Complexes of C60 Fullerene with Simple Donor Molecules: Theoretical Study

LIOUDMILA FOMINA, ABRAHAM REYES, SERGUEI FOMINE

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán DF 04510, México

ABSTRACT: The complex formation between fullerene C60 and simple donor molecules such as dimethyl ether, dimethylamine, dimethylsulfide, furan, pyrrole, and thiophene has been studied applying the hybrid MP2/6-31G(d'):PM3 ONIOM approach for geometry optimization. Local implementation of Møller–Plesset perturbation theory in combination with 6-31G(d) and 6-311G(d,p) basis sets was used for binding energies estimation of fullerene complexes. Two factors were found to contribute most to the complex stability: the polarizability and molecular volume of donor molecule. As follows from positive stabilization energies at the Hartree–Fock level, the stabilization of fullerene complexes is entirely due to dispersion interactions in accordance with available experimental data. The calculations show that for donors of similar molecular volume the binding energy of molecular complex increases with polarizability of donor molecules. Similarly, for such complexes the partial charges on molecules increase with decreasing of ionization potentials of donor molecules. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 89: 477–483, 2002

Key words: fullerene; van der Waals complexes; local MP2 theory; ONIOM

Introduction

The discovery of superconductivity in the alkali metal intercalated fullerides led to the exploration of C60 complexes [1] with organic donors searching for metallic state or superconducting properties.

Correspondence to: S. Fomine; e-mail: fomine@servidor.unam.mx

Recently, many donor–acceptor complexes involving fullerenes have been prepared [2–13]. Electronic absorption spectra of some of these show charge transfer (CT) bands so that these compounds can be considered as charge transfer complexes (CTC) [3–10]. In most cases, C60 CTC are neutral insulating compounds in which C60 cocrystallize with donor molecules. Only strong electron donors like decamethylnickelocene, Fe(C$_5$H5)(C$_6$Me$_6$), cobaltocene, or tetrakis(dimethylamino)-ethylene produce ion-radical salts with C60 [14–16].

TABLE I _____

Stabilization energies of T-shaped benzene dimer (kcal/mol).

MP2/6-31G(d') geometry					
MP2/6-31G(d)	MP2/6-311G(d,p)	LMP2/6-31G(d)	LMP2/6-311G(d,p)	LMP2/aug-ccPVTZ($-$f)	CCSD(T)/aug-ccPVDZ//MP2/DZ+2P[b]
−3.42 (−1.18)[a]	−4.12 (−2.11)[a]	−1.56	−1.95	−2.42	(−2.34)[a]

[a] BSSE-corrected energies.
[b] Ref. [32].

C60 also forms CTC with polymers bearing electron donor groups like polyvinylcarbazole, polythiophenes, and polyparaphenylenevinylenes [17, 18]. Similarly to many weak CT polymeric complexes, they show high photoconductivity due to photoinduced electron transfer from a polymer to a C60 molecule forming metastable C60 anions and mobile holes in the polymer [17]. This property of polymeric CT fullerene complexes is currently of a great interest because these materials can be utilized in xerography, energy phototransdusers, and molecular swithes [19]. Despite the great interest in fullerene CT complexes, few articles dealing with molecular modeling of these complexes have been published to date to the best of our knowledge. This is no surprise because to model van der Waals interactions with reasonably accuracy at least the MP2 level of theory with a polarizable basis set is needed that is still out of reach for such large molecules.

Less costly density functional theory (DFT) methods, although succeeding in predictions of the geometries for some hydrogen bonded and ionic complexes [20], are not able to reproduce dispersion interactions [21], of primary importance for weakly bounded C60 CTC. On the other hand, local correlation methods have recently emerged as alternatives for the study of intermolecular interactions [22, 23]. Reduced step dependence of the computational cost on the size of molecule and reduced basis set superposition error (BSSE) are two important advantages of local MP2 method (LMP2) [24]. In particular, it has been shown that LMP2 and counterpoise-corrected MP2 equilibrium geometries of water and water clusters are fairly closed [22, 23]. In this work, we present first results of molecular modeling for CT C60 complexes with simple organic molecules that can be considered as models of C60 complexes with polymers like polythiophene polypyrrole, polyethylenesulfide, polyethyleneimine, and polyethyleneoxide. Supposing

that in CTC consisting of large molecules the closest atoms contribute most to the interaction energy, the ONIOM two-layer method [25, 26] has been adopted for the geometry optimization where some atoms were treated at the MP2/6-31G(d') level and for the rest of them PM3 model [27] was applied. LMP2 was used to evaluate the binding energy of CT complexes.

Computational Details

All geometry optimizations and DFT calculations were carried out with Gaussian 98 suite of programs [28]. LMP2 single-point calculations were performed with the Jaguar 3.5 package [29]. To test the reliability of selected computational models, preliminary calculations on simple molecules were carried out. While BSSE correction is of importance for the binding energies estimation, it implies significant additional computational costs in the case of large complexes. LMP2 has already been designed to avoid BSSE. The BSSE arising in LMP2 is coming from the Hartree–Fock (HF) part of calculations. Because HF energies converge much faster with the basis set size compared to MP2 ones, we attempted to verify whether LMP2 can be used without BSSE correction. T-shaped benzene dimer was fully optimized at the MP2/6-31G(d') level and the stabilization energy was estimated at different levels of theory (Table I) with and without BSSE correction. To calculate BSSE correction, the counterpoise correction method was applied [30]. As seen from Table I, LMP2 stabilization energies for benzene dimer are close to these BSSE-corrected MP2 energies and in the case of the aug-ccPVTZ($-f$) basis set the stabilization energy is almost identical to the BSSE-corrected one obtained from high-level CCSD(T)/MP2 calculations [31].

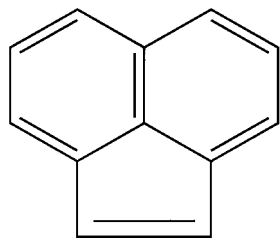Other test calculations were carried out to justify the applicability of the two-layer MP2:PM3 ONIOM

FIGURE 1. Naphthacene molecule.

model to van der Walls complexes modeling. The stabilization energy of N_2-naphtalene complexes were calculated using LMP2/6-31G(d) and LMP2/6-311G(d,p) models on MP2/6-31G(d') and ONIOM MP2/6-31G(d'):PM3 geometries, where nitrogen molecule and one benzene ring with four hydrogens belong to a high [MP2/6-31G(d')] level and the rest of naphthalene ring to a low (PM3) one with the N_2 molecule being parallel to the naphthalene plane. The LMP2/6-31G(d) stabilization energies were found to be of -1.56 and -1.53 kcal/mol using MP2/6-31G(d') and ONIOM geometries, respectively. It has been demonstrated recently that for naphthalene trimer even optimization at the MP2/6-31G level appears to provide a good compromise between accuracy and computational efficiency [32]. Taking the above into account, it seems that a reasonably good description of van der Walls π-complexes can be obtained making use of the two-layer ONIOM model for the geometry optimization where closest interacting atoms are treated at the MP2/6-31G(d') level while the rest of them are described in terms of the semiempirical PM3 model. Single-point energy calculations using the LMP2 model produced binding energies with little BSSE contamination.

Results and Discussion

Six different molecules containing oxygen, nitrogen, and sulfur atoms have been selected as donor parts of complexes: dimethyl ether, dimethylamine, dimethylsulfide, furan, pyrrole, and thiophene. The first three molecules represent models of polyethyleneoxide, polyethylenimine, and polyethylenesulfide polymers while pyrrole and thiophene are repeating units of polypyrrole and polythiophene. All these molecules are weak donors with ionization potentials ranging from 9.98 eV for dimethylether to 8.2 eV for pyrrole [33, 34]. The high ONIOM level [MP2/6-31G(d')] was applied to all

atoms of donor molecules and the "naphthacene" fragment of the C60 molecule (Fig. 1). The rest of the atoms were treated at the PM3 level.

