

Chalcanthrene–fullerene complexes: A theoretical study

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Received 6 September 2007; received in revised form 28 September 2007; accepted 28 September 2007

Available online 24 October 2007

Abstract

In this work we have considered a series of 10 chalcanthrenes–fullerene complexes that were studied by the BLYP density functional theory (DFT) approach. A complete series of chalcanthrenes ($C_{12}H_8XY$, in which X, Y = O, S, Se, Te) were computed in several combinations in order to demonstrate the effect of structural changes on the electronic properties of the complexes under consideration. The optimized geometries, dissociation energies, and vibrational spectra of the chalcanthrenes–fullerene complexes are reported.

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Keywords: Chalcanthrenes; Fullerenes; Interaction energies; Structures; Frequencies; BLYP

1. Introduction

Charge-transfer materials have been extensively studied in recent years due to their unusual electrical, magnetic and optical properties [1]. Chalcanthrene compounds have attracted great interest of scientists due to their thermal stability and potential capabilities in inorganic–organic materials [2]. These molecular species serve as excellent donating systems in charge transfer complexes [3]. The electron donating properties arise from interactions between the two benzene rings which occur through the chalcanthrenes.

The fullerene species possess unique photophysical properties that can be implemented as electron acceptor units in the design of donor–acceptor systems [4–9]. Fullerenes and their derivatives are ideal electron acceptors because of their unusually high electron affinity. They can reversibly accept up to six electrons [10]. Because of this property, many donor–acceptor systems containing the fulleropyrrolidine moiety have been synthesized as candidates for photovoltaic devices [11–13].

The supramolecular complexes formed by this type of molecule have been the subject of intensive studies, in

which a variety of these compounds have been prepared. The purpose of these studies was geared towards studying electron and energy transfer process [6,8,14–17]. Systems of this nature generally consist of a donor–acceptor pair. The donor (D) group is covalently linked to an acceptor (A) group through a rigid or flexible bridging unit (i.e. bicyclic or alkyl chain bridges). In order to create a new donor–acceptor pair, we have studied the possibility of the electron transfer between the chalcanthrenes (donor) and the fullerene C_{60} (acceptors).

In this work, we have been examined a series of ten chalcanthrenes–fullerene complexes by performing DFT calculations. The complete series of chalcanthrenes ($C_{12}H_8XY$, whereby X, Y = O, S, Se, Te) were studied in order to show the effect of such structural change on the structural and electronic properties of the complexes studied. The optimized geometries, dissociation energies, electronic density plots and vibrational spectra of chalcanthrenes–fullerene complexes are examined by the use of DFT.

2. Computational methods

The electronic structure calculations in this work were performed using the DMol³ [18] numerical-based density-functional computer software implemented in the

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Materials Studio Modeling 3.1 package from Accelrys, Inc. Additionally, geometrical optimizations and frequency calculations were carried out with the BLYP general-gradient potential approximation in conjunction with the double-numerical plus diffusion basis set (denoted as DND). This basis set is equivalent to a double-zeta DZP basis set, however, it has extra diffuse functions. Fine convergence criteria and global orbital cutoffs were employed on basis set definitions. Calculations have demonstrated that the proposed methods used are ideal when studying C_{60} van der Waals interactions, and adequately account for BSSE effects and dispersion forces [19,20]. Test calculations demonstrate that the basis set used reduces the BSSE error and is ideal for calculations on molecules of this type.

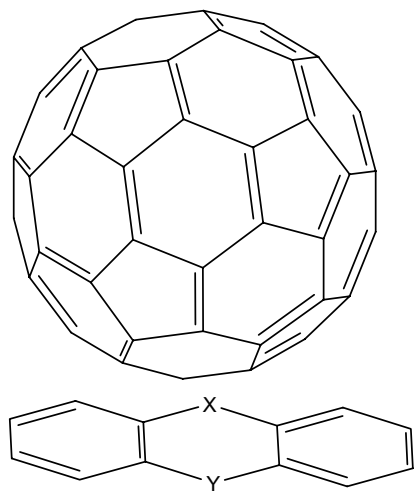
The dissociation energies (ΔE) for the complexes have been presented in order to determine their relative stability with respect to chalcathrenes–fullerene interactions:

$$\Delta E = E_{C_{60}\text{-Chalcathrene}} - (E_{C_{60}} + E_{\text{Chalcathrene}}).$$

Hessian matrices were studied to ensure that the structures obtained are experimentally viable from the DFT computations performed in this work on the described systems.

3. Results and discussion

Scheme 1 depicts a graphical representation of the chalcathrenes– C_{60} complexes, whereby X,Y = O, O, S, S, Se, Se, Te, Te, O, S, O, Se, O, Te, S, Se, S, Te, Se, Te. Fig. 1 shows the optimized geometrical structures of the systems calculated at the BLYP/DND level of theory. As we can see from the figure, the geometrical parameters are shown by which bond lengths are in angstroms (Å) and bond angles are in degrees (°). Fig. 2 displays the HOMO orbital plots for the species. Table 1 displays the HOMO/LUMO band gap for the isolated chalcathrenes and the gap for the chalcathrenes– C_{60} complexes. Also shown are the dis-



Scheme 1. The general structure of the chalcathrenes– C_{60} complexes described in this work. We have considered the following combinations for X and Y: O, O, S, S, Se, Se, Te, Te, O, S, O, Se, O, Te, S, Se, S, Te, Se, Te.

sociation energies for the studied species in kcal/mol. The structures have been ordered according to dissociation energies (ΔE) as we will discuss later. To further characterize the physical properties of these systems, vibrational frequencies (displayed in Table 2) are presented.

The table depicts the closest contact distances between the X and Y atoms with the fullerene surface. In all species considered in this work the isolated chalcathrene species undergoes minimal distortions when compared to the chalcathrenes–fullerene complex. For the O, O case it is readily observed that the intermolecular separation is about 3.8 Å and that the C–O bond length is 1.4 Å. If we replace the O, O atoms with Se, Te species we can see that the intermolecular distance increases by around 2.0 Å. The C–Se bond length in this case is 1.94 Å and the C–Te length is 2.17 Å as the figure clearly shows. It is evident from the figure that the structure has undergone structural distortions and increased ring puckering.

For the Te, Te species the intermolecular separation is slightly extended, with an even higher grade of ring puckering. The rings of the molecule appear to further interact with the fullerene species as the calculations demonstrate. If we next consider the O, S case, it can be seen that the intermolecular separation reduces to around 4.2 Å. If the oxygen atom is changed to sulfur in the S, S, case we obtain an intermolecular separation of about 5 Å. For the S, S case we also obtain longer C–S bond lengths than in the O, S case as a consequence of ring puckering. In the O, Se case the molecule is stabilized by chalcogenide interactions [21–23] which tend to stabilize complexes containing Se. The intermolecular separation is lower than in the S, S case and the bond angle distortions minimized. If we change Se for Te, this causes a slight elongation of the intermolecular separation; however, the geometries are rather consistent.

The S, Te case exhibits a large degree of ring puckering similar to the S, Te case while the intermolecular separation are smaller. For the S, Se and Se, Se cases the intermolecular separations is 4.7 Å and the C–X, Y–C angles have decreased. The final Se, Se structure is again the lowest energy structure with respect to dissociation as we will address later. Additionally, since Se has a larger atomic size, this permits coordination to the molecular surface much more feasible.

From the first table, it is clear that the HOMO/LUMO band gaps of the chalcathrenes molecules are higher than the complexed species. Upon interaction with the C_{60} species they reduce drastically. The most significant reduction can be observed for the Se, Te, and O, Se cases. The dissociation energies as the table shows vary from 70 kcal/mol (the O, O case) to 104.5 kcal/mol (the Se, Se case). This is significantly higher than other studies that propose metals as a binding factor in porphyrin– C_{60} complexes [20]. There does not appear to be a clear relationship between intermolecular separation, band gaps or dissociation energies, but it is clear that the Se containing species tend to be more stable with respect to dissociation.

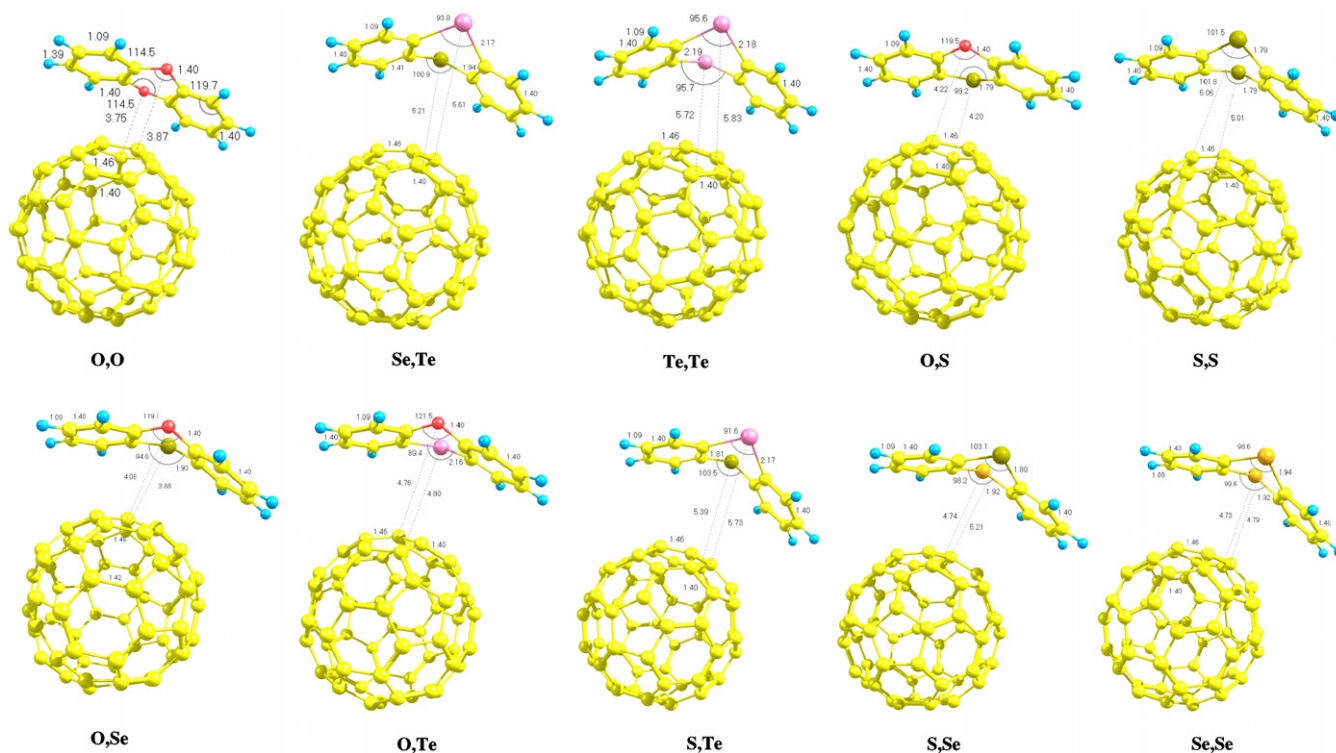


Fig. 1. Various geometrical parameters for the chalcathrenes- C_{60} complexes, where bond lengths are in angstroms (Å) and bond angles in degrees (°).

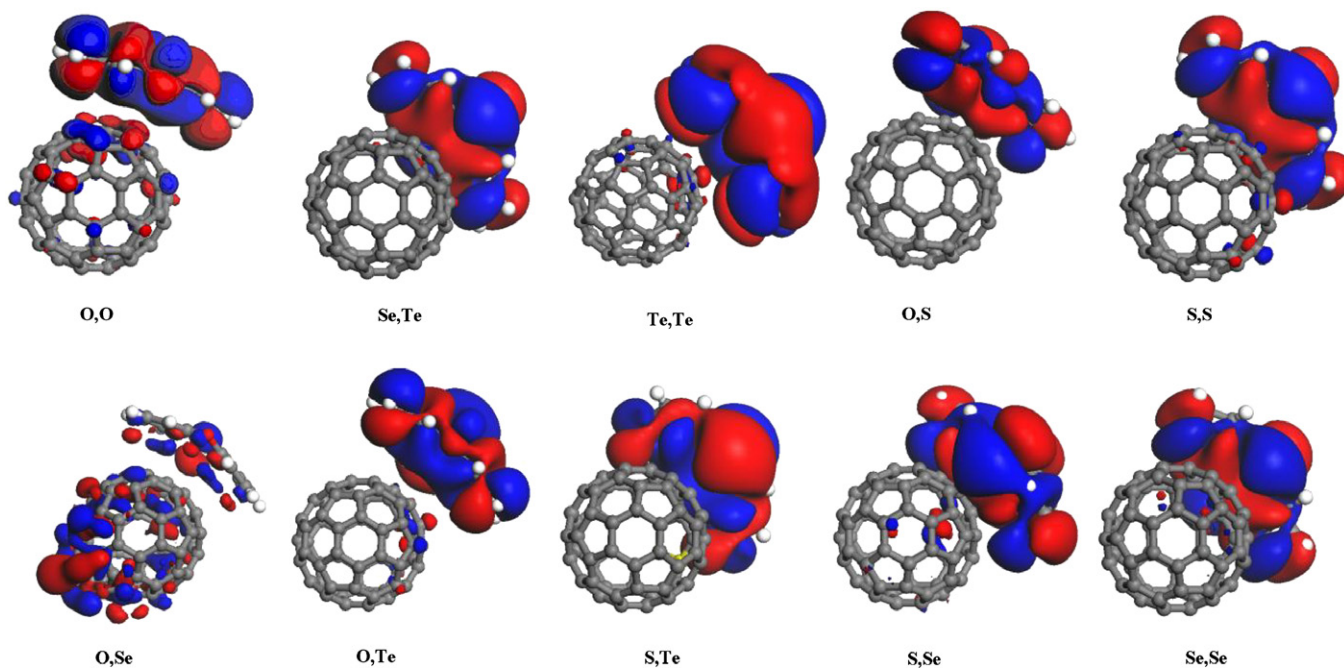


Fig. 2. HOMO isosurfaces (at a 0.022 a.u. contour level) for the chalcathrenes- C_{60} complexes.

Fig. 2 shows the HOMO plots for the species presented in this work. The systems which have higher dissociation energies tend to have a greater degree of electron density localized on the chalcathrene ring. The O, O-S, S cases appear to have a uniform distribution which is quite similar in all studies examples. How-

ever, the O, Se substituted molecule demonstrates an interesting deviation. In this species the electron density is localized along the fullerene species. In the Te, and Se containing frameworks the chalcathrenes have an extensive cloud of electron density masking the fullerene structure.

Table 1
HOMO/LUMO band gaps and dissociation energies in kcal/mol

X, Y	X–C ₆₀	Y–C ₆₀	Gap ^{Ch}	GAP ^{Com}	ΔE
O, O	3.75	3.87	84.7	28.9	70.0
Se, Te	5.21	5.61	69.3	15.7	72.9
Te, Te	5.72	5.83	63.7	20.7	73.0
O, S	4.20	4.22	75.2	25.1	82.7
S, S	5.01	5.06	63.2	26.4	89.2
O, Se	3.88	4.08	78.2	13.8	89.8
O, Te	4.76	4.80	65.1	21.3	99.2
S, Te	5.39	5.73	68.8	23.2	101.1
S, Se	4.74	5.21	74.8	25.2	102.3
Se, Se	4.73	4.79	79.5	25.0	104.5

In this table Gap^{Ch} corresponds to the chalcathrenes gap and Gap^{Com} corresponds to the the C₆₀ complex. Also shown are the nearest intermolecular distances in angstroms (Å) between the X, Y atoms and C₆₀.

Table 2
Selected vibrational modes in cm⁻¹

X, Y	ν ₁	ν ₂	ν ₃	ν ₄	ν ₅	ν ₆
O, O	110.1	167.6	224.3	261.9	304.6	335.9
Se, Te	40.6	95.7	172.9	231.3	302.8	335.4
Te, Te	31.2	94.0	155.0	229.3	303.5	336.7
O, S	86.7	117.1	220.8	246.5	300.8	337.3
S, S	57.1	206.0	231.4	235.9	310.6	335.9
O, Se	116.6	194.4	233.9	274.9	308.4	336.3
O, Te	55.1	163.5	219.1	284.4	318.7	337.8
S, Te	24.4	69.8	158.5	231.4	309.6	336.1
S, Se	48.7	91.3	178.9	231.8	310.1	338.3
Se, Se	40.6	95.7	172.9	232.0	313.8	339.1

ν₁ is the chalcathrenes–C₆₀ stretching, ν₂ = chalcathrenes bending, ν₃ is X, Y bending, ν₄ is chalcathrenes–C₆₀ rocking, ν₅ is a fullerene rocking mode, and ν₆ is a chalcathrenes–C₆₀ twisting mode.

Finally, we have also analysed a set of vibrational modes which can be used to characterize the presented species. Table 2 displays these modes whereby ν₁ is the chalcathrenes–C₆₀ stretching, ν₂ is chalcathrenes bending, ν₃ is X, Y bending, ν₄ is chalcathrenes–C₆₀ rocking, ν₅ is a fullerene rocking mode, and ν₆ is a chalcathrenes–C₆₀ twisting mode. It appears that the strongest ν₁ mode is observed for the O, Se case followed by the O, O case. The trend observed can be due to O–Se interactions which increase the vibrational frequencies of the interacting complex [22,23].

The increased value of the ν₂ vibrational frequency for the S, S case can be attributed to the modified geometry of the chalcathrene molecule. The largest ν₃ mode is seen for the O, Se system which can be accounted for by the small degree of ring puckering and O–Se interactions. The remainder of the vibrational frequencies are quite similar, but it appears that the O, Te species has the largest value for these frequencies. This can be explained by the larger intermolecular separations and smaller fullerene distortions caused by complexation. Upon complexation with the chalcathrene molecule the C₆₀ species undergoes slight changes in geometry and electronic properties which can manifest as changes in vibrational frequencies.

4. Conclusions

In this work we have studied the effect of chalcathrene–C₆₀ interactions by the use of the GGA-BLYP/DND method. The calculations demonstrate that Se–chalcogenide interactions can influence the stability of the selected species and have adverse effects on their binding energies as well as vibrational frequencies. We demonstrated that when the chalcathrene molecule is substituted with Se at both positions (see Scheme 1) the interaction energy with the fullerene increases dramatically. It is thereby important to understand effects of substitution and the transformation in the ability of C₆₀ to interact with other molecular species.

It is primarily dispersion forces that are responsible for the interaction between the fullerene and the chalcathrene. Dispersion forces (also referred as London forces) are long-range attractive forces that act between separated molecules even in the absence of charges or permanent electric moments. These forces are purely quantum mechanical in nature and arise from interplay between electron densities of the two interacting systems. We have compared the results to other GGA DFT approaches (i.e. PW91, PBE, HCTH, BOP) as well as local density approximation (LDA) methods (i.e. VWN, PWC) and have observed similar trends in the geometries and energies of the structures. Also, the strength of the dispersion forces for simple van der Waals complexes has been shown to be adequately computed by the BLYP/DND method. The advantage of the BLYP method is that it has a correction term implemented for dispersion forces in weakly bound complexes which tends to downplay the errors which arise from such an approximation. While DFT methods generally possess flaws when discussing dispersion forces, the methods employed appear to partially account for this. While full correlation methods are ideal (i.e. HF, MP2, CCSD(T)) for systems of this size it not possible due to limitations of computational resources. Even on large scale supercomputers such calculations are cumbersome and very time consuming.

The accurate characterization of these species requires detailed knowledge of the electronic structure of the interacting molecules. As mentioned the methods employed partially are corrected for dispersion forces and should provide at least qualitatively useful information. We believe that this report should serve as a benchmark for investigators performing DFT computations on weakly bound fullerene–chalcathrene complexes.

Acknowledgements

Special thanks are extended to DGSCA of the UNAM for valuable resources and to the University of Arizona for supercomputer time.

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