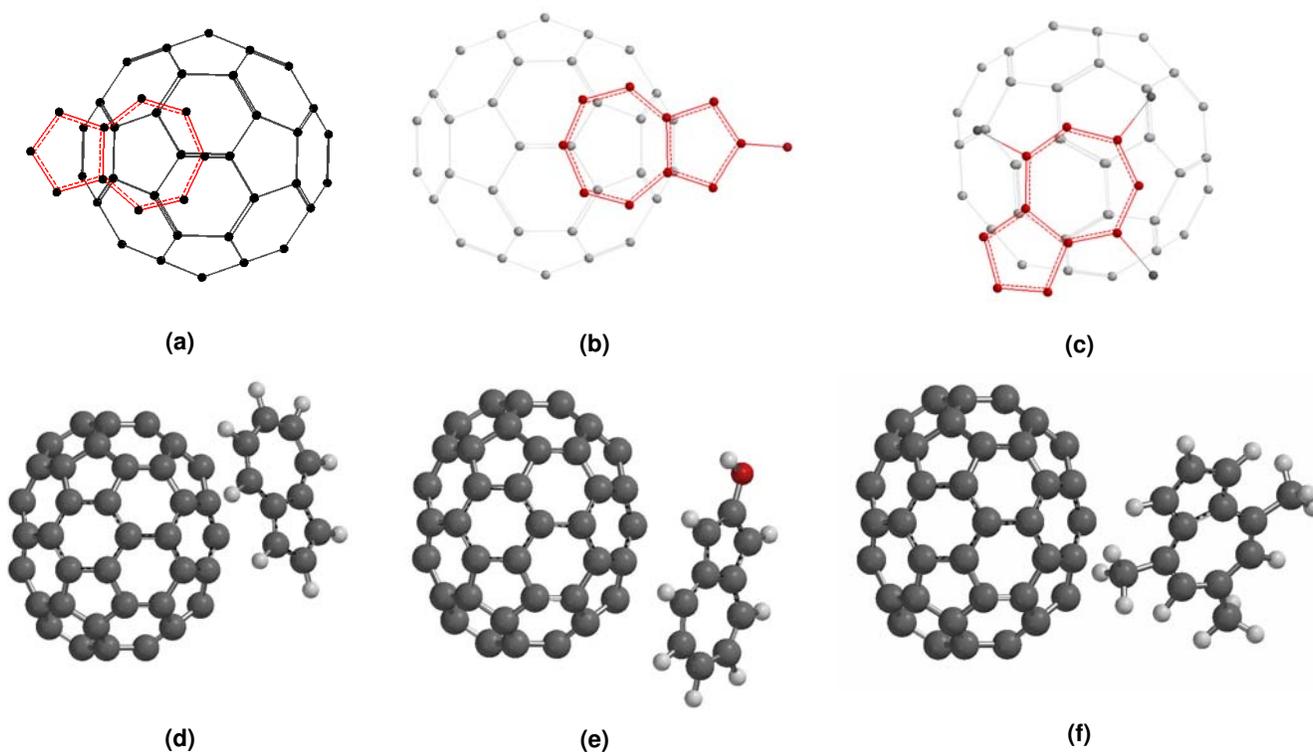


Fig. 1—Stereoscopic structures of the C_{60} complexes of [(a) **1**, (b) **3**, (c) **4**] and C_{70} complexes of [(d) **1**, (e) **3**, (f) **4**] obtained after DFT/B3LYP/6-311G* calculations.

Table 2—Comparison of the five highest occupied and five lowest unoccupied orbital levels (eV) for the C_{60} complexes of **1**, **3** and **4** obtained by DFT/B3LYP/6-311G* calculations

State	$C_{60}/1$	$C_{60}/3$	$C_{60}/4$
HOMO - 4	-6.3725	-6.3669	-6.3781
HOMO - 3	-6.3703	-6.3651	-6.3721
HOMO - 2	-6.3694	-6.3638	-6.3704
HOMO - 1	-6.3674	-5.9560	-6.1758
HOMO	-5.4094	-5.5215	-5.2946
LUMO	-3.5425	-3.8586	-3.5491
LUMO + 1	-3.5389	-3.5348	-3.5447
LUMO + 2	-3.5385	-3.5346	-3.5434
LUMO + 3	-2.3310	-2.3272	-2.3355
LUMO + 4	-2.3246	-2.3209	-2.3311

comparison of the five HOMOs and five LUMOs for the optimized structures of the EDA complexes of azulene and functionalized azulenes with C_{60} in *vacuo* using 3-21G, 6-31G* and 6-311G* basis sets for *ab initio*, DFT/B3LYP/6-31G* and DFT/B3LYP/6-311G* calculations, respectively. However, it has already been reported that C_{70} favors end-on orientation over side-on during its complexation with another molecule²². For this reason, we have presented the results of HOMO and LUMO at various electronic states for the optimized C_{70} -azulene

Table 3—Comparison of the five highest occupied and five lowest unoccupied orbital levels (eV) of the C_{70} complexes of azulene and substituted azulenes obtained by DFT/B3LYP/6-311G* calculations

State	$C_{70}/1$	$C_{70}/2$	$C_{70}/3$	$C_{70}/4$
HOMO - 4	-6.5392	-6.1449	-6.3402	-5.9928
HOMO - 3	-6.3420	-5.9392	-6.2854	-5.9482
HOMO - 2	-6.2879	-5.8905	-6.2834	-5.9407
HOMO - 1	-6.2841	-5.8894	-5.9539	-5.8927
HOMO	-5.4473	-5.2327	-5.5199	-4.9935
LUMO	-3.5373	-3.1202	-3.5347	-3.1711
LUMO + 1	-3.5361	-3.1194	-3.5337	-3.1685
LUMO + 2	-3.3543	-2.9528	-3.3520	-3.0070
LUMO + 3	-3.0309	-2.5886	-3.0291	-2.6426
LUMO + 4	-2.6705	-2.2639	-2.6677	-2.2983

molecular complexes in end-on orientation of C_{70} . Tables S5, S6 and 3 list the energy values of various HOMO, LUMO, HOMO - n and LUMO + n (where $n = 1$ to 4) states for the C_{70} complexes of azulenes and functionalized azulenes using 3-21G basis set for HF and 6-31G*, 6-311G* basis sets for DFT calculations. It is interesting to note here that while the LUMO energy levels for all the fullerene-azulene molecular complexes compare well with the fullerene (acceptor moiety), the HOMO energy level of the same complex is close to that of the

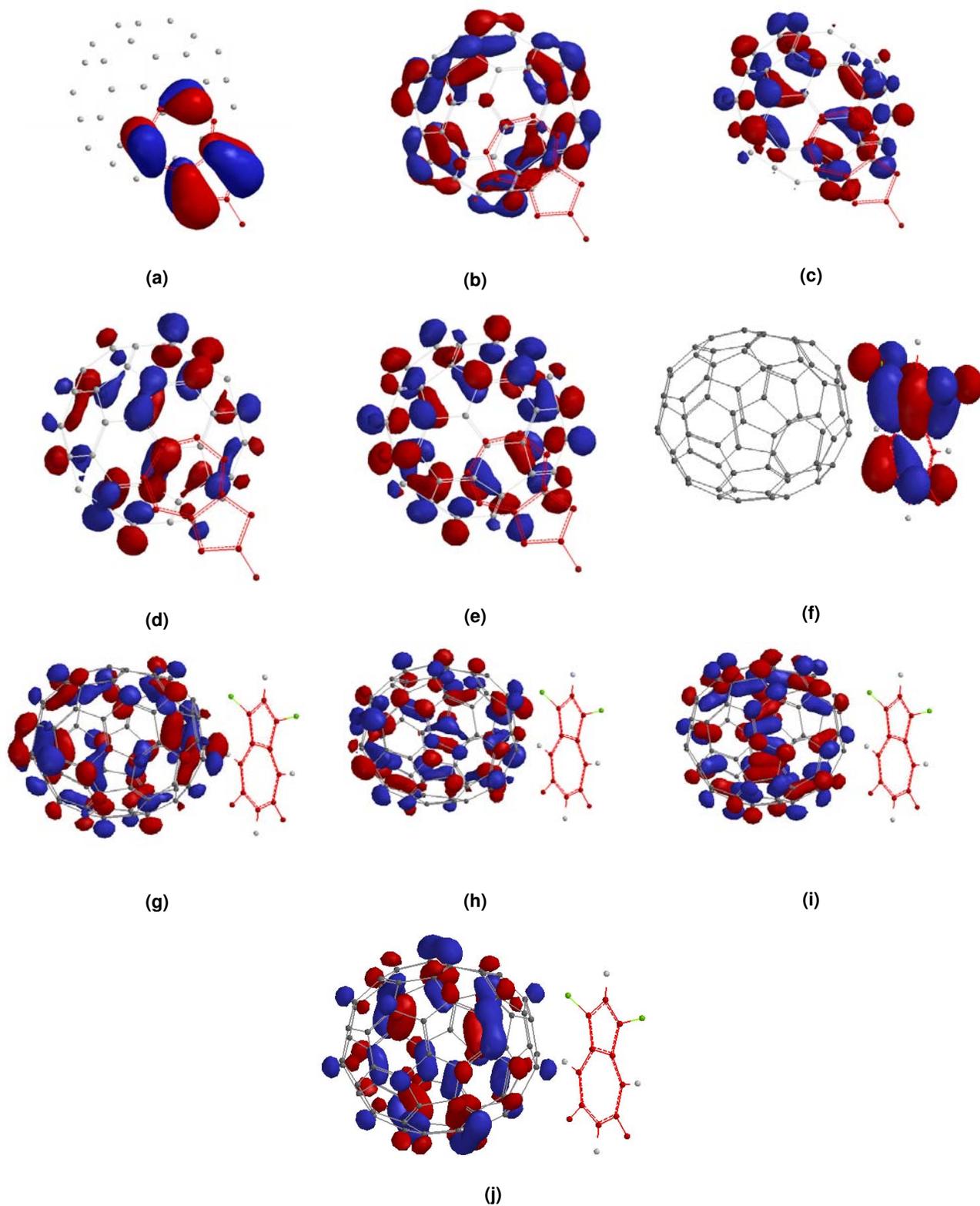


Fig. 2—Spatial orientation diagrams for the molecular orbital distribution for (a) HOMO, (b) LUMO, (c) LUMO + 1, (d) LUMO + 2, (e) LUMO + 3 energy levels for the C₆₀-3 complex and for (f) HOMO, (g) LUMO, (h) LUMO + 1, (i) LUMO + 2, (j) LUMO + 3 energy levels for the C₇₀-3 complex estimated by DFT/B3LYP/6-31G* calculations.

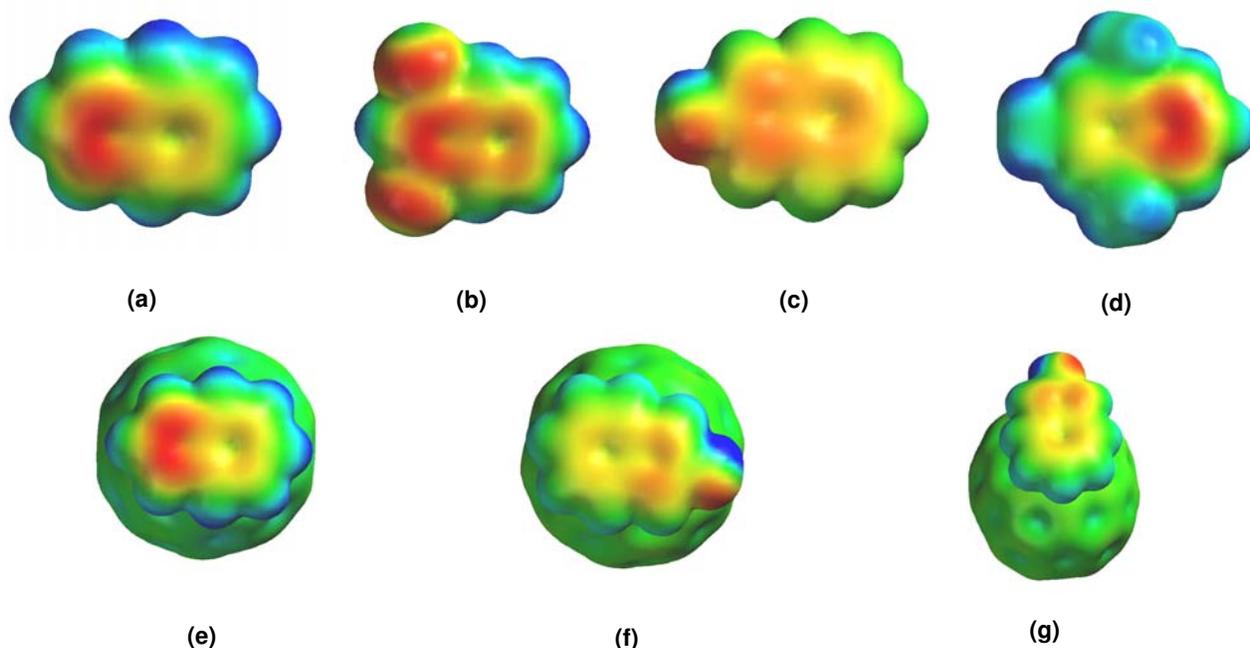


Fig. 3—MESP of (a) **1**, (b) **2**, (c) **3**, and (d) **4**, along with the MESP of (e) C_{60} -**1**, (f) C_{60} -**3** and (g) C_{70} -**3** systems estimated by DFT/B3LYP/6-311G* calculations.

uncomplexed azulene (donor moiety). However, the features and difference of the energy levels of the C_{60} - and C_{70} -complexes of **2**, **3** and **4** are affected by the functional group of the donor, i.e., chloro, hydroxy and methyl group. The same strategy can be seen in rectifier molecules having a similar sort of reported localization^{29,30}. Figure. 2 shows the spatial orientation diagram for the molecular orbital distribution for the HOMO, LUMO, LUMO + 1, LUMO + 2 and LUMO + 3 energy levels of the C_{60} -**3** and C_{70} -**3** complexes, determined by DFT/B3LYP/6-311G* calculations. The above figures envisaged that the LUMO, LUMO + 1 and LUMO + 2 are localized on the acceptor, while the HOMO and LUMO + 3 are positioned on the donor side. It should be noted at this point that the same tendency for the localization of the frontier orbitals has been reported previously for other fullerene-donor systems^{31,32}. It is noteworthy to mention here, that in all cases, DFT calculations validate the results obtained in the *ab initio* calculations.

Moreover, molecular electrostatic potential (MESP) map calculations reveals that the regions of high negative electrostatic potential of the azulene (the five membered ring) face the regions of strong positive electrostatic potential of the fullerenes (the centers of hexagons and pentagons) and vice versa (6:6 bond is high negative electrostatic potential

and seven membered ring in azulene is the center of high positive electrostatic potential). This result is consistent with the notion that fullerenes are generally accepted as good electron acceptors in forming EDA complexes with various electron donors^{33,34}. However, the complex structure of C_{70} with various azulenes reveals that the distribution of electronic potentials over the surface area of both the donor (azulene) and acceptor (fullerenes) molecules of fullerene-azulene EDA complexes takes place in such a manner that electrostatic interactions play a dominant role behind the mode of approach of C_{70} towards the plane of the azulenes. The same reasoning can be made in terms of high and low charge density regions. In this particular system, therefore, the electrostatic interaction eventually determined the absorption geometry of the azulene and derivatized azulenes with respect to fullerenes. Some typical MESP plots of azulenes and fullerene-azulene complexes are shown in Fig. 3.

Conclusions

The present study describes the ground state geometric and electronic structures of various fullerene-azulene complexes using *ab initio* and DFT calculations. The ground state electronic distributions for the fullerenes and azulenes, before and after complexation, have been analyzed on the

basis of spatial distribution of their frontier orbitals (HOMO and LUMO). It is observed that while the HOMOs are localized on the donor subunit, the LUMOs are positioned on the acceptor moiety. The analysis of the frontier orbitals is expected to be useful in assisting the interpretation of spectroscopic analysis. From an application perspective, combination of azulene with various macrocyclic receptor molecules like porphyrin has already attracted much attention as a potential candidate for development of molecular logic circuit⁴⁵. In this connection, the present study provides useful insight into the factors that control the propensity of electrostatic interaction in fullerene-azulene complexes and forms a platform for further studies involving the incorporation of such species into molecular devices.

Acknowledgement

This work was financially supported by Department of Science and Technology, New Delhi through Fast Track scheme of sanction no. SR/FTP/CS-22/2007. TM is thankful to The University of Burdwan, Burdwan, West Bengal, India, for providing basic research support to him.

Supplementary Data

Optimized structures of various fullerene-azulene molecular complexes using *ab initio* and DFT/B3LYP/6-31G* methods are given in Figs S1-S6 and data for various theoretical calculations at *ab initio* and DFT/B3LYP/6-31G* are provided in Tables S1 – S6. These data (Figs S1-S6 and Tables S1-S6) may be obtained from the authors on request.

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