



THEORETICAL STUDY OF THE INTERACTION NATURE OF CHALCANTHRENE WITH FULLERENE C60

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ABSTRACT

The interaction between the two molecules of the chalcantrene–fullerene complex was studied and demonstrated by using Becke's 3-parameter, Lee-Yang-Parr method (B3LYP) with double-zeta basis set (DZP) to demonstrate the influence of stereo effects (the intermolecular distance, the rotation about the intermolecular axis, the chalcantrene molecule rotation about its longitudinal axis and the chalcantrene molecule rotation about its transverse axis) on the stability of the chalcantrene–fullerene complex. The optimized geometry, binding energy and molecular orbitals contributions to HOMO/LUMO and the energy gap is reported.

KEYWORDS: Density functional theory, chalcantrene, fullerene, binding energy, rotation, energy gap.

INTRODUCTION

Fullerene molecules are considered as the best electron acceptor in donor-acceptor systems (Haddon *et al.*, 1993 and Bracher *et al.*, 2002) where it has special photo-physical properties due to their high electron affinity, because of the fullerene molecule's ability to accept up to six electrons, it is synthesized as candidates for photovoltaic devices (Bracher *et al.*, 2002, Imahori *et al.*, 1999, Imahori *et al.*, 1997 and Mizuseki *et al.*, 2003). The thermal stability of chalcantrene compounds make them to be of great potential as bridging ligands in organic-inorganic materials (Kacholdt *et al.*, 1987). Chalcantrene molecules are considered as very good donors in charge transfer complexes (Andrews, 2005). Their electron donating behaviors appears to be due to interactions between the two benzene rings of the chalcantrene molecule. The charge transfer materials have been extensively studied due to their optical, electrical and magnetic properties (Amato *et al.*, 1993). All previous studies seek to examine the nature of electron transfer in

these complexes (Imahori *et al.*, 2001, Modin *et al.*, 2005, Holzwarth *et al.*, 2001, Imahori *et al.*, 2001, Mizueski *et al.*, 2003 and Muller *et al.*, 2010). The aim of this study was to examine the electron transfer between chalcantrene (as donor) and fullerene C60 (as acceptor) as a function of the four stereo effects (the intermolecular distance x , the chalcantrene molecule rotation about the intermolecular axis θ , the chalcantrene molecule rotation about its longitudinal axis ϕ and the chalcantrene molecule rotation about its transverse axis ψ).

COMPUTATIONAL METHODS

Initially, the geometrical optimizations of fullerene-chalcantrene complex were carried out by the Restricted Hartree-Fock method (RHF) and then by the Density Functional theory B3LYP with base set DZP. The B3LYP is the Becke's three-parameter hybrid functional using the Lee-Yang-Parr correlation (LYP) (Becke, 1993). The B3LYP exchange-correlation functional is:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

Where $a_0 = 0.2$, $a_x = 0.72$ and $a_c = 0.81$. E_x^{GGA} and E_c^{GGA} are generalized gradient approximations for the Becke 88 exchange functional (Becke, 1998) and the correlation functional of Lee, Yang and Parr (Lee *et al.*, 1989, and Miehlich *et al.*, 1989), respectively, while E_c^{LDA} is the local density approximation (LDA) to the correlation functional (Vosko *et al.*, 1980). DZP is the double-zeta basis set, which has diffuse functions (Kamiya *et al.*, 2002). Calculations have illustrated that the implemented methods are ideal when studying fullerene C60 van der Waals interactions, and adequately account for the basis

set superposition error (BSSE) effects and dispersion forces (Basiuk *et al.*, 2005).

All calculations were carried out using the Amsterdam Density Functional (ADF) software [www.scm.com]. All molecular structures were prepared with the graphics program Chem Draw from Cambridge Soft [www.camsoft.com].

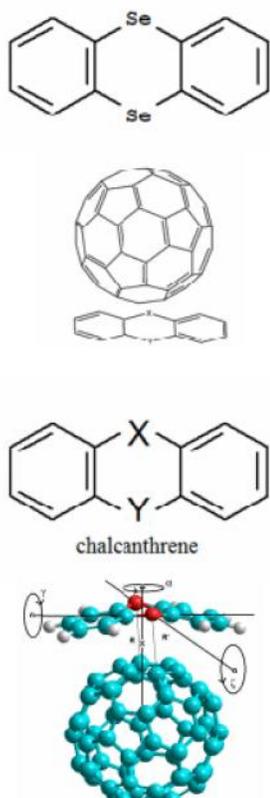
The initial geometry optimization results in the table-1 below shows a good agreement with other results (Jallbout *et al.*, 2008).

