Intermolecular Interaction In C_{60}-Based Electron Donor-Acceptor Complexes

Elena F.Sheka

People Friendship University of Russia, ul.Miklukho-Maklaya 6, Moscow 117198, Russia
sheka@icp.ac.ru

Abstract: Quantum-chemical testing of donor-acceptor properties of binary molecular complexes, related to the singlet state, is suggested as QCh calculations of both studied systems and their constituents by using spin-nondependent (RHF) and spin-dependent (UHF) version of the exploited computational tool in common. The avoided crossing of intermolecular interaction terms of neutral molecules $E_{\mathrm{int}}(A^0B^0)$ and molecular ions $E_{\mathrm{int}}(A^+B^-)$, lays the analysis foundation. The dependence of D-A complex properties on the type of the ground state interaction term, space positions of its minimum as well as interrelation of the corresponding energies is discussed. The suggested approach has been applied to binary complexes C_{60}+X (X= TAE, TDAE, DMMA, COANP, 2Li, Mg).

Key words: quantum chemistry; electron donor-acceptor complexes; diabatic charge transfer; fullerene C_{60}

1. Introduction

For more than a half of century, intermolecular interaction (IMI) in molecular donor-acceptor (D-A) complexes has mainly been associated with a long wavelength absorption band, known as a *charge-transfer band* (CTB) [1-4]. Widely used expression for the band position has the form

$$h\nu_{CT} = I_D - \varepsilon_A - \left(\Delta E_{ext} - \Delta E_N\right), \qquad (1)$$

where I_D and ε_A are the molecular donor ionization potential (IP) and the molecular acceptor electron affinity (EA), respectively, while ΔE_{ext} and ΔE_N are the formation energies of complexes $\left[A^+B^-\right]$ and $\left[A^0B^0\right]$. The CTB recording has been always considered as a qualitative indication of the D-A character of a binary molecular complex. But actually, CTB is only a consequence of the IMI, complex by nature [5]. As has been still shown by Polanyi [6], a qualitative description of the interaction, detailed enough, can be suggested when comparing IMI potentials, IMI terms below, of complexes $\left[A^+B^-\right]$ and $\left[A^0B^0\right]$. The difference of the terms asymptotes at the infinity is equal to $I_D - \varepsilon_A$. Since accordingly to (1) the difference is always positive and the $\left[A^+B^-\right]$ term is below that of the $\left[A^0B^0\right]$ complex within the main range of the intermolecular distances, there is always a space region where these terms intersect. However, the breakdown of adiabaticity between electrons and nuclei in the region causes replacing the terms intersection by their splitting [5,7], so that a region of an *avoided crossing* arises where a number diabatic processes such as photosynthesis, photodissociation, spin-exchange reactions, and other processes, among which charge transfer, occur (see review [7]). This viewpoint has obtained a large development when studying charge transfer at colliding alkali metal atoms with halides and other molecules with high EA (see reviews [8,9]). The suggested model of *chemoionization* is of a general nature and can be fruitfully applied to the consideration of the D-A properties of molecular complexes.

Suggested in the current study is a practical implementation of the IMI analysis in D-A complexes within the framework of the chemoionization model performed as an extended computational quantum-chemical (QCh) experiment. The following basic concepts form the ground of thus formulated QCh testing:

- a multi-well IMI term of the complex ground state arises due to avoided crossing;
- the term parameters are of determining significance for the type of the complex formed;
- a comparative study of the constituent molecules structure in both neutral and ionic states lays the foundation of the complex structure prediction.

As a consequence, the computational experiment involves QCh calculations of a binary complex as well as constituent molecules and their ions. Indispensable use of both spin-nondependent (RHF) and spin-dependent (UHF) versions of the QCh code at each stage of the calculations is a distinctive feature of the experiment. In the current study, the approach has been applied to C_{60}–based complexes. As shown below, that has allowed not only to reveal specific features provided by fullerene, but to determine leading parameters and to classify the complexes over the IMI term types.

The paper is organized in the following way. The main concepts are given in Section 2. Charge transfer in D-A complexes is discussed in Section 3. Section 4 concerns the methodology of QCh testing of D-A complexes. Details of computational experiment are described in Section 5. Section 6 is devoted to QCh testing of six C_{60}–based complexes. Conclusion summarizes essentials of the study.

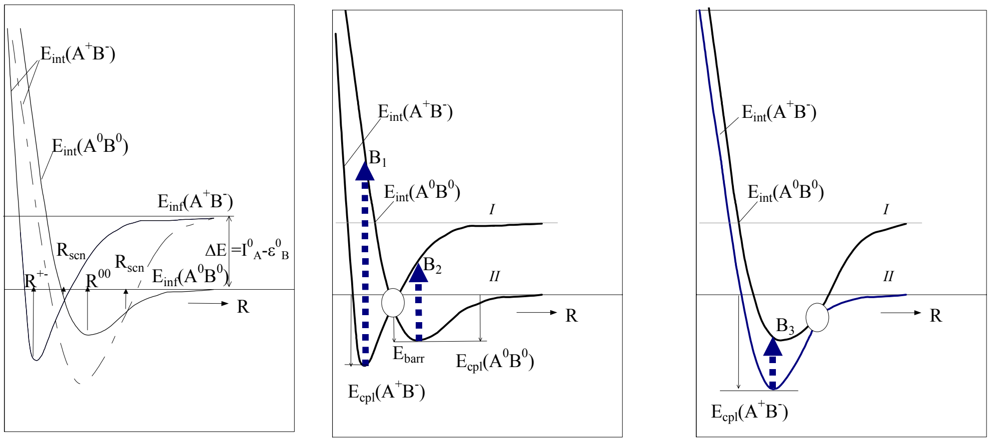
2. Intermolecular interaction in D-A complexes

Intermolecular interaction is complex by nature and is difficult for theoretical description. Repeatedly a question has risen to divide the total interaction into constituents, each of clear physical meaning, for the further determination of those to be possible. Thus the concepts on electrostatic (E_{es}), inductive (E_{pl}), exchange (E_{ex}), dispersion (E_{disp}) as well as charge transfer (E_{ct}) interactions have appeared [5]. Concurrent with individual consideration of the above terms, there have been attempts to tackle them jointly within the framework of a unique computational scheme. Suggested by Morokuma et al. [10, 11] should be accepted as the most successful. The total IMI is presented as a sum

$$E_{\text{int}} = E_{es} + E_{pl} + E_{ex} + E_{ct} + E_{mix}\,, \tag{2}$$

each term of which is determined within one session of HF SCF calculations. The term E_{mix} completes contributions by interactions unable to be determined by SCF calculations, by dispersion interaction in particular. Morokuma's analysis has been usually performed for a fixed geometry of the complex described by sets of internal $\{r_{io}\}$ and external $\{R_{jo}\}$ coordinates. But actually, $E_{\text{int}}(r, R)$ is a complex function of the coordinates.

Analysis of interaction of alkali metal atoms with various molecules showed [6,8], that both complex stabilization and complex structure depend on a composite IMI term of the ground state that is composed of $E_{\text{int}}(A^0B^0)$ and $E_{\text{int}}(A^+B^-)$ terms which describe the ions and neutral molecules interaction, respectively, that results in the ion coupling at $R^{(+\ -)}$ and neutral molecules at $R^{(0\ 0)}$. If $I_A - \varepsilon_B > 0$, the terms are splitted in the avoided crossing region thus forming two branches of composite terms. Figure1 presents a sketch of a one-dimensional cross-section of the potential energy surface that demonstrates the formation of the above discussed two branches of the IMI term of complex AB for two different terms $E_{\mathrm{int}}(A^+B^-)$ in Figure 1a. Horizontal lines $E_{\mathrm{inf}}(A^+B^-)$ and $E_{\mathrm{inf}}(A^0B^0)$ mark asymptotic summary energies of molecular ions and neutral molecules at the infinity, respectively. The latter is usually taken as the reference level. The lower branch is attributed to the ground state while the upper describes the excited one. Circles mark the avoided crossing regions. Quantities $\overset{+-}{E}_{cpl}$, $\overset{00}{E}_{cpl}$ and E_{barr} are the main energetic parameters of the ground state. E_{barr} determines the chemoionization barrier. Coupling energies are counted from the reference level.

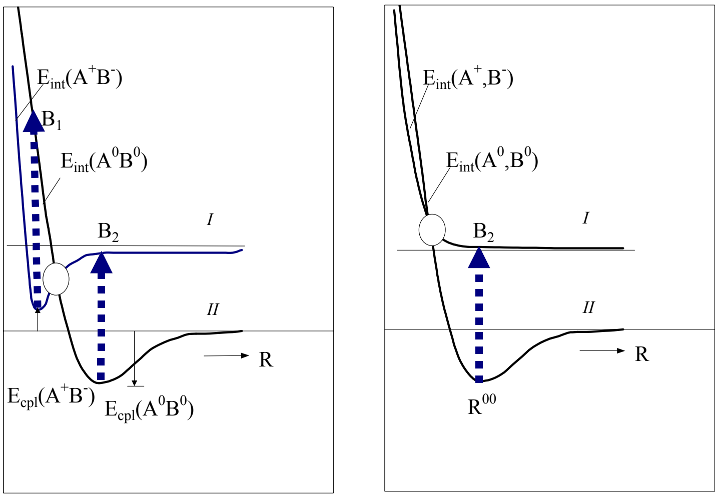


(a) (b) (c)

Figure 1. A sketch of the formation of two branches of IMI terms; $\overset{+-}{E}_{cpl} < \overset{00}{E}_{cpl}$ .a. IMI terms for neutral molecules and molecular ions; b. and c. IMI terms of complexes of type 1 and type 2, respectively.

As shown in the figure, summary term of the ground state may be either of two- or one-well type depending on the position of the intersection point R_{scn} on either the left- or right-hand side from the point $R^{(0\ 0)}$. In the first case (Figure1b), classified as type 1, the complex is characterized by two bound states which correspond to coupling at $R^{(+\ -)}$ and $R^{(0\ 0)}$. The former can be conditionally called as ionic implying that the structure and electronic properties of the relevant complex are mainly determined by the interaction of molecular ions. The latter state can be called neutral since the interaction of neutral molecules is mainly responsible for the complex properties. In the second case (Figure 1c), classified as type 2, the only bound state, mainly ionic by nature, is responsible for the complex formation. In both cases $\overset{+-}{E}_{cpl} < E^{00}_{cpl}$ and minimum $R^{(+\ -)}$ plays the main role.

IMI terms shown in Figure 2 correspond the condition when $\overset{+-}{E}_{cpl} > E^{00}_{cpl}$. As seen in the figure, the ground state term can also be either two- or one-well depending on the depth of the term $E_{\text{int}}(A^{+}B^{-})$ minimum. In both cases presented in the figure, the minimum $R^{(0\ 0)}$ is the lowest by energy. A limit case of the one-well IMI term (Figure 2b) is related to the term $E_{\text{int}}(A^{0}B^{0})$, showing a lack of coupled ionic state. Four types of the IMI term of the ground state introduced above offer a good ground for qualitative classification of D-A complexes.



(a) (б)

Figure 2. A sketch of the formation of two branches of IMI terms; $\overset{+-}{E}_{cpl} > E^{00}_{cpl}$. a. and b. IMI terms of complexes of type 3 and type 4, respectively.

If the complex structure at $R^{(0\ 0)}$ is generally clear, that one at $R^{(+\ -)}$ will depend, as shown in [8], on the state of ions that are produced at the intersection point. This is caused by two circumstances. Firstly, the diabatic transition molecule → ion is vertical that means that the space configuration of the formed ions corresponds to the equilibrated configuration of neutral molecules at the intersection point. Available types of such transitions are schematically shown in Figure 3: the left part of the figure is related to the positive ion formation, the right part deals with negative ions. As seen in the figure, the state of a formed ion is greatly dependent on shifting equilibrium position of atoms under ionization [14]. If the shifting is small or is absent at all, the formed ions are stable (case a). If the shifting is large, vibrationally excited ions are formed under ionization (case b), energy of the vibrational excitation of which may approach or even exceed dissociation limit (case c).

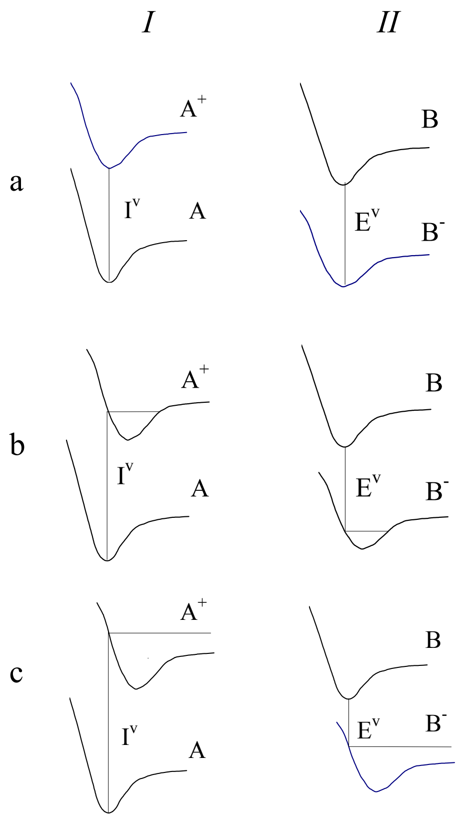


Figure 3. Scheme of "neutral molecule → ion" vertical transitions.

Secondly, the produced ions are subjected to Coulomb interaction at the intersection point, energy of which is of $\approx I_A - \varepsilon_B$ by order of magnitude [8]. As a result, the ions or products of their dissociation can form molecular compounds of the $M = A^{\delta+}B^{\delta-}$ and $M = (A_1 + A_2)^{\delta+}B^{\delta-}$ types, where A_1 and A_2 are dissociation products of, say, donor in accordance with scheme *Ic* in Figure 3. Applied to beams of neutral atoms and molecules, harpoon reactions were introduced to match the case [6,8,9]. Similar reactions with participation of C_{60} fullerene will be discussed below in Sections 6.3 and 6.4.

3. Charge transfer in D-A complexes

3.1 Charge transfer under light absorption

Every time when analyzing a long-wavelength absorption band, which is characteristic for *any* D-A complex, one must give oneself an account of which type of the IMI term is concerned with. As seen in Figures 1 and 2, three types of absorption bands, namely B_1, B_2, and B_3, correspond to optical transitions shown by broken arrows. Among the others, only position of B_2 band is described by Eq.(1). Positions of B_1 and B_3 bands cannot be analytically described. The charge transfer, that accompanies photoexcitation, is determined by a partner composition of wave functions of the states that participate in the optical transition. Transitions of B_2 traditionally imply a complete crossed partitioning of the wave functions. This means that the ground state wave function is fully determined by molecular partner *A*, while molecule *B* determines the excited state function. The partner composition of the wave functions participating in B_1 and B_3 transition is not known *a priori* and must be determined in due course of QCh calculations.

3.2. Charge transfer in the ground state

Caused by avoided crossing, the splitting of terms $E_{\text{int}}(A^+B^-)$ and $E_{\text{int}}(A^0B^0)$ at R_{scn} results in mixing ionic and neutral states of the complex that can be generally expressed by mixing the corresponding wave functions which has the following form

$$\Psi(AB) \sim \Psi(A^0B^0) + c\Psi(A^+B^-) \tag{3}$$

for the states determined by the term $E_{\text{int}}(A^0B^0)$. For states belonging to the term $E_{\text{int}}(A^+B^-)$ mixing has the form

$$\Psi(AB) \sim \Psi(A^+B^-) + c'\Psi(A^0B^0)\,. \tag{4}$$

Coefficients c and c' determine the contribution of the added states. As a result, molecules *A* and *B*, neutral in gaseous state, may acquire a charge. On the other hand, pure ionic states (ion charges, in particular) may be partially smoothed by adding neutral states.

As to the value of the transferred charge, it can be evaluated as the difference

$$\delta e = e_B - e_A = \sum_{\nu \in B} e_\nu - \sum_{\mu \in A} e_\mu \tag{5}$$

where e_A and e_B present charge of molecules A and B, respectively, calculated via atomic charges e_ν and e_μ, which are obtained in the performed QCh calculation according to Mulliken's scheme.

Besides obtaining the charge value, one is interested in characteristic quantity, which could be a distinguishing factor of the action occurred. As shown in numerous works (see [2-4, 15, 16]), for initially neutral molecules the charge transfer is of quantum nature and is connected with electron exchange in a quantum system. Thus, following [17] generally, the charge transfer integral J_{AB} can be expressed as

$$J_{AB} = \left[E_R + \Delta E_R + E_{es}\right] S_{AB}\,. \tag{6}$$

Here E_R is the energy of resonance (exchange) interaction between molecules *A* and *B*; ΔE_R presents the correction to the resonance term caused by polarization of orbitals of molecules *A* and *B;* E_{es} is the energy of electrostatic interaction with induced dipole moments of the molecules; S_{AB} describes overlapping integral of molecular orbitals of molecules *A* and *B*. Numerous attempts of this integral determination as well as the charge transfer probability can be found in review [15] and monograph [16]. As occurred, in the general case the problem is sufficiently complex. Among few successes in the field, the approach suggested by Kitaura and Morokuma [11] should be mentioned. The approach concerns the determination of the probability to find a charge at a space point *r*, $\rho(r)$, within the framework of the HF SCF technique. Fock's matrix partitioning over members of the total interaction energy in form of Eq.(2) lays the approach foundation.

However, when coefficient c in Eq.(3) is small, one may attempt to undertake an indirect evaluation of the transfer integral by using broken symmetry approximation in the form suggested by Noodleman [18] when considering magnetic properties of odd electrons in a molecule. The matter is that for odd electrons a singlet one-determinant open shell HF function, Ψ_B^{UHF}, is spin-mixed or broken by symmetry [18]. As shown in [18-20], the function symmetry breaking is caused by an intramolecular charge transfer contamination to the UHF function. This contribution can be characterized by the difference of the electron energy determined by using RHF and UHF functions. Actually, the electron energy, calculated in the UHF approximation is less that calculated in the closed-shell spin-nondependent RHF approximation. If there is no mixing with ionic states, the relevant difference in energy is equal to zero. Developing Noodelman's concept, in [21] it was suggested to use the relevant difference energy

$$\Delta E_{tot} = E_{rad}(M) = E_0^{RHF}(M) - E_0^{UHF}(M) \tag{7}$$

for testing the extraction of odd electrons from the covalent pairing that leads to a partial radicalization of the molecule. $E_0^{RHF}(M)$ and $E_0^{UHF}(M)$ present in Eq.(7) the energies of the singlet state of the studied molecule that are calculated by using the RHF and UHF versions of the same computational tool. $E_{rad}(M)$ is considered as a qualifying energetic parameter of mixing or radicalization of odd electrons.

Taking into account mixing of neutral and ionic states of both molecular constituents of a complex and the complex as a whole, the difference energy for a D-A complex at the minimum $R^{(0\ \ 0)}$ of the IPI term can be written in the following way

$$\begin{aligned}\Delta E_{tot} &= E_0^{RHF}(compl) - E_0^{UHF}(compl)\\ &= E_0^{RHF}(A) + E_0^{RHF}(B) + E_{coupl}^{RHF} - E_0^{UHF}(A) - E_0^{UHF}(B) - E_{coupl}^{UHF} + E_{chg}\\ &= E_{rad}(A) + E_{rad}(D) + \Delta E_{coupl} + E_{chg}.\end{aligned} \tag{8}$$

$E_{rad}(A)$ and $E_{rad}(B)$ present the radicalization energies of molecules A and B. At least, one of the composing terms in Eq.(8) has been always presented for the complexes studied below due to the presence of fullerene C_{60}, which is characterized by a rather large E_{rad} [21]. $\Delta E_{coupl} = E_{coupl}^{RHF} - E_{coupl}^{UHF}$ describes the difference in the complex RHF and UHF coupling energies. E_{chg} takes into account remaining effects caused by function mixing according to Eq. (3), including a molecule charging. Let us call it conditionally as *charge energy* and take it as a qualifying parameter. It can be expressed as

$$E_{chg} = \Delta E_{tot} - E_{rad}(M_1) - E_{rad}(M_2) - \Delta E_{coupl}. \tag{9}$$

All terms of Eq.(9) can be independently calculated thus allowing determination of the E_{chg} value. Naturally suppose that $E_{chg} = 0$ when there is no charge transfer. On the other hand, non-zero E_{chg} may evidence the charge transfer occurrence in the ground state of a D-A complex.

For D-A complexes at minima $R^{(+\ -)}$, the charge energy in the above form is obviously meaningless. Presenting a tightly bound molecular compositions of ions A^+ and B^-, the complexes must be considered as integral molecules which in case of the odd electron availability may be characterized by non-zero energy difference ΔE_{tot} according to Eq.(7). The latter should be considered as the radicalization energy of the complex that traces the odd electron behavior in the case of strong interaction between the complex partners. .

4. Methodology of quantum-chemical testing of D-A complexes

The following sequence of computational actions can be suggested, aiming at QCh testing of a complex under study.

1. Testing is opened by QCh calculations of free molecules *A* and *B* as well as their ions. The calculations involve structure optimization when seeking the energy minimum by using both RHF and UHF versions of a selected computational tool.

Among the other energetic parameters, IP and EA of both molecules are determined on this stage as the eigenvalues of Fock's operator related to the molecules HOMOs and LUMOs, respectively. Both quantities are related to vertical transitions at fixed geometry of the ground state. A readiness of the selected molecule pair to form a D-A complex is analyzed by meeting requirements $\Delta E = I_A^0 - E_B^0 > 0$, $I_A < I_B$, and $\varepsilon_A < \varepsilon_B$. Radicalization energies of the molecules are determined. Structure of molecules and ions is analyzed by comparing valence bond distribution to evaluate the equilibrium position shifting.

2. Complex calculations start by selecting sets of initial configurations which differ by molecules A and B positions in the neighborhood of minima $R^{(+\ -)}$ and $R^{(0\ 0)}$.

Distance $R^{(+\ -)}$ is evaluated as either chemical bond length, formation of which is expected for the molecule pair, or as a distance of maximum coming together for ions in the case of ionic coupling. Distance $R^{(0\ 0)}$ is assumed to start from a sum of van-der-Waals radii of atoms that form the shortest intermolecular contacts.

3. A full QCh calculation cycle is performed for each initial configuration of D-A complex in the singlet state by using both RHF and UHF versions of the selected computational tool.

Calculation results involve equilibrated structures, heats of the complex formation, coupling energies E_{coupl}, difference energy ΔE_{tot} as well as charge energy E_{chg}, IP and EA, charge of molecular fragments e_A and e_B, partner composition of HOMO and LUMO.

5. Details of computational experiment

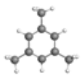
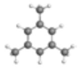
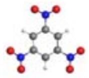
Molecular partners of D-A complexes. A vast number of C_{60} –based complexes have been synthesized and thoroughly studied experimentally by now (see [15,22,23] and references therein), many of which show a promising application. Besides the fullerene, the second partners of the complexes selected for the current study were presented by molecules of 2-cyclooctylamin-5-nitropyridine (COANP), dimethylenemethylamine (DMMA), tetrakisaminoethylene (TAE), and tetrakis(dimethylamino)ethylene (TDAE). Concise complex nominations C_{60}+COANP; C_{60}+DMMA; C_{60}+TAE and C_{60}+TDAE will be used below. Additionally, complexes C_{60}+2Li and C_{60}+Mg involving two Li atoms and one Mg atom have been tested. Thus selected complex family made possible to reveal four types of the IMI terms, shown in Figures 1 and 2.

Calculation technique. Selected complexes contain from 62 to 97 atoms so even a single QCh calculation within the family is not a simple problem. Obviously, the problem is greatly complicated when attempting to follow the analytical scheme described above, even when applying to a single complex. Nothing to say about a QCh testing of the complex collection within a real time limits without using effective and time-conserving calculation techniques. In view of requirements to be met, indisputable advantages of modern semi-empirical (SE) techniques are particularly evident. As is well known, accuracy of results provided by the techniques is as good as that obtained by best *ab initio* (AI) tools, not to mention widely used DFT methods as DFT-B3LYP and others. A SE AM1 method of SCF HF calculations [24] implemented in the CLUSTER-Z1 code [25] has been used in the current study. Acknowledging tradition of unwarranted arrogance towards SE techniques from a part of quantum chemists, a comparative study of a probing complex of trimethylbenzene+trinitrobenzene (TMB+TNB) by using the SCF-RHF version in the 6-31G** basis of GAMESS software [26] and the AM1 technique of the CLUSTER-Z1 codes has been performed. The data obtained are presented in Table 1. Structures inserted in the table correspond to equilibrate configurations obtained in due course of a complete geometry optimization.

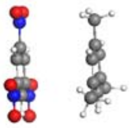
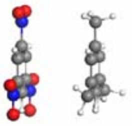
As seen from the table, SE and AI series of the free molecules calculations differ by both structural and electronic data. A comparison of bond lengths, molecular symmetry, and EA, in particular, with experimental data clearly favors SE calculations. AI results on negative EAs of both molecules are fully non-real, while SE consideration correctly reproduces EA of the TNB molecule, large by value and positive by sign, accepting properties of which in intermolecular complexes are well known. According to SE calculation, EA of the TMB molecule is negative but reliably small by absolute value. SE calculations reveal as well small radicalization energy of the molecule that evidences a partial extraction of odd electrons of benzene ring from the covalent pairing.

The complex calculations have been carried out for initial arrangement of benzene rings of both molecules parallel to each other at the distance of 0.450nm. Equilibrated structures in all calculations preserve practically the initial configuration, subjected to a slight increasing of the distance between two rings (0.452-0.456nm). In

Table 1. Characteristics of electron states of TMB+TNB complex

Calculation technique	SSC-RHF GAMESS		AM1 (CLUSTER-Z1)			
Molecules	*TMB*	*TNB*	*TMB*[1]		*TNB*[1]	
Chemical formula: *TMB*: $C_6H_3(CH_3)_3$ *TNB*: $C_6H_3(NO_2)_3$						
Calculated quantities: singlet	RHF	RHF	RHF	UHF	RHF	UHF
Heat of formation, *ΔH, kcal/mol* [2]	not determ.	not determ.	-0.72	-0.95	44.66	44.66
Ionization potential, *I, eV*	8.43	11.86	9.16	9.18	12.25	12.25
Electron affinity, *ε, eV*	-4.02	-0.37	-0.57	-0.64	2.53	2.53
Dipole moment, *Db*	0.0	0.0	0.12	0.12	0.0	0.0
Squared spin (S**2)	-	-	0.0	0.182	0.0	0.0
Bond length C-C, *A*	1.391-1.387 (H) 1.511 (Me)	1.403	1.398 (H) 1.482 (Me)	1.400 (H) 1.481 (Me)	1.403	1.403
Bond length C-H, *A*	1.078 (H) 1.086 (Me)	1.111	1.100 (H) 1.118-1.119 (Me)	1.100 (H) 1.118-1.119 (Me)	1.111	1.111
Bond length C-N, *A*	-	1.493	-	-	1.493	1.493
Bond length N-O, *A*	-	1.199	-	-	1.199	1.199
Symmetry	C_s	C_{3h}	C_3	C_3	C_{3h}	C_{3h}
Radicalization energy, E_{rad}, *kcal/mol*	-	-	0.23		0	

Complex TMB+TNB

	SSC-RHF GAMESS	AM1 (CLUSTER-Z1)[1]	
			
Calculated quantities: singlet	RHF	RHF	UHF
Heat of formation, *ΔH, kcal/mol*	not determ.	42.41	42.25
Coupling energy, E_{coupl}, *kcal/mol*	-2.43	-1.53	-1.46
Difference energy, ΔE_{tot}, *kcal/mol*	-	0.16	
Recharge energy, E_{chg}, *kcal/mol*	-	0.00	
Squared spin, (S**2)	0.0	0.0	0.187
Ionization potential, *I, eV*	8.85	9.52	9.53
Electron affinity, *ε, eV*	-0.15	2.40	2.40
Dipole moment, *Db*	0.29	0.37	0.37
Symmetry	C_1	C_1	C_3
Partner charge, *TMB/TNB, am.eð.*[3]	0.003/-0.003	0.003/-0.003	0.003/-0.003
Partner composition of HOMO, *TMB/TNB,* %	-	100/0.0	100/0.0
Partner composition of LUMO, *TMB/TNB,* %	-	0.0/100	0.0/100
Time, *min*[4]	~6700	5	188

[1] Presented are UHF structures.

[2] $\Delta H = E_{tot} - \sum_{A} E^{A}_{elec} + EHEAT^{A}$, where $E_{tot} = E_{elec} + E_{nuc}$, E_{elec} and E_{nuc} are electron and nucleus energies while E^{A}_{elec} and *EHEAT*^{A} correspond to the electron energy and heat of formation of an isolated atom *A*. All quantities are calculated within the same calculation session.

[3] Notation *TMB/TNB* means that the data divided by slash from the next rows should be related to the relevant partners, say, TMB and TNB .

[4] SE and AI calculations have been performed on PC with two Intel-PIII-660MGz processors and Atlon-1.7 GGz processor, respectively.

spite of a noticeable difference in details of the molecules structure, both SE and AI coupling energies of the complex occurred to be close by value and rather significant.

As in the case of free molecules, the AI results concerning IP and EA are clearly inconsistent with the reality. Largely time-costly, AI calculations have been performed in the RHF version only. Increasing the needed time by order of magnitude has made the UHF calculation practically non-feasible [27].

As seen from Table 1, the transferred charge is practically zero that well correlates with the zero value of the charge energy E_{chg}. A complete cross partitioning of the partner composition of the complex HOMO and LUMO convincingly evidences towards D-A nature of the complex that can be characterized by the charge transfer from TMB to TNB under photoexcitation. The relevant CTB of B_2 type should be observed in the complex absorption spectrum.

6. Quantum-chemical testing of C_{60}-based complexes

6.1. Molecular partners

Calculation results for molecules C_{60}, TAE, DMMA, TDAE and COANP are summarized in Table 2.

Fullerene C_{60}. Electron states of the molecule are presented by the last by time QCh investigation that was aimed at revealing a partial exclusion of the molecule odd electrons from covalent pairing. For a detailed discussion see [21]. Here we shall limit ourselves only by a short note that the molecule is characterized by ~ 30-20%th radicalization of all 60 electrons in average, that means that only ~70-80% of each electron are involved in interatomic coupling leaving them partially free and causing a considerable radicalization energy.

Dimethylenemethylamine– DMMA. The molecule exhibits well seen radical properties provided by two methylene radicals. Radicalization of the C-C bonds of methylene units is of 40%, in what connection E_{rad} is of more than 20% of the molecule heat of formation and $<S^{**}2>$ is non-zero. For the C_{60}(A)+DMMA(B) pair the requirements $I_A > I_B$ and $\varepsilon_A > \varepsilon_B$ are met, therewith DMMA is an electron donor while fullerene may accept the electron.

Tetrakis(dimethylamino)ethylene-TDAE. The molecule is a rather strong covalent compound with a small, but not zero anyway, energy E_{rad}. The requirements $I_A > I_B$ and $\varepsilon_A > \varepsilon_B$ are hold for the pair C_{60}(A)+TDAE(B), at which TDAE can serve as an electron donor while fullerene plays the acceptor role.

Tetrakisaminoethylene –TAE. Substitution of amino units by dimethylamines somewhat weakens the covalent bonding of the ethylene bridge comparing to that of TDAE that results in increasing E_{rad}. Otherwise both molecules behave similarly so that TAE is a proper donor partner for fullerene C_{60}.

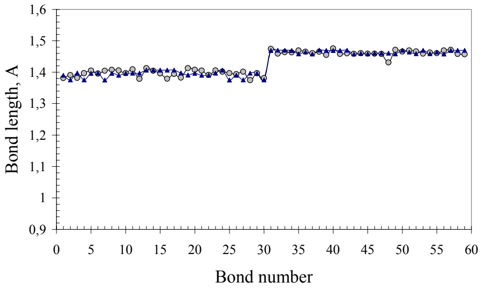
2-cyclooctylamine-5-nitropyridine–COANP. The molecule is an example of a complete covalent pairing with the zero energy E_{rad} and offers suitable characteristics for donor-acceptor coupling with fullerene C_{60}.

6.2. Molecular ions

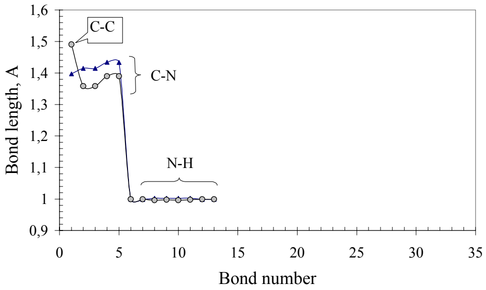
As follows from the analysis performed in the previous Section, the fullerene C_{60} molecule acts as electron acceptor in all cases while the other molecules are electron donors. This makes possible to limit oneself by the calculations of its negative ion and positive ions of other molecules. Table 3 presents basic QCh characteristics of single-charged ions in the doublet ground state. Figure 4 compares the ion structures with those of the neutral molecules in terms of valence bond lengths. As seen from the table, the negative ion formation lowers the molecule heat of formation while the positive ion formation results in a considerable increase of the latter. Simultaneously, IPs and EAs of all positive ions increase while, oppositely, the quantities decrease for the negative ions. The deviation of the (S**2) value from the exact value of 0.75 characterizes a spin-mixing of the considered doublet states.

As follows from the data, the considered molecules form two groups. The first group covers fullerene, DMMA, and COANP, ionization of which does not cause lengthening of valence bond more than by 0.002nm. It should be noted that this is equally related to both negative and positive fullerene ions. As for the TAE and TDAE molecules belonging to the second group, the ionization results in a considerable lengthening of the C-C bond of the ethylene bridge by 0.010 and 0.012nm, respectively. Consequently, it can be said that the molecular ion formation is accompanied by a significant shifting of the atom equilibrium positions along this internal coordinate. According to schemes in Figure 3, the shifting is escorted by the ions vibrational excitation during vertical diabatic transition. As a result, the ion dissociation along the C-C bond is greatly facilitated.

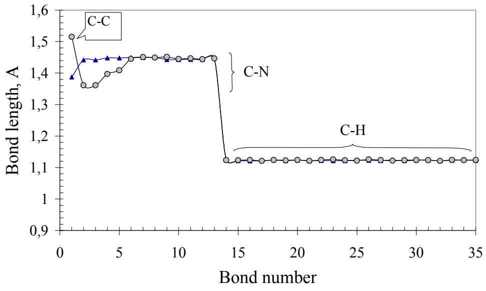
C_{60}



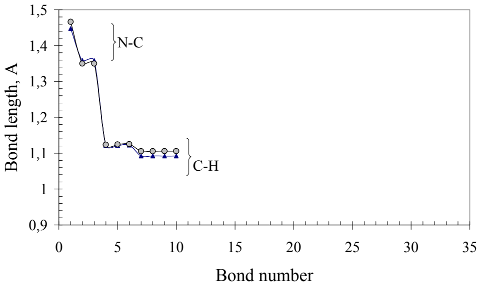
TAE



TDAE



DMMA



COANP

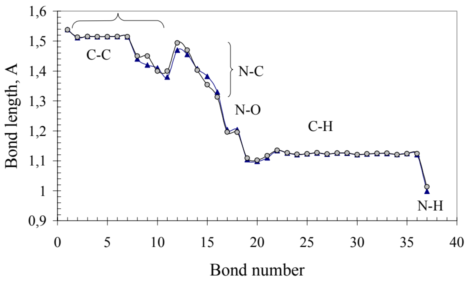


Figure 4. Structure of neutral molecules and molecular ions in terms of valence bonds.

Table 3. Characteristics of electron states of single-charged ions

Calculated quantities (AM1), doublet	*$(C_{60})^-$*	*$(C_{60})^+$*	*$(DMMA)^+$*	*$(TDAE)^+$*	*$(TAE)^+$*	*$(COANP)^+$*
	UHF	UHF	UHF	UHF	UHF	UHF
Heat of formation, ΔH, *kcal/mol*	878.79	1166.68	200.99	193.57	157.17	199.61
Ionization potential, I, *eV*	4.23	12.89	15.17	11.63	12.43	14.03
Electron affinity, ε, *eV*	-0.40	6.83	5.94	3.99	4.59	5.45
Squared spin, (S**2)	5.44	5.36	0.86	0.76	0.76	1.07
Symmetry	C_i	C_i	C_1	C_1	C_2	C_1

The following predictions can be made concerning features of the C_{60}–based complexes with the studied molecules, based on the data obtained. The complex formation of C_{60} with the TAE, TDAE, and DMMA molecules must be subordinated to two-well IMI term of the first type, shown in Figure1b, with great probability.
Strong complexes with the molecules coupled to fullerene C_{60} via chemical bond that provides a deep minimum on the IMI term at $R^{(+\ -)}$, should be expected in the region of small *R*. As well known [29], a central double C-C bond of the naphthalene-core fragment of the C_{60} molecule is taken as the most chemically active site. The bond is willingly opened towards any partner that provides involving two odd electrons of the two carbon atoms into covalent bond formation. For simplicity, in what follows the atoms will be referred to as reference ones. The TAE and TDAE dissociation will undoubtedly promote the bond formation. As for the DMMA molecule, the radical character of its two methylene units assists the process from the very beginning. In contrast to the above said, the formation of similar bonds for the C_{60}+COANP pair is not obvious. The complex formation for the pair is expected to subordinate IMI term of type 3 or 4 (see Figure 2) when the process in the region $R^{(+\ -)}$ depends on the depth of the corresponding minimum.

6.3. D-A complexes C_{60}+TAE and C_{60}+TDAE

Complex C_{60} + TAE. Results of the complex testing are given in Table 4. Calculations have shown that the complex configuration depends of the starting intermolecular distance. The quantity is presented in the Table by parameter R_{st} that corresponds to the shortest starting distance between carbon atoms of the C-C bond of the TAE molecule and one of the reference carbon atoms of the fullerene $C_{60.}$ At $R_{st} \geq 0.20$nm, the distance in the final complex is enlarged up to 0.37–1.5nm depending on the TAE orientation with respect to the fullerene. The heat of formation is changed therewith from the value given in the table to that which exceeds the former by ~20 kcal/mol. The structure and the heat of formation of the C_{60} molecule do not change therewith. As to TAE, both its structure and charge distribution over atoms at keeping the molecule charge neutrality as well as the molecule heat of formation significantly change. At the same time both coupling energies E_{coupl}^{RHF} and E_{coupl}^{UHF} in all cases occur to be small and consistent with an averaged value given in the table. The charge distribution well exhibits that changes in both heat of formation and the molecule structure should be attributed to considerable polarization effects that resulted from inductive IMI [5] and are sensitive to the mutual orientation of both molecules. As known [18], this effect is fairly significant in molecular crystals, coupled by weak IMI, which is conventionally attributed to van-der-Waals one [30], so that its appearance in the studied complex is absolutely natural.

Variations in the complex heat of formation as well as the TAE structure effect the other complex characteristics only slightly. As seen from the table, both the radicalization energy and squared spin are mainly determined by the C_{60} molecule. EA is also originated from the molecule value while IP has clearly seen TAE origin. Complex dipole moment is rather significant that evidences a charge polarization between the complex components discussed earlier. Transferred charge and charge energy are equal to zero, partner composition of HOMO and LUMO tells about complete cross partitioning of these orbitals over the complex components. The latter provides appearing a CTB of a B_2 type in the complex absorption spectrum.

At $R_{st} \leq 0.20$nm, the only equilibrated complex configuration has been formed. That is related to a di(diamino)fulleroid [31] (TAE-fulleroid) which is formed due to dissociation of the TAE molecule along its C-C bond [32]. The reaction occurs without barrier. The fulleroid heat of formation is determined as

$$E_{coupl} = \Delta H_{compl} - \Delta H_{C_{60}} - \Delta H_{TAE} - E_{diss}(R_{eq}). \qquad (10)$$

$E_{diss}(R_{eq})$ is the dissociation energy of TAE at the C-C distance (0.166nm) that is observed in the complex equilibrate configuration. The relevant RHF and UHF values are 42.16 and 32.02 kcal/mol, respectively. The newly formed C-C bonds between fullerene and TAE are of 0.158nm (RHF) and 0.159nm (UHF) in length.

As seen from the table, the fulleroid is characterized by a considerable coupling energy and a pronounced radicalization energy caused by odd electrons of the fullerene. The coupled ions charge constitutes about 14% of that of free ions and provides a considerable increasing of the dipole moment. As for complex orbitals, both calculations show that LUMO is provided by fullerene only. At the same time, HOMO is partner-mixed: RHF composition favors fullerene while UHF one evidences in favor of TAE. Here we have firstly faced a qualitative difference in RHF and UHF results. A large experience gathered during numerous calculations tells that this is not connected with the SE nature of the technique used. The matter is in the nature of the UHF approximation itself that is undoubtedly preferable when electrons are located on spatially different fragments. That is why through over the paper a preference has been given to UHF equilibrated structures that are shown through over the tables. For the discussed C_{60}+TAE complex, a B_1 type band should be expected in the absorption spectrum, whose excitation is accompanied by a considerable charge transfer in addition to the charge available in the ground state.

The discussed data obviously show that the complex formation for the binary system C_{60}+TAE is related to the case $\overset{+-}{E}_{cpl} << E^{00}_{cpl}$ and is subordinated to two-well IMI term of the first type with deep minimum at $R^{(+\ -)}$.

Complex C_{60}+TDAE. When comparing data from Table 4, it becomes obvious that binary systems C_{60}+TAE and C_{60}+TDAE behave quite similarly in many aspects. Thus, in the latter case, as previously, there are two regions of starting parameter R_{st} , that marks the distance between carbon atoms of the ethylene bridge in the TDAE molecule and reference carbon atoms of fullerene. At $R_{st} \geq 0.20$nm, a traditional weak D-A complex is formed with the only difference that instead of numerous final configurations of the C_{60}+TAE system the only configuration of the C_{60}+TDAE pair is formed where R_{st} is substituted by R_{fin} equal to 1.04 and 0.75nm in the RHF and UHF states, respectively. The relevant coupling energies are small that is consistent with a shallow minimum on the IMI term at $R^{(0\ 0)}$. However, just this very minimum is responsible for the formation of the C_{60}+TDAE molecular crystal with experimental R_{fin} value within the range of 0.38-0.40nm [33]. The discrepancy between the calculated and experimental value can be easily explained by a natural tendency of crystalline structure to a dense packing [30] that is resulted from the interaction of the TDAE molecule with surrounding C_{60} molecules and vice versa. As known, the interaction can shorten intermolecular distances in a binary system at least by half [30]. A presence of a B_2 type CTB in the absorption spectrum of the crystal is well supported by the partner composition of HOMO and LUMO, shown in Table 4.

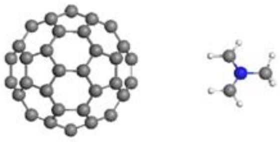
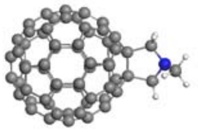
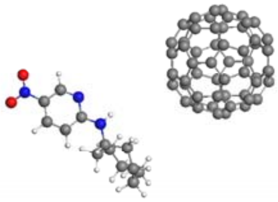
Ar $R_{st} \leq 0.20$nm, as in the case of C_{60}+TAE, a barrierless reaction occurs of two dimethylamine radicals addition to two reference carbon atoms of the fullerene C_{60}. The radical formation is promoted by the TDAE dissociation along the C-C bond. Thus formed TDAE-fulleroid is similar to the TAE-fulleroid in many aspects. It is characterized by a large coupling energy (deep minimum) that is determined in accordance with Ex.(10). $E_{diss}(R_{eq})$ is equal to 94.97 (RHF) and 83.24 (UHF) kcal/mol at the C-C distance (0.280nm) observed in the relevant equilibrate configurations of the fulleroid. The radicalization energy is similar to that of the TAE-fulleroid. Oppositely to TAE-fulleroid, TDAE-one practically losses its ionic character if follow the UHF charge value. As for the partner composition of HOMO and LUMO, it is of cross-partitioning character, typical to traditional D-A complexes with CTB of B_2 type. That is why a photoexcitation of the complex band will be accompanied by charge transfer.

Summarizing the data obtained, a conclusion can be made that, analogously to the binary system C_{60}+TAE, the complex formation in the C_{60}+TDAE system is well described by two-well IMI term with a deep minimum at $R^{(+\ -)}$.

6.4. D-A complexes C_{60}+DMMA and C_{60}+ COANP

Complex C_{60} + DMMA. Similarly to two previous cases, the studied complex structure is sensitive to initial starting distances R_{st}. In the current case, the parameter describes C-C distance between a carbon atom of a methylene unit and a reference atom of the fullerene molecule. At $R_{st} \geq 0.35$nm (the lower limit is ranged between 0.25-0.35 nm), the complex consists of the C_{60} and DMMA molecules largely separated by the final distance R_{fin} of 0.542 (RHF) and 0.588nm (UHF), and, as seen from Table 5, exhibits all characteristics of weak D-A complexes: coupling energies of the RHF and UHF complexes are small and comparable; the molecules preserve their individuality to a great extent; transferred charge and charge energy are zero; both RHF and UHF partner compositions of HOMO and LUMO show a complete cross partitioning providing the appearance of a traditional CTB of B_2 type in the absorption spectrum.

Table 5. Characteristics of electron states of D-A complexes C_{60}+DMMA and C_{60}+ COANP

						
Calculated quantities(AM1), singlet	*C_{60}+DMMA*				*C_{60}-COANP*	
	R_{st}=0.354 nm		R_{st}=0.252 nm		R_{st}=0.353 nm	
	RHF	UHF	RHF	UHF	RHF	UHF
Heat of formation, *ΔH*, *kcal/mol*	1022.56	995.50	948.40	927.67	982.01	964.75
Coupling energy, E_{coupl}, *kcal/mol*	-0.11	-0.21	-58.53	-68.04	-0.11	-0.23
Difference energy, ΔE_{tot}, *kcal/mol*	27.06		20.73		17.26	
Charge energy, E_{chg}, *kcal/mol*	0.00		-		0.00	
Squared spin, (S**2)	0.0	5.69	0.0	5.50	0.0	4.94
Ionization potential, *I*, *eV*	7.14	7.98	9.29	9.64	9.32	9.32
Electron affinity, *ε*, *eV*	2.90	2.64	2.84	2.44	2.99	2.70
Dipole moment, *Db*	2.35	1.38	2.75	2.52	7.63	7.63
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1
Partner charge, C_{60}/*XXX*, *am.ed.*	0.0/0.0	0.0/0.0	-0.206/0.206	-0.208/0.208	0.00/0.00	0.00/0.00
Partner composition of HOMO, C_{60}/*XXX*, %	0.0/100	0.0/100	99.0/1.0	99.0/1.0	0.0/100	0.0/100
Partner composition of LUMO, C_{60}/*XXX*, %	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0

At $R_{st} \leq 0.25$nm (upper limit is in interval of 0.25-0.35nm), as in the previous cases, a strongly coupled DMMA-fulleroid is formed. The formed substance can be called differently, in particular, as suggested in [34], as N-methyl-pyrrolo[3,4] C_{60} (MPC). The RHF data for the species from Table 5 are well consistent with results of similar calculations by using the AM1 version of MOPAC package [34]. DMMA and fullerene are connected by two single C-C bonds of 0.156nm. Coupling and radicalization energy are comparable with the previously studied. This is quite reasonable since the same pair of the fullerene carbon atoms participates in the fulleroid formation. Ion charge is rather considerable. The fragment composition of both HOMO and LUMO is one-fragmental in favor of fullerene, so that phototransitions that are responsible for the band of B_1 type occur between fullerene states and are not accompanied by the charge transfer [35].

The obtained data clearly show that the complex formation in the considered binary system, similarly to two previous cases, should be attributed to the case $E_{cpl}^{+-} << E_{cpl}^{00}$ and is subordinated to two-well IMI term of the first type with deep minimum at $R^{(+\ -)}$.

Complex C_{60}+COAN. If for configurations in the vicinity of $R^{(0\ 0)}$ at large intermolecular distances a setting of an initial configuration is quite trivial, in the region of small intermolecular distances close to $R^{(+\ -)}$ structural features of the COANP molecule determine parameter R_{st} as the distance between nitrogen atom of the molecule amine unit and the reference carbon atom of the fullerene. According to the data discussed in Section 6.2, the equilibrate structures of the COANP molecule and its ion are practically coincident so that a stable molecular ion $[COANP]^+$ is formed at vertical diabatic transition without any indication to the N-H bond dissociation. Three initial configurations of the binary system C_{60}+COANP have been chosen for calculations with R_{st} =0.14, 0.22, and 0.35nm. In all cases not only short final distances R_{fin} compared with chemical bond length are obtained but even shortened intermolecular contacts are absent and values R_{fin} constitute 0.45, 0.46, and 0.38nm. In spite of clear difference in the mutual orientation of the partners, the complex energetic parameters are practically identical. Therefore, the binary system C_{60}+COANP forms a typical weak D-A complex [37]: the charge transfer does not occur in the ground state and the charge energy is zero; there is a complete cross partitioning of HOMO and LUMO so that a CTD of B_2 type is observed in the absorption spectrum of the complex [38]. From this follows, that minimum at $R^{(0\ 0)}$ plays the main role on the IMI term, which should be attributed to term of the fourth type shown in Figure 2b.

6.5.D-A complexes C_{60} + 2Li and C_{60} + Mg

The diversity of the properties of C_{60}-based D-A complexes will be incomplete without considering alkali and alkali-earth atoms as partners to fullerene. Such complexes have been largely studied [39,40] and form a good testing ground for the suggested approach.

Complex C_{60} + 2Li. Two Li atoms allow to preserve the even number of the electrons and to consider a singlet ground state. When calculating, one had to reject the use of the AM1 technique due to the lack of reliable atomic parameters for both metal atoms. PM3 technique [41] of the CLUSTER-Z1 codes has been used instead with Li and Mg parameters from [42] and [43]. The calculation results are given in Table 6.

When setting a starting configuration, Li atoms have been placed in the center of two parallel hexagons at the R_{st} distance from the hexagon carbon atoms varying in limits of 0.22-0.50nm. As occurred, the final configuration of the complex, shown in the table, does not depend on the R_{st} values. The data in Table correspond to R_{st}=0.323nm. After structure optimization the metal atoms are placed at the distances of 0.252-0.256nm (RHF) and 0.242-0.250nm (UHF) to carbon atoms of the relevant hexagons. Wiberg's bond indices [44] show that each metal atom interacts with six carbon atoms of a hexagon practically in equal way that leads to a large coupling energy. The complex is characterized by a large value of ion charge (of 1.13a.u. in both RHF and UHF states) so that IMI between the complex partner is mainly ionic by nature. The obtained data show that the IMI term $E_{\text{int}}(r,R)$ of the complex has only one minimum at $R^{(+\ -)}$ and can be attributed to the term of the second type shown in Figure 1c. As follows from the fragment composition of HOMO and LUMO, phototransitions that correspond to a band of B3 type occur between states belonging to fullerene and are not accompanied by charge transfer.

Complex C_{60} + Mg. Two starting configurations have been tested. In the first case, Mg atom has been placed over C-C bond, which joins reference atoms, at the distance R_{st} of 0.184 and 0.185nm from the atoms. A search of the energy minimum results in a new position of the atom at 0.192nm from both reference atoms. The value is well consistent with a conventional length of the Mg-C bond in magnesium carbide. Carbon atoms, coupled to the metal, form three equal C-C single bonds of 0.150nm in length with neighboring ones. In both RHF and UHF states 1.79 a.u. participate in covalent bonding, 0.76 a.u. is involved in the formation of each Mg-C bond, besides what from 0.03 to 0.01 a.u. take part in interaction of metal atom with other carbon atoms of the selected naphthalene-core fragment. Charge on the metal atom is of +0.44 a.u. (RHF) and +0.45 a.u. (UHF). The same by value but negative charge is located at the fullerene. The complex coupling energy is rather big but positive that evidences about endothermic character of the reaction of the metal atom addition to the fullerene. It should be reminded nevertheless, that the coupling energy is counted off from the reference term $E_{\inf}(A^0B^0)$. A stability of the ionic compound is determined by the depth of minimum of the IMI term $E_{\rm int}(A^+B^-)$ with respect to asymptotic term magnitude $E_{\inf}(A^+B^-)$. Counted from this term, the coupling energy of the complex constitutes –88.91kcal/mol. Energy of the complex radicalization is related to that of the C_{60} molecule practically in the same proportion as in the previous case with two carbon atoms involved in the coupling as well. In this connection, an about two-times increasing of the value for the C_{60} + 2Li complex should be pointed out as showing the effect of the type of metal-fullerene binding on fullerene odd electrons behavior. The RHF partner composition of HOMO and LUMO shows that fullerene states dominate in both orbitals. In the case of the URF state, this dominating vanishes and the fragment composition approaches to typical for weak D-A complexes with a traditional CTB of B_2 type. Therefore, an additional charge transfer from metal atom to fullerene must accompany a photoexcitation.

In the second starting configuration the distance from metal atom to reference atoms of fullerene has been increased up to 0.480nm. After structure optimization the distance has been enlarged up to 0.942nm. The complex formed therewith can be considered as a typical weak D-A complex. Charge transfer is absent, the charge energy is zero, HOMO and LUMO are fully cross-partitioned, a traditional CTB of B_2 type should be observed in the absorption spectrum of the complex. Attention should be drawn to the fact that the RHF coupling energy is positive. Generally, it means an impossibility of a stable complex formation of neutral component. However, the UHF heat of formation is much less and the UHF coupling energy is both negative and of a reasonable value. It should be supposed that this very result fits the real situation so that the above described weak complex of the binary C_{60}+Mg system must exist at nanometer distances. This might be a most appropriate case for demonstration of the RHF application disadvantage to the systems with largely separated parts. Analyzing the considered system behavior at small and large intermolecular distances, a conclusion can be made that the complex formation in the system is related to the case $E_{cpl}^{+-} > E_{cpl}^{00}$ and is subordinated to the two-well IMI term of the third type shown in Figure 2a.

7. Conclusion

Suggested in the current paper is a quantum-chemical testing of donor-acceptor properties of C_{60}-based binary systems. The testing concept is based on mixing states of neutral molecules and their ions. The mixing assists in avoided crossing of the IMI terms related to neutral molecules $E_{\text{int}}(A^0B^0)$ and molecular ions $E_{\text{int}}(A^+B^-)$ that results in formation of two branches of the composite IMI terms. Generally, the IMI term of the ground state possesses a few minima. Representing it as a function of a single intermolecular coordinates makes possible to reveal four types of the term, two of which (two-well and one-well) correspond to inequality $E_{cpl}^{+-} < E_{cpl}^{00}$, terms of type 1 and 2, respectively, while two other (two-well and one-well) correspond to inequality $E_{cpl}^{+-} > E_{cpl}^{00}$, terms of type 3 and 4, respectively. Quantities E_{cpl}^{+-} and E_{cpl}^{00} determine complex coupling energies at small and large intermolecular distances. The complex properties depend directly on the type of the IMI term of the ground state.

The current study has been aimed at elaborating a methodology of the binary systems testing with respect to the above four types of the IMI terms. The methodology suggested in the paper is related to the singlet ground state and is based on joint QCh calculations by using both spin-nondependent (RHF) and spin-dependent (UHF) versions of the same computational tools. The approach has a rather general meaning and does not depend on the very computational technique in use. Practical implementation of the approach is possible by using efficient time-saving computational programs, among which SE techniques have offered so far supreme advantages.

The testing involves the following stages:

- QCh analysis of free molecules *A* and *B* as well as their ions that involves equilibrate structures of the species together with a number of electron characteristics;

- QCh analysis of binary systems A + B with different relative positions of the partners in the initial configurations which might correspond to different minima of the IMI term of the ground state;
- a quantitative analysis of equilibrated structures based on heats of formation, coupling energies E_{coupl}, difference energies $\Delta E_{tot} = E_0^{RHF}(compl) - E_0^{UHF}(compl)$ as well as charge energies E_{chg}, ionization potentials and electron affinities, charges of molecular partners e_A and e_B, as well as partner composition of the complex HOMO and LUMO.

Being applied to binary systems, each containing the C_{60} fullerene molecule with high EA additionally to other organic or metallic atom component with relatively low IPs, the suggested testing methodology has made possible to exhibit the following.

The complex formation in the binary systems C_{60}+TAE, C_{60}+TDAE and C_{60}+ DMMA are subordinated to the IMI terms of the first type with two minima at $R^{(+\ -)}$ and $R^{(0\ 0)}$, respectively. In the $R^{(+\ -)}$ region, strongly coupled complexes presented by the correspondent fulleroids are formed, which are characterized by the intermolecular chemical bond formation that was predicted by a comparative study of neutral molecules TAE, TDAE, and DMMA and their positive ions. All complexes demonstrate a significant charge transfer from the organic molecule to fullerene. The partner composition of HOMO and LUMO is generally partner-mixed and changes from a one-partner type (C_{60}+DMMA) to fully cross partner-partitioned type (UHF state of C_{60}+TDAE). While optical excitation is not accompanied by an additional charge transfer in the first case, a rather significant adding to the transferred charge is provided by the excitation in the second case.

All systems form in the $R^{(0\ 0)}$ region weak D-A complexes, which are characterized by small coupling energy, zero transferred charge in the ground state and zero charge energy. Optical excitation, occurred between fully cross- partner-partitioned HOMO and LUMO, provides the appearance of a traditional CTB in the complex absorption spectrum.

Oppositely to the above three systems, the binary system C_{60} +COANP offers only characteristics of weak D-A complexes and does not exhibit any complexing in the $R^{(+\ -)}$ region. The findings force to attribute the system to those that are subordinated to the IMI term of the fourth type.

Two additional binary systems C_{60} + 2Li and C_{60} + Mg have been tested to make the obtained results more general. A strong D-A complex was obtained in the first case. The correspondent IMI term is attributed to the term of the second type with a single deep minimum at $R^{(+\ -)}$. The complex is characterized by a big coupling energy , mainly ionic by nature, with large ion charge. The binary system C_{60} + Mg can be characterized by a two-well IMI term of the third type. Strong and weak D-A complexes are formed in the $R^{(0\ 0)}$ and $R^{(+\ -)}$ regions, respectively.

Radical properties of the fullerene molecule remain unchanged for weak D-A complexes while considerably changing in the case of tight binding that results in fulleroid formation. Those are characterized in the paper by radicalization energy that occurred to be sensitive to extra electron attack.

Calculations performed in the current study on personal computer with two Intel-PIII processors have taken less than two months of computational time. That clearly shows that QCh testing of complicated molecular systems is well feasible and can be introduced in the laboratory practice of chemical analysis.

References

1. Mulliken, R.S. J.Amer.Chem.Soc. 1950, 72, 600; ibid., 1952, 74, 811; J.Phys.Chem., 1952, 56, 801; J.Chim.Phys. 1964, 61, 20.
2. Mulliken, R.S.; Person, W.B. Molecular complexes.-N.Y.: Willey Interscience, 1969.
3. Forster, R. Organic charge-transfer complexes, London and New York: Academic Press, 1969.
4. Rose, J. Molecular Complexes, Oxford:Pergamon, 1967.
5. Kaplan, I.G. Vvedenie v teoriu mezhmolekuljarnukh vzaimodeistvij (Introduction to the theory of intermolecular interaction), Moskva: Nauka, 1982, Ch.1.
6. Evans, M.G.; Polanyi,J. Trans.Far.Soc ;1939, 35, 178.
7. Yarkony, D.R. J.Phys.Chem. 1996, 100, 18612.
8. Herschbach, D.R. Adv. Chem. Phys. Vol.10. Molecular Beams 1966, 319.

9. Leonas, V.B.; Kalinin, A.P. Uspekhi Fiz. Nauk (Soviet Physics Uspekhi) 1977, 121, 561.
10. Morokuma, K. , J.Chem.Phys. 1971, 55, 1236.
11. Kitaura, K.; Morokuma, K. Int.Journ.Quant.Chem. 1976, 10, 325.
12. Umeyama, H.; Morokuma, K., Yamabe, S. J.Amer.Chem.Soc. 1977, 99, 330.
13. Umeyama, H.; Morokuma, K., J.Amer.Chem.Soc. 1976, 98, 7208.
14. Actually, the matter is about changing the molecule valence bonds length under ionization.
15. Soos, Z.G.; Klein, D.J. in Molecular Association, vol. 1, Ed. R.Foster, London and New York: Academic Press, 1975, p.1.
16. Silinsh, E.A. Organic Molecular Crystals: Their Electronic States, Springer:Berlin, 1980.
17. Glaeser, R.M.; Berry, R.S. J.Chem.Phys. 1966, 44, 3797.
18. Noodleman, L. J Chem Phys 1981, 74, 5737.
19. Benard, M. J Chem Phys 1995, 71, 2546.
20. Hay, P.J.; Thibeault, J.C.; Hoffman, R. J Amer Chem Soc. 1975, 97, 4884.
21. Sheka, E.F. Lecture Notes in Computer Science, Computational Science – ICCS2003, Eds. P.M.A.Sloot, D.Abramson, A.V.Bogdanov, J.Dongarra, A.Y.Zomaya, Y.E.Gorbachev, Springer : Berlin, 2003, Part II, 386.
22. Konarev, D.V.; Lyubovskaya, R.N. Russian Chem.Rev. 1999, 68, 1938.
23. Konarev, D.V.; Kovalevsky, A.Yu.; Litvinov, A.L.; Drichko, N.V.; Tarasov, B.P., Coppens, P.; Lyubovskaya, R.N. J.Solid State Chem. 2002, 168, 474.
24. Dewar, M.J.S.; Zoebisch, E.G.; Healey; E.F., Stewart, J.J.P. J Amer Chem Soc 1985, 107, 3902.
25. Zayets, V.A. CLUSTER-Z1: Quantum-Chemical Software for Calculations in the *s,p*-Basis: Institute of Surface Chemistry, Nat. Ac.Sci. of Ukraine: Kiev, 1990.
26. Schmidt, M.W.; Baldridge, K.K.; Boatz, J.A.; Elbert, S.T.; Gordon, M.S.; Jensen, J.J.; Koseki, S.; Matsunaga, N.; Nguyen, K.A.; Su, S.; Windus, T.L.; Dupuis, M.; Montgomery, J.A. J.Comput.Chem. 1993, 14, 1347.
27. Stimulating by a referee, one more comparing of SE and *ab initio* results has been done by using DFT (BLYP) [28] technique. However, the results occurred to be rather poor even for individual molecules. Thus, spin-restricted data for the TNB species lengths of bonds C-C, C-H, C-O, and O-N are of 0.140nm, 0.109nm, 0.150nm, and 0.124nm, respectively. Similarly, not sufficiently accurate reproducing of the TMB molecule geometry has been obtained as well. Energetic

parameters, namely IP (8.26eV for TNB) and EA (5.18eV for TNB) are much worse: the former are too low while the latter are too big. Time expenses exceed those of SE technique by two orders of magnitude.

28. Delley, B. J.Chem Phys. 1990, 92, 508; ibid. 2000, 113, 7756.
29. Wudl, F. Acc. Chem. Res. 1992, 25, 157.
30. Kitaygorodski, A.I. Molekulyarnye kristally, Moskva:Nauka, 1971.
31. Term fulleroid has a meaning suggested by Wudl [29].
32. The fulleroid structure, recently obtained when starting from free ions $(C_{60})^-$ and $(TAE)^+$, is fully identical to shown in Table 4 and does not depend on the starting distance between ions.
33. Narymbetov, B.; Omerzu, A.; Kabanov, V.V.;Tokumoto, N.; Kobayashi, H.; Mihailovich, D. Nature 2000, 407, 883.
34. Liu, Y.; Zhang, D.; Hu, H.; Liu, Ch. J.Mol.Struct. (Theochem) 2001, 545, 97.
35. Recent study of the MPC molecule absorption spectrum has revealed a close similarity of the latter to that of the C_{60} molecule [36].
36. Razbirin, B.S. Book of Abstracts 6-th Biennial International Workshop "Fullerenes and Atomic Clusters", June 30- July 4, 2003, St.Petersburg, P.16.
37. The above shown non-dependence of the coupling energy of weak D-A complexes on mutual orientation of molecular partners well explains a stability of molecular crystals belonging to an extended class of intermolecular configurations of the C_{60}+X type [12,33], in spite of practically free rotation of the fullerene in these crystals at ambient temperature.
38. Kamanina, N.V.; Sheka. E.F. Book of Abstracts 6-th Biennial International Workshop "Fullerenes and Atomic Clusters", June 30- July 4, 2003, St.Petersburg, P.178. Optika i spektroskopia (in press).
39. Nagase, S. ; Kobayashi, K.; Akasaka, T. J. In Fullerene Chemistry, Physics, and Technology; K.M.Kafish, R.S.Rueff, eds. Wiley Interscience: N-Y, 2000, p. 357.
40. H.Shinohara. In Fullerene Chemistry, Physics, and Technology; K.M.Kafish, R.S.Rueff, eds. Wiley Interscience: N-Y, 2000,p. 395.
41. Stewart, J.J.P. J Comp Chem 1989, 10, 209, 221.
42. Anders, E.; Koch, R., Freunscht, P. J. Comp. Chem 1993, 14, 1301.
43. Stewart, J.J.P. J. Comp. Chem. 1991,12, 320.
44. Wiberg, K.B.:Tetrahedron 1968, 24, 1083.

Table 2. Characteristics of electