J. Phys. Chem. A **1997,** *101,* 5692−5695

Structural Effects on the Direction of Charge Transfer in $C_{60}\cdots X_2$ (X = I, Br)

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Received: January 13, 1997; In Final Form: March 12, 1997[⊗]

In contrast to many organic halogen complexes, the bromine and the iodine complexes of C_{60} behave differently. Interaction of bromine with C_{60} may be sufficiently strong to break the Br−Br bond, while iodine forms layered intercalation compound. Charge transfer (CT) in the interaction of $C_{60}\cdots X_2$ (X= I, Br) system is investigated by EHT involving IMOD function. The calculation reproduces the observed experimental results and spectroscopic data. The direction of CT might be the consequence of structural effects of halogen docking.

Introduction

Many oxidatively or reductively[1,2] doped fullerenes show interesting properties such as superconducting and ferromagnetism.[3] Such electronic modifications are attempted based on the electronic structures of the host and guest materials. But there are cases that experimental results could not interpret ordinarily. For example, while alkaline metal doping of C_{60} produces electron doped balls consistently, halogen doping does not seem to produce simply a hole-doped fullerene.

In a number of charge transfer (CT) complexes, bromine and iodine behave similarly.[4] However, bromine with C_{60} results in a different structure from that of iodine. Interaction of bromine and C_{60} may become sufficiently strong enough to break the Br−Br bond. Thus, reduced bromide ion forms bond at the apices of (C(sp^3), (**1(A)**)) truncated dodecahedron axially with C−Br distance (1.99 Å), and evidence of Br−Br bond was not observed in both structural[5] and Raman data.[6]

On the other hand, no spectroscopic evidence was found for the I−I bond breakage for the $C_{60}\cdots I_2$ complex. Furthermore, it has been controversial about the role of iodine as acceptor[6] or donor[7] or neither.[8] In fact, it is quite unusual to consider iodine as a donor. But the most recent spectroscopic results of the Mössbauer[7a] and XANES[7b] studies seem to support that iodine acts as an electron donor to C_{60}. And Raman study shows donor property as well, but not quite quantitatively. Usually, X−X vibration is red-shifted by more than 20 cm^{-1} for the acceptor halogen for the most of known halogen complexes in the Raman and IR spectra.[9] However, recent Raman study on the iodine intercalated C_{60}[7b] shows that I_2 stretching frequency (212 cm^{-1}) is blue-shifted by 4 cm^{-1} from that of free I_2 (198 cm^{-1}). This supports that iodine behaves differently in the $C_{60}\cdots I_2$ system than any other organic⋯iodine complexes. But the blue shift by 4 cm^{-1} is too small for the force change accompanied with the experimental I−I bond contraction.[1] *Ab initio* calculation[10] shows that this is smaller than expected too. This number is appropriate for the force change associated with weak hydrogen bond like C−H⋯O.[11]

Any X−X distance alteration upon complexation would be important evidence to judge the direction and the degree of CT between donor and acceptor molecule. There are two structural reports on the I−I distance contradicting each other, but indicating CT. The I−I distance of 2.53 Å reported by Zhu et al.[1] is slightly shorter than 2.67 Å[12] in the molecular I_2 while 3.90 Å by Kobayashi et al.[8e] is rather close to the van der Waals (vdW) contact limit (3.96 Å)[13]. Experimental X-ray diffraction profile of the former shows much higher resolution than that of the latter, though.

It is not very difficult to find out the bond alteration upon charge transfer in the halogen-involved complexes. But most of the known halogen complexes show X−X bond elongation.[4] For example I−I distance (2.91 Å) in the diamagnetic $C_4H_8Se\cdots I_2$ is elongated by 0.24[14] and 0.12 Å in the 1,4-dithiane⋯iodine (1:2) complex.[15] Both of these compounds have the structure where iodine docked axially over the organic molecules. In fact, the iodine-doped C_{60} might be the first example of a sizable I−I bond contraction as much as 0.14 Å.[1] This CT interaction may look not so strong for $C_{60}\cdots I_2$ to show any magnetism, but it is even reported as a ferromagnet with a T_c of ∼20 K.[7b] No further proved experimental result has been published about the magnetism yet. There may be other reasons such as crystal defect or impurity which might be responsible for the observed magnetism.

Ionization enthapy (IE) and electron affinities (EA) data might explain the role of bromine or iodine as an oxidizing agent, but not the role of iodine as donor in the $C_{60}\cdots I_2$ system.[1,5,7b] In fact, the forward CT from the C_{60} to the halide (IE of C_{60} (7.6 eV);[16] EA[17] of I_2 (2.49 eV) and Br_2 (2.59 eV)) requires much less energy barrier than the backward CT when EA of C_{60} (2.65 eV)[18] and IE of I_2 (9.40 eV) and Br_2 (10.52 eV)[19] are compared. Therefore, it is of interest to study such different CT behavior of halogens and its origin upon interaction with C_{60}. Up to now, intercalation modes of the halogen or the reaction leading to halides associated with C_{60} is not studied.