TABLE-1 the geometry optimized results of the complex fullerene- chalcanthrene, energy gap, binding energy using B3LYP/DZP

Parameter	Present work	Other work [21]
R_{O-C60}	3.689 Å	3.75 Å
R_{O-C60}	3.688 Å	3.87 Å
(C-O-C)	103.71	104.5
(C-O-C)	103.71	104.5
Eg(Kcal/mol)	28.71(Kcal/mol)	28.9(Kcal/mol)
BE(Kcal/mol)	-68.79(Kcal/mol)	70.0(Kcal/mol)

RESULTS & DISCUSSION

Scheme 1, shows a graphical representation of the fullerene-chalcanthrene complex, where the chalcanthrene molecule is substituted (X, Y) with oxygen at both positions. There are four effects, below, that this study considers of their effects on the binding energy, BE and the energy band gap Eg; The four effects are 1) the change of the intermolecular distance, x , with steps of 0.5 Å; 2) the chalcanthrene molecule rotation about the intermolecular axis, θ , from angle 0, corresponding to the optimized structure, to rotation angle 90 with steps of 10; 3) the chalcanthrene molecule rotation about its longitudinal axis, ϕ , in front of the fullerene molecule, from angle 0 to 60 with steps of 10; and 4) the chalcanthrene molecule rotation about its transverse axis, ψ , in front of the fullerene molecule, from angle 0 to 25 with angle steps of 5 for each.



Scheme 1. Graphical representation of the fullerene-chalcanthrene complex with four stereo effects (x , θ , ϕ , ψ).

INTERMOLECULAR DISTANCE

To investigate the relationship between the intermolecular distances, x , BE and Eg, the intermolecular distance was changed by 0.5 Å steps. The binding energy of the complex, $BE = E_{\text{fullerene-chalcanthrene complex}} - (E_{\text{fullerene}} + E_{\text{chalcanthrene}})$, as a function of intermolecular distance, x is shown in Figure. 1; BE decreased as the chalcanthrene molecule shifted from the optimized intermolecular distance, x_0 . The binding energy disappeared when x was 1.0 Å more than the optimized distance, x_0 . Also, there was a rapid growth in the anti-binding energy as the chalcanthrene molecule moved closer toward the fullerene molecule. Moving the chalcanthrene molecule away from the fullerene was easier than becoming closer.

The range of attractive forces appeared when the molecule of chalcanthrene had distance from the $x_0 - 0.4$ Å to the $x_0 + 1.0$ Å. Thus, the molecules of fullerene and chalcanthrene, if separated beyond this distance of $x_0 + 1.0$ Å, would be in the gas phase. x_0 is limited in two directions: $x > x_0$ points toward a gas phase region or non-complex form, while $x < x_0$ points toward repulsion force or forbidden region. The molecular orbital coefficients (MOC) contributions of the two molecules in the complexes to the HOMO/LUMO levels are shown in Figures 2 and 3. As the chalcanthrene shifted out from the optimized distance ($x = x_0$) the chalcanthrene made major contributions of the HOMO electrons, where a greater electron density localized on the chalcanthrene molecule. So that it is similar to a gas phase region. The fullerene molecule does not make any contribution to the HOMO electrons at large shifting of the intermolecular distance. From Figure 2, the chalcanthrene shows a constant contribution to the HOMO as the intermolecular distance $x > -0.5$ Å. So there may be charge transfer at the intermolecular distance, x_0 . The fullerene molecule contribution to the HOMO begins growing below as intermolecular distance of ~ 2.5 Å, also as the intermolecular distance, x , decreases. The molecule of fullerene makes a contribution to the LUMO level in comparison with the chalcanthrene (Fig. 3) which has only a small down contribution to the LUMO level from the intermolecular distance $x = 1.5$ Å to the optimized distance. From this figure the chalcanthrene appears to have an inverse behavior to the contribution of fullerene molecules. If there is any probability of electron transmissions to the LUMO, the electron will be localized in the fullerenes orbitals, where the fullerene molecules have a high electron affinity. the contribution to HOMO and LUMO of the fullerene-chalcanthrene complex as a function of the intermolecular distance, x . Generally, the total contribution to HOMO shows only a slight growth in the gas phase region, but this growing more increases in

the complex region. The LUMO level does not appear to be influenced with the intermolecular distance through the gas phase and complex regions, except when the two molecules become very close, to each other, in the forbidden region. Figure 4 shows the energy gap of the fullerene-chalcanthrene complex as a function of the intermolecular distance, x . The energy gap first increased as the intermolecular distance decreased through the

forbidden region, but, at the intermolecular distance of -0.5\AA , it began to decrease sharply. At the optimized intermolecular distance x_0 , and when the energy gap $=28.71\text{Kcal/mol}$ there will be a decrease for the energy gap towards the gas phase region or non-complex form. The energy gap will be more stable around the value 15Kcal/mol when x was 1.0\AA more than the optimized distance, x_0 .

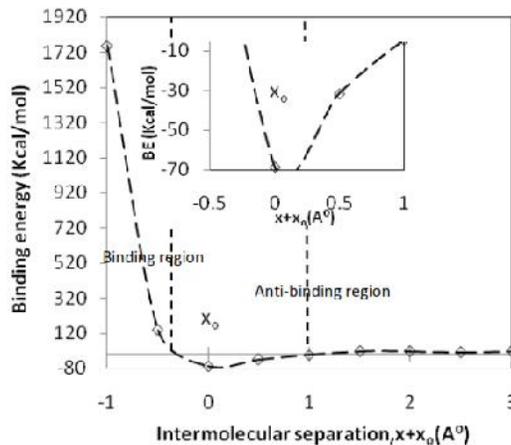


FIGURE 1: Binding energy of the complex as a function of the intermolecular distance, x , using B3LYP/DZP

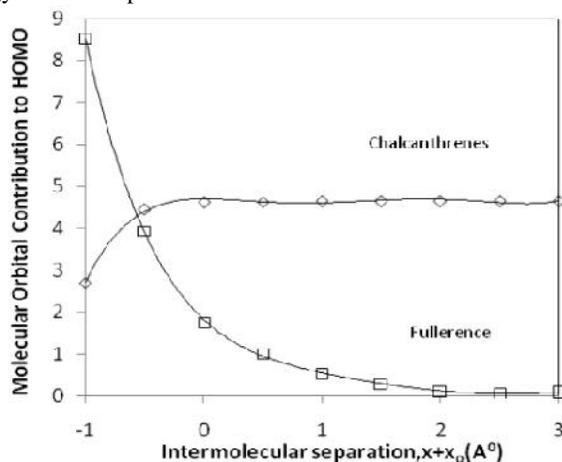


FIGURE 2: Molecular orbital coefficients of the molecules of chalcanthrene and fullerene to the HOMO level as a function of the intermolecular distance, x , using B3LYP/DZP.

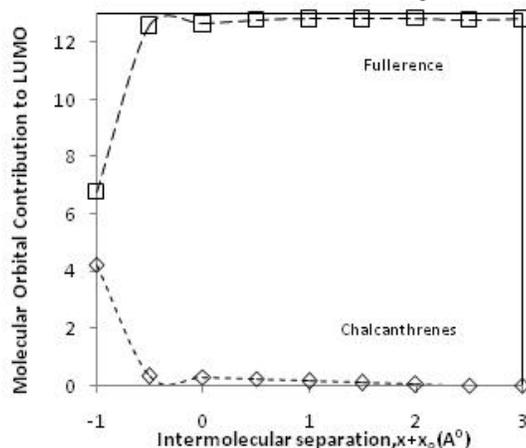


FIGURE 3: Molecular orbital coefficients of the molecules of chalcanthrene and fullerene to the LUMO level as a function of the intermolecular distance, x , using B3LYP/DZP.