Although all carbons are equivalent in the C60 molecule, it consists of fused pentagons and hexagons. The naphthacene fragment includes both of them still maintaining the job size reasonably small to allow optimization of weakly bonded van der Waals complex with flat potential energy surface. Initial geometries for molecular complexes were obtained with the Monte Carlo conformational search method using the MMF94 force field. During the conformational search, the heteroatom–pentagon center or heteroatom–hexagon center distances were set to 2.5 Å. Lowest-energy structures were picked up and used as input geometries for ONIOM (MP2/6-31g(d'):PM3) geometry optimizations. Figures 2, 3, and 4 show minimized geometries of van der Waals complexes and in Table II are listed binding energies of C60 complexes at different levels of theory.
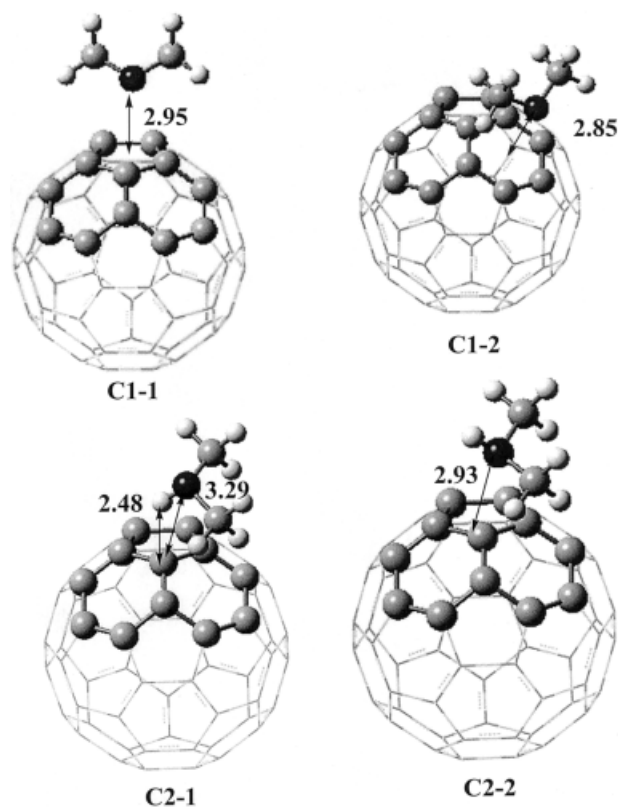

FIGURE 2. ONIOM-optimized geometries of C60–dimethyl ether (**C1-1, C1-2**) and C60–dimethylamine (**C2-1, C2-2**) complexes [ball-&-stick and wireframe rendering shows MP2/6-31G(d') and PM3 levels of the ONIOM model, respectively].

Analyzing the data of Tables II and III one can easily see that no clear correlation exists between ionization potentials of donor molecules and the binding energies of C60 complexes, suggesting that charge transfer contributes little to their stabilization, in line with experimental observations. Similar conclusion can be made examining charge distributions in C60 complexes. Unfortunately, Jaguar code is not able to do population analysis using LMP2 density while for conventional MP2 Gaussian's 98 method the molecules are too large to obtain density matrix even at the MP2/6-31G(d) level. To remedy this problem, MP2/6-31G(d') population analysis results (Mulliken and NBO) for naphthalene–N_2 complexes were compared with these obtained with a series of density functionals. Three parameter B3PW91 functional [35, 36] reproduced closely results of the MP2 model and was used to analyze the charge distribution in C60 complexes. As can be seen from Table II, both Mulliken and NBO analysis show little charge transfer in the ground state.
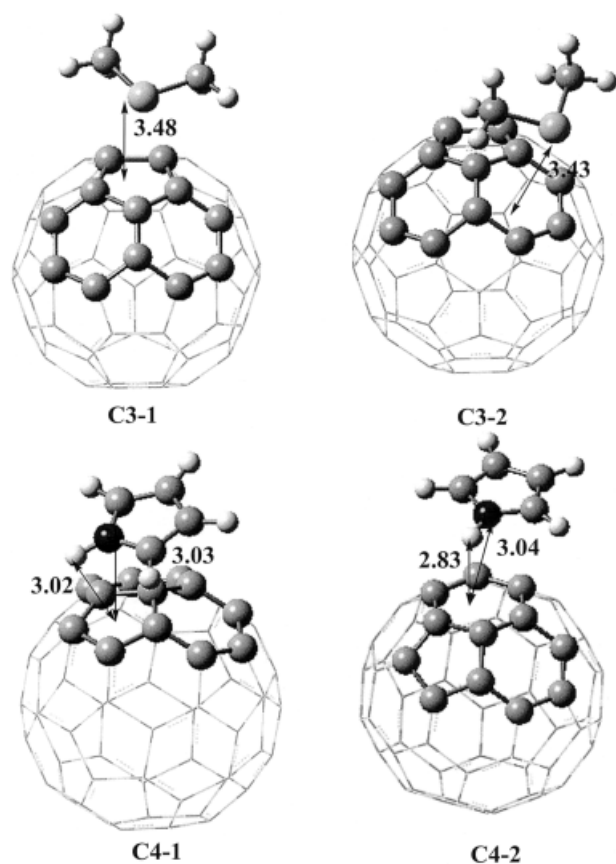

FIGURE 3. ONIOM-optimized geometries of C60– dimethyl sulfide (**C3-1, C3-2**) and C60–pyrrole (**C4-1, C4-2**) complexes [ball-&-stick and wireframe rendering show MP2/6-31G(d') and PM3 levels of the ONIOM model, respectively].

As can be seen from Table I, ONIOM stabilization energies are much more negative compared to LMP2 ones due to the fact that the ONIOM energies are not BSSE corrected, thus overestimating the binding energy. As to relative stabilization energies, the ONIOM model predicts molecular complexes to be significantly more stable in the case of aromatic donors (pyrrole, thiophene, furan) than in the case of simple dimethyl-substituted heteroatoms. This effect can also be attributed in part to the absence of BSSE correction (the basis set is more complete in the case of aromatic molecules). On the other hand, the LMP2 model, while maintaining general trends shown by the ONIOM method, smoothes out the difference in binding energies between aromatic and aliphatic complexes. Surprisingly, the most stable complex at the LMP2 level of theory is that formed by dimethyl ether.
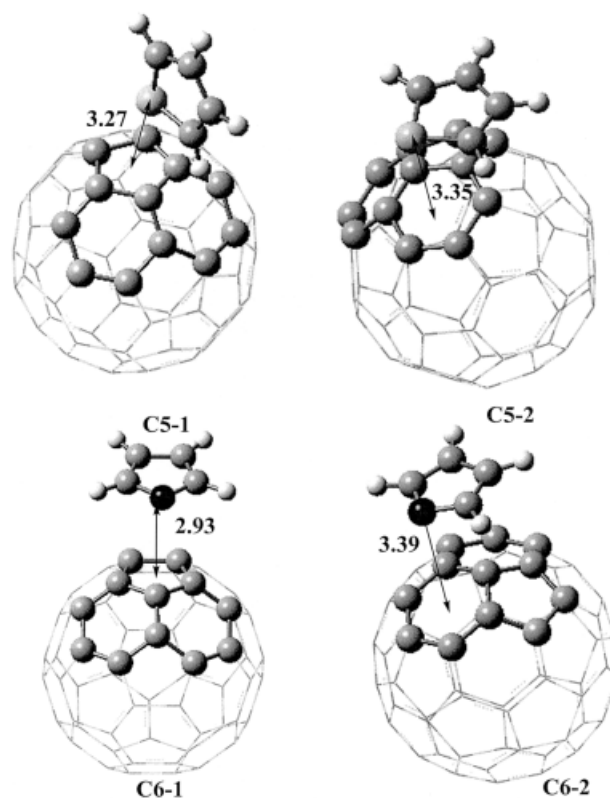

FIGURE 4. ONIOM-optimized geometries of C60– thiophene (**C5-1, C5-2**) and C60–furan (**C6-1, C6-2**) complexes [ball-&-stick and wireframe rendering show MP2/6-31G(d') and PM3 levels of the ONIOM model, respectively].

However, it is seen that complexes with pyrrole, the donor with lowest ionization potential, show maximal charge transfer according to both Mulliken and NBO charge partitioning schemes.

Important information about the interaction nature in C60 complexes can be obtained by the comparison of the binding energies at the HF and LMP2 levels of theory. As can be seen from Table II, all molecular complexes are unstable at the HF level while the binding energy is negative in most cases at the LMP2/6-31G(d) and in all cases at the LMP2/6-311(d,p) level. Therefore, the attraction forces in C60 complexes are entirely due to electron correlation effect. When examining ΔE_{corr} (Table II), which represents the difference between the correlation energies of separate molecules and the complex, one can see that ΔE_{corr} is more negative for the LMP2/6-311G(d,p) level of theory compared to the LMP2/6-31G(d) one due to the fact that the more complete 6-311G(d,p) basis set recovers more correlation energy compared to the 6-31G(d) one. As has been shown [37], at distances where the overlap of valence shells can be neglected the correlation energy has a physical meaning of dispersion energy. Therefore, it is reasonable to expect that ΔE_{corr} of C60 complexes correlates with polarizabilities of donor molecules. This is in general the case as can be seen from the comparison of polarizabilities (Table III) of donor fragments and ΔE_{corr} of C60 complexes (Table II). Thus, the complexes formed by aromatic donors show more negative ΔE_{corr} compared to these of aliphatic ones due to larger polarizabilities. However, pyrrole complexes are better stabilized by dispersion interactions compared to thiophene ones despite higher polarizability of thiophene. A similar trend can be observed when comparing ΔE_{corr} for dimethyl sulfide and dimethylether complexes. Despite higher polarizability of dimethylsulfide compared to dimethylether, the latter forms complexes with more negative ΔE_{corr}. This phenomenon can be understood taking into account the size of donor molecule. Because the correlation energy has physical meaning of dispersion energy at distances where intermolecular molecular overlap can be neglected, the correlation contribution in binding energy of C60 complexes can be presented as a sum of three terms,

$$\Delta E_{\mathrm{corr}} = -[C_6/r^6 + C_8/r^8 + C_{10}/r^{10}], \qquad (1)$$

where dipole–dipole (r^{-6}), dipole–quadrupole (r^{-8}), and dipole–octapole plus quadrupole–qua-

drupole (r^{-10}) are taken into account and C_n are dispersion coefficients. As can be seen from Eq. (1), ΔE_{corr} decreases strongly with intermolecular distance. It has been established recently that the geometry and energies of molecular complexes are more a result of the system trying to minimize repulsive interactions than an increase in attractive interactions [24]. When comparing the molecular volumes of dimethylether with dimethylsulfide and pyrrole with thiophene, one can see that volumes of sulfur-containing donors are significantly larger. Therefore, sulfur-containing donors should form looser and less stabilized complexes according to the concept of minimizing repulsive interactions. As seen from Figures 2, 3, and 4, the differences in heteroatom—C60 distances in **C1-1** and **C1-2** complexes are 0.55 Å shorter than those in **C3-1** and **C3-2** complexes. Similar trends hold for **C4-1/C4-1** and **C5-1/C5-2** complexes, where S–C60 distances are about 0.3 Å larger compared to corresponding N—C60 distances. In the case of molecules of similar size and shape, like furan and pyrrole, the correlation stabilization of complexes governs the polarizabilities of donors. For molecules of similar size, a direct correlation between ionization potential and positive charge on donor molecule is observed as can be seen in series of pyrrole, furan, and dimethylsulfide complexes.

The starting geometries of all complexes showed more or less T-shaped structure, while after the optimization aromatic donors become parallel with respect to hexagon or pentagon planes of C60 molecules. In one particular case (**C5-1** complex), the thiophene ring is practically perpendicular to the pentagon plane. At first sight, the stability of this complex could be attributed to an H-bond of C—H . . . π-electron type (C2—H . . . π-electrons of hexagon). However, the comparison of C2—H thiophen bond lengths in **C5-1** and in free thiophene gives 1.085 and 1.086 Å, respectively, thus providing no evidence of existence of such an H-bond. A similar situation holds for the **C2-1** complex formed by dimethylamine. Two minimum structures were located for a complex of C60 with dimethylamine: with N—H bond pointing to (**C2-1**) and out (**C2-2**) of the C60 molecule. As can be seen from Table II, at any level of theory [LMP2/6-31G(d) or LMP2/6-311(d,p)] the **C2-2** complex is more stable (or less unstable) compared to the **C2-1** one. N—H bond lengths are identical in two complexes (1.018 Å). These two examples suggest that neither C—H . . . C60 nor N—H . . . C60 hydrogen bonds exist in C60 complexes, at least at the level of theory

TABLE II

Interaction energies (kcal/mol) for C60 complexes at different levels of theory.

	SCF		LMP2		ΔE_{corr} [a]		ONIOM	Partial charge larger 0.02 e on C60 molecule[b]	
Complex	6-31G(*d*)	6-311G(*d*,*p*)	6-31G(*d*)	6-311G(*d*,*p*)	6-31G(*d*)	6-311G(*d*,*p*)	MP2/6-31G(*d′*):PM3	Mulliken	NBO
C1-1	3.5	1.3	−1.9	−3.0	−5.4	−4.3	−5.3	—	—
C1-2	3.8	2.5	−1.3	−3.9	−5.1	−6.4	−5.5	—	—
C2-1	3.5	3.3	1.0	−1.8	−2.5	−5.1	−4.9	—	—
C2-2	3.8	2.9	0.6	−2.5	−3.2	−5.4	−5.3	−0.02	−0.03
C3-1	3.1	2.3	0.1	−1.5	−3.0	−3.8	−4.8	—	—
C3-2	4.2	2.3	0.5	−2.4	−3.7	−4.4	−5.0	—	—
C4-1	6.8	6.0	0.1	−1.9	−6.7	−7.9	−7.7	−0.05	−0.05
C4-2	6.5	5.2	−0.8	−3.1	−7.3	−8.3	−6.6	−0.06	−0.07
C5-1	3.9	2.5	−0.9	−2.0	−3.0	−4.5	−5.1	—	—
C5-2	6.8	4.5	0.4	−3.7	−6.4	−8.0	−7.2	−0.03	−0.04
C6-1	5.8	4.9	−0.4	−1.7	−6.2	−6.6	−6.0	−0.03	−0.03
C6-2	6.5	5.0	−1.8	−2.7	−8.3	−7.7	−7.0	−0.05	−0.06

[a] ΔE_{corr} is defined $[E_{AB}^{(LMP2)} - (E_A^{(LMP2)} + E_B^{(LMP2)})] -$ as $[E_{AB}^{(SCF)} - (E_A^{(SCF)} + E_B^{(SCF)})]$ where $E^{(SCF)}$ and $E^{(LMP2)}$ are SCF and LMP2 level energies of molecule A, B and molecular complex AB, respectively.
[b] B3PW91/6-31G(*d*)//ONIOM level of theory.

applied in this study. On the other hand, there have been found by high-level *ab initio* calculations that such bonds exist in $NH_3 \ldots$ benzene complexes [38]. In these complexes, NH_3 behaves as a proton donor. Because C60 has lower ionization potential compared to benzene (7.58 vs. 9.24 eV) [39, 40], it is reasonable to expect stronger π—H interaction in the case of C60. This is not the case, however, for C60–dimethylamine complexes The viable explanation for this apparent contradiction could be steric hindrances caused by methyl groups of dimethylamine. This observation confirms again the concept of minimizing the repulsion interactions.

Conclusions

It seems that by making use of a mixed ONIOM–LMP2 model useful information can be obtained for large van der Waals complexes. According to molecular modeling data, the stability of studied molecular complexes is totally attributed to dispersion interactions with little charge transfer contribution in the ground state, in agreement with experimental observations. The binding energies of fullerene complexes depend on two factors: polarizability and size of donor molecule. As a result, complexes formed by small donors often are more stable compared to looser complexes formed by larger and more polarizable molecules. On the other hand, for complexes involving donors of similar volumes the direct correlation between binding energy and polarizability of donor molecule is observed. In much the same way, for such complexes the excessive

TABLE III

Comparison between average polarizabilities, molar volumes, and ionization potentials of donor molecules.

Donor	α [a] $(10^{-24}$ cm$^3)$	V [b] (cm^3/mol)	IP [c] (eV)
$O(CH_3)_2$	5.15 (5.29)[d]	48.0	9.98[e]
$HN(CH_3)_2$	5.91 (6.37)[f]	51.7	9.1[g]
$S(CH_3)_2$	7.52	58.0	8.68[g]
Furan	7.42	55.6	8.89[g]
Pyrrole	8.31	56.8	8.20[g]
Thiophene	9.71 (9.67)[f]	65.1	8.86[g]

[a] Average polarizability calculated at the B3LYP/aug-cc-pVTZ//MP2/6-31G(*d′*) level of theory using CPHF method.
[b] Molecular volume computed as the volume inside a contour of 0.001 electrons/bohr^3 density at the MP2/6-31G(*d′*) level of theory.
[c] Ionization potential obtained from photoionization data.
[d] Experimental average polarizability [41].
[e] Ref. [33].
[f] Experimental average polarizability [42].
[g] Ref. [34].

negative charge on the C60 molecule increases with decreasing of ionization potential of donor molecule. Unlike complexes of benzene with first-row hydrides where hydrides of carbon, nitrogen, and flour form a H—π hydrogen bond, these kinds of interactions have not been detected for complexes of C60 with dimethylamine. The obtained data are in line with the minimizing repulsion interactions concept for van der Waals complexes.

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