Models and the Method of the Calculation

A molecular $C_{60}\cdots X_2$ model is utilized throughout this work to identify the interaction between the guest (X_2) and the host (C_{60}). The fullerene model with two different C−C bond distances of 1.45 and 1.39 Å is used.[1] And two X_2 (X = Br, I) docking fashions, axial (end-on) (**1A**) and resting (**1B**) over the C_{60} peripheral, were considered in our calculation. Although no intermediate structure leading to bromides for the $C_{60}Br_{24}$ compound[5] is known, the linear geometry (axial docking) is assumed as found in the pyridine⋯iodine complex.[4] Also since I_2 is intercalated between the C_{60} layers with the resting fashion (after Mulliken's notation)[20] over the cage peripheral experimentally, resting docking is considered as well.[1,8e] **1B** shows that iodine docking over the 56 bond (56 resting docking hereafter), which is one of the energetically favorable positions

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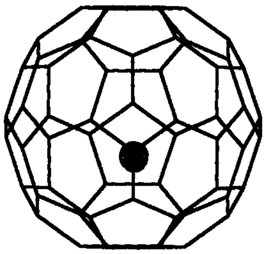
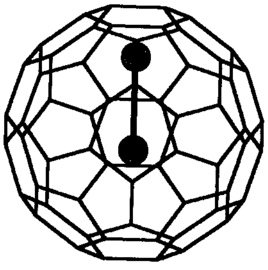
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)00200-4 CCC: $14.00



1(A)



1(B)

with the resting fashion. Nevertheless, it is difficult to observe the ordering of carbon atoms. Also, the iodine molecules are statistically disordered too. The first example of crystallographically ordered C_{60} at the room temperature was $C_{60}\cdot CH_2I_2\cdot C_6H_6$, but ^{13}C NMR experiment shows dynamic effects also.[21]

Extended Hückel theory[22] involving MOD (molecular orbital displacement) or IMOD (integrated MOD) function[23] was utilized in our calculation. For MOD or IMOD, displacement function of molecular orbitals involving no translational symmetry is utilized in the studied system. The idea about these functions originates from COD (crystal orbital displacement) or ICOD (integrated COD), which is described in detail elsewhere.[23] These functions were designed to be useful to extract out the secondary forces such as CT, vdW, and hydrogen bonding associated with the weak interaction from the strong primary force of composite donor or acceptor molecule.[23]

Results and Discussion

The CT of each composite orbital of the donor and the acceptor molecule upon host−guest interaction and its effect can be understood easily if the associated electronic structures are drawn. In **2**, the electronic configurations of diatomic X_2 (X = Br, I) and HOMO (h_u), HOMO-1 (h_g), LUMO (t_{1u}), LUMO+1 (t_{1g}) of C_{60} are shown. X_2 molecules have only one empty orbital available to accept electron, which has σ antibonding character. And $1\Sigma_u$* and $2\Sigma_g$ are nonbonding in nature. If one considers guest X−X bond distance alteration associated with CT, taking bonding X_2 electron out or adding electron to antibonding X_2 level leads to bond elongation (bond weakening) while taking antibonding electron out leads to bond contraction (bond strengthening). The degree of alteration is of course a function of the strength of the complexation.

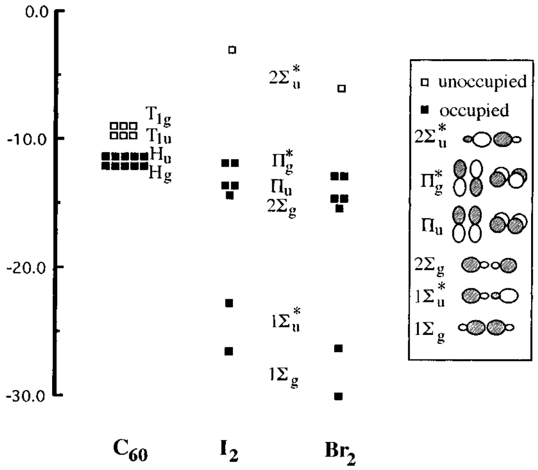


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TABLE 1: Values of IMOD Functions of Molecular Orbitals of X_2 (X = I, Br) up to HOMO Level (×10^4) in the $C_{60}\cdots X_2$ in Decreasing Order of Energy

	$C_{60}\cdots I_2$ (R)[a,b]	$C_{60}\cdots I_2$ (A)[b,c]	$C_{60}\cdots Br_2$ (A)[c,d]
$2\Sigma_u$*	1.6	6.6	364.2
Π_g*	−84.4	−0.6	−105.1
Π_g*	−59.6	−0.9	−101.8
Π_u	−12.4	−0.2	−37.6
Π_u	−10.2	−0.3	−38.6
$2\Sigma_g$	−4.8	−7.1	−2007.1
$1\Sigma_u$*	−1.1	−0.6	−302.6
$1\Sigma_g$	−0.4	−0.2	−130.6
X−X OP[e]	0.4945	0.4902	0.3415

[a] I_2 docked over the 56 edge in resting fashion(R). [b] I−C and I−I distance at 3.60 and 2.53 Å. [c] I_2 docked over C (sp^3) axially(A). [d] Br-C and Br−Br distance at 1.99 and 2.28 Å. [e] Overlap populations.

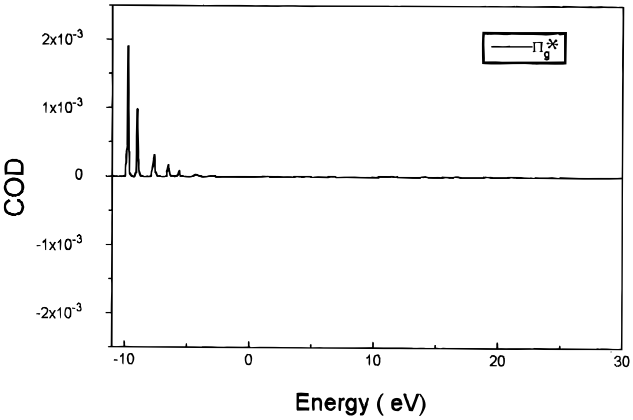

Figure 1. MOD curves for the occupied Π_g* of I_2 in the energy range of the empty orbitals of the host C_{60}.

The $C_{60}\cdots I_2$ is a weak complex. Thus, CT of individual molecular orbital (MO) of guest molecule was analyzed by utilizing IMOD function for $C_{60}\cdots I_2$ (resting), $C_{60}\cdots I_2$ (axial), and $C_{60}\cdots Br_2$ (axial) and is listed in Table 1. Geometric description of each model is given as notes in Table 1. Especially, MOD and IMOD functions are handy in judging the degree and the direction of CT of each composite MO's for the complexes of secondary force. The positive sign means the electron transfer from host to guest MO level and the negative sign from guest to host.

For $C_{60}\cdots I_2$ (R) model in which iodine is complexed with resting docking fashion, CT from both Π_u and Π_g* of iodine to the empty levels of C_{60} are dominant. This means that I_2 π type orbital overlaps better than any σ type orbitals for this orientation. The degree of electron transfer from Π_g* is more than that from Π_u level, because degree of transfer is also an inverse function of energy difference between donor and acceptor levels.[24] This is better seen with MOD function for the Π_g* of this model in Figure 1. An intense peak is observed in the region of LUMO (T_{1u}) and less in LUMO+1 (T_{1g}) of C_{60} and the gradual decrease of peak height as the energy level goes up. Thus one could tell that primary host−guest interaction with the resting fashion occurs between occupied Π_g* of iodine and empty T_{1u} and T_{1g} of C_{60} leading to X−X bond contraction.

Indeed, population analysis shows that net 0.0205 e^- is transferred backward from I_2 to C_{60} for the 56 resting docking position and 0.004 e^- for the 66 resting docking position in agreement with the spectroscopic data.[7] This reveals that the degree of CT varies with docking positions, besides fashions like resting or axial. The 56 position (**1(B)**) is more reactive than the 66 position for the resting docking fashion. This phenomenon could be understood within the frontier density theory scheme.[25] Since the occupied Π_g^* level of the guest is the one where the CT occurs mostly for the resting docking fashion, then the counterpart should be the position with the larger LUMO density of host for better overlap. The 56 bond does have more LUMO density than the 66 bond as pointed out by previous authors.[26] However, I_2 of solid $C_{60}\cdots I_2$ is known to be statistically disordered on the $\bar{3}$ position in resting fashion.[1] Thus one cannot determine if it is ordered over 56, 66, or any other intermediate positions because of the disorder of carbon and the iodine atoms at the present time as pointed out earlier. It is confirmed experimentally to date that iodine travels over the cage peripheral in resting fashion. It may be necessary to cool $C_{60}\cdots I_2$ down to a low temperature to determine its structure by diffraction or to obtain STM image.

Even though the iodine intercalated in the C_{60} with axial docking fashion of iodine is not observed experimentally, $C_{60}\cdots I_2$ (A) is listed in column 2 of Table 1 to illustrate the axial docking effect. And another hypothetical axially docked model ($C_{60}\cdots Br_2$ (A)) utilizing observed C−Br distance of 1.99 Å[5] is listed in column 3 for comparison.[4] The numbers in column 2 and 3 show the same trend, but with much larger numbers in column 3. In contrast to the resting docking model, CT from $2\Sigma_g$ level to unoccupied C_{60} levels is the most noticeable for both axial docking samples because of better overlap due to outward lobes of this orbital from the I−I bond axis and better energy matching than $1\Sigma_u^*$ (see **2**). However, this is nonbonding level which should not affect X−X bond distance. Instead, notice electron filling of antibonding $2\Sigma_u^*$ in column 2, and much more in column 3. Thus, one can see that bond weakening is essential in axial docking fashion. In the extreme case, filling two electrons on this level should break the X−X bond leading to the zero bond order. This might be happening for the $C_{60}Br_{24}$ system[5] as in the pyridine$\cdots$iodine complex.[22] Furthermore, $2\Sigma_u^*$ level of Br_2 is much close in energy to the HOMO of C_{60} than that of I_2 as seen in **2** such that Br_2 is more susceptible to accept electron than I_2 upon complexing with C_{60}. However, this orbital interacts to its utmost limits only for axial docking fashion as seen throughout our discussion.

Bond alterations depending on docking fashions are much clearly seen in numerical overlap population data. The I−I overlap population varies from axial to resting docking as shown in Table 1. Compare 0.4945 for the resting or 0.4902 for the axial model to 0.4922 for free I_2 with I−I distance (2.53 Å). And 0.4377 for free Br_2 with Br−Br distance (2.28 Å) is significantly reduced to 0.3415 for the model in the third column. Indeed, axial docking results in weakened X−X bond while resting docking do strengthen it.

Nevertheless, our calculation shows that axial docking fashion over C(sp^3) position is energetically more favorable than any other resting docking models by 2.0−5.7 kcal/mol for the $C_{60}\cdots I_2$ system. This is the consequence of maximum overlap principle[9] for which the orientation is decided solely by the quantity of overlap when other factors are not considered. However, iodine requires much more space in the real solids than bromine for an axial docking due to the steric reason. By comparing the van der Waals radii (2.2 Å for I_2[1] *vs* 1.85 Å for Br_2[13]), the required volume ($4/3\pi r^3$) for iodine is ∼1.68 times larger than that of bromine. There may not be enough space for axial intercalation of iodine unless the stronger interaction exist to separate balls apart. But, the energy gain of $C_{60}\cdots I_2$ should be less than that of $C_{60}\cdots Br_2$ as can be understood by the energy difference between HOMO of C_{60} and $2\Sigma_u^*$ level (**2**). Thus, these might explain why only resting docking is observed in the $C_{60}\cdots I_2$ system.

However, the evident directionality of X_2 toward C(sp^3) lobes in our docking calculation for both models confirms that CT force takes part in the description of the bonding scheme in these complex in addition to the spectroscopic and geometric X−X and C−X bond distance data. The shortest C−I distance of 3.60 Å[1] is within the vdW radii sum (3.68 Å), and the C−Br distance of 1.99 Å is comparable to the known covalent bond distance. Thus vdW nonbonding[8] or repulsive force for explaining the resulted C−X distance is excluded to describe the bonding forces of X_2 intercalated C_{60}. Even though the reaction steps for bromine reduction are not known, the bond breaking might be proceeded by the axial docking at the earlier step as known in the organic complexes.[4]

Many inconsistent experimental results about the $C_{60}\cdots I_2$ might be associated with the dynamic behavior of C_{60} and statistical disorder of iodine. For example, the iodine molecule in resting fashion to one ball could be in intermediate or axial fashion to the other ball in the next layer such that the resting docking effect is canceled out at an arbitrary moment. It may be called the polymorph effect, but it is not included in our calculation. Thus, it is better that the reliability should be checked for any experimental characterizations for this system.

Another interesting experimental result is about the intermolecular interaction between guests.[27] This should cancel out the blue shift effect in the Raman spectrum, since they form chain conformation which is end-on fashion to each other.[27] Then it might be more reasonable to compare the observed I−I vibration peak (212 cm^{-1})[7b] in the $C_{60}\cdots I_2$ system with that at 180 cm^{-1} of the solid $(I_2)_x$[6] rather than that at 198 cm^{-1} of the molecular I_2.[6]

In conclusion, it seems that docking fashion is critical in describing the nature of the $C_{60}\cdots X_2$ complex. The utilized MOD and IMOD function analysis can be useful and simple tools for the qualitative study including structural effects or spectroscopic analysis of the complicated system with weak host−guest interactions involving CT force. Also, EHT calculation in the studied system is shown to be reliable to reproduce the experimental results as for many other systems containing the carbon atom.[22]

Acknowledgment. Generous donation of the SGI computer time made by Prof. C. J. Yoon at the Catholic University of Korea at the beginning of this work is greatly appreciated.

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