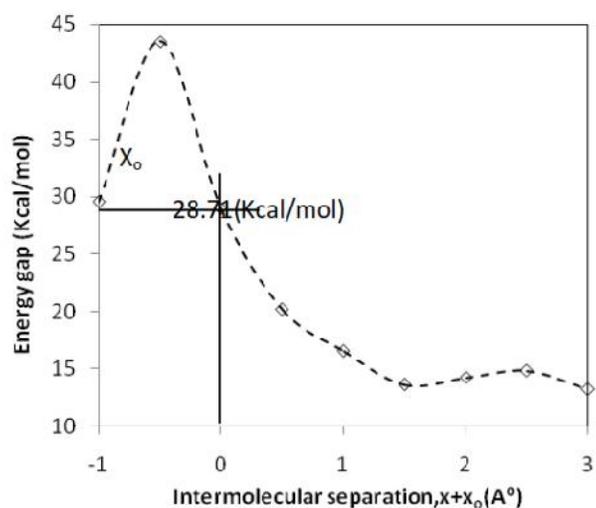


FIGURE 4: Energy gap of the complex as a function of the intermolecular distance, x , using B3LYP/DZP.

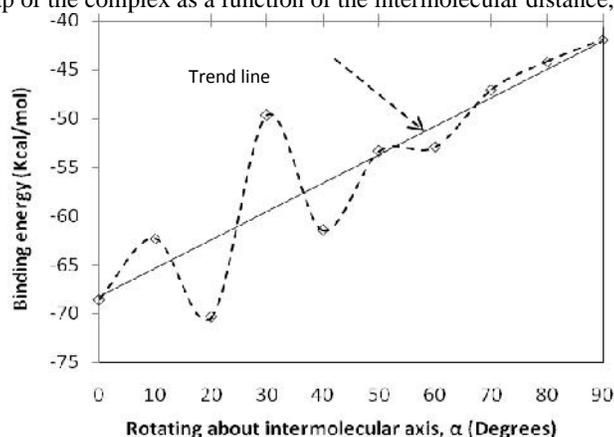


FIGURE 5: Binding energy as a function of the rotation of the chalcantrene around the intermolecular axis, α , using B3LYP/DZP.

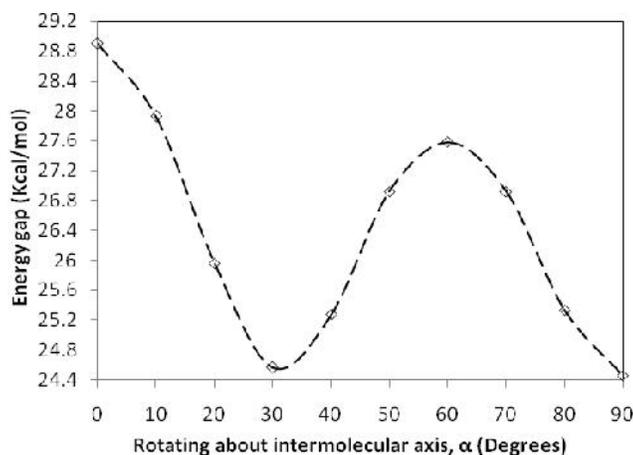


FIGURE 6 Energy gap as a function of the rotating the chalcantrene about intermolecular axis, α , using B3LYP/DZP.

Rotation about the intermolecular axis

An attempt was made to explore the response of BE, MOC to HOMO/LUMO and Eg of the complex with the rotation of the chalcantrene molecule about the intermolecular axis, α . Figure 5 displays BE as a function of the degree of rotation, where the BE decrease as the chalcantrene rotates, but with some fluctuation. At $\alpha = 20$, the binding energy became more negative point corresponding to the

initial optimized ($\alpha = 0$). Generally, these are rotations will reduce the stability of the complex due to the stereo effect, but the necessary energy to do it is not very high. The chalcantrene rotation about intermolecular axis does not show a noticeable effect on the contributions of the chalcantrene and the fullerene to the HOMO and LUMO, The figure 6 shows that the Eg of the fullerene-chalcantrene complex decreased as the molecule of

chalcantrene rotated from angle $\theta = 0$ to the angle $\theta = 30$, and then increased to reach a maximum at angle $\theta = 60$, then again decreased toward angle $\theta = 90$. If the complex has enough energy, $E = E(0) - E(30)$, it may rotate to the angle of $\theta = 30$ with $E_g(\theta = 30) = 24 \text{ Kcal/mol}$. Also thus with an energy of $E = E(0) - E(90)$, the $E_g(\theta = 90) = 24.3 \text{ Kcal/mol}$. This system may have some applications in molecular switching devices.

Rotation about the chalcantrene longitudinal axis

The rotation of chalcantrene molecule about its longitudinal axis, θ , in front of the fullerene molecule, leads to the lowering of the stability of the complex. The binding energy decreases to zero at the rotating angle $\theta = 20$, and then the anti-binding energy appears and grows rapidly toward the rotating angle of $\theta = 60$. The calculations for $\theta > 60$ did not converge. This behavior may reflect a steric effect, which appears for $\theta > 20$, and hence it is considered as a forbidden region. Due to the high energy because of the steric effect, it may not happen in this complex in comparison with rotation effect. The rotating of the chalcantrene about its longitudinal axis, θ , shows also results in only same in contributions of the chalcantrene and fullerene to the HOMO level from $\theta = 0$ to the rotating angle $\theta = 30$. For $\theta > 30$, the contribution of chalcantrene rapidly decreases, while the fullerene rapidly increases. This may be due to a large electronic charge transfer between these two molecules, where the change in electron density is localized. From Figure 10, however $\theta > 20$ is forbidden and therefore this behavior will not occur. The contribution of the chalcantrene and fullerene to LUMO again does not show any interesting effect of rotating of the chalcantrene about its longitudinal axis, θ . There was an increase in the E_g as the chalcantrene rotates from $\theta = 0$ to the angle $\theta = 40$, and then it decreases to a value lower than the energy gap at the optimized point. In the complex region, $\theta < 20$, there is no interesting change in the energy gap.

Rotation about the chalcantrene transverse axis

The last case in this study was rotation of the chalcantrene molecule about its transverse axis, θ , in front of the molecule of fullerene behavior of $BE(\theta)$, vs. rotation of the chalcantrene molecule about its transverse axis. It is similar to the behavior of $BE(\theta)$ as a function of rotation of chalcantrene about its longitudinal axis, except that it occurred at lower angles θ . However the BE vanished at rotating angle $\theta = 10$. At $\theta > 10$ an anti-binding energy appeared as a forbidden region. All calculations for $\theta > 25$ did not converge. Generally, this rotation about the chalcantrene transverse axis seems even less possible from the rotation about the chalcantrene longitudinal axis. The molecular contributions to HOMO/LUMO vs. rotation of the chalcantrene molecule about its transverse axis, θ ; they are also similar to the behaviors of the LUMO as a function of the rotating of chalcantrene about its longitudinal axis and the energy gap as a function of the rotating of chalcantrene about its longitudinal axis, although again at a smaller angle, here $\theta = 15$. Thus there is a forbidden region for $\theta > 10$. Also the energy gap E_g as a function of the rotation of chalcantrene about its transverse axis, θ , was studied, where E_g increased as the chalcantrene rotates from $\theta = 0$ to the angle $\theta = 20$ $E_g(\theta)$ then rapidly decreased to a value lower than the energy gap at

the optimized point, $E_g(\theta = 0)$. By noting the behavior E_g with rotation within the allowed region of complex ($\theta < 10$), there is no interesting change in the energy gap, so that it can have good applications in molecular switching devices.

CONCLUSION

In this work, the nature of the interaction was studied by using the B3LYP/DZP method employing ADF software. The results demonstrated that the stability of chalcantrene–fullerene complex and its binding energy as a function of the stereo effect (intermolecular distance, the rotation about the intermolecular axis, the chalcantrene molecule rotation about its longitudinal axis and the chalcantrene molecule rotation about its transverse axis): $BE(x, \theta, \phi) \sim -68.79 \text{ Kcal/mol}$. So that, there are conditions for these variables: 1) $x_0 - 0.3 \text{ \AA} < x < x_0 + 1.0 \text{ \AA}$, 2) $0 < \theta < 90$, 3) $0 < \phi < 20$ and 4) $0 < \phi < 10$. The interaction energy decreased dramatically when the intermolecular distance, x , shifted from the optimized distance. The contributions of chalcantrene and fullerene molecules to the HOMO/LUMO levels, within the complex region, showed interesting changes only with the intermolecular distance, x . The energy gap showed an interesting response to changes in x , and in comparison with θ . The rotation of chalcantrene about the intermolecular axis is easier than the other two rotations with two forbidden at angles $\theta = 20$ and $\theta = 40$.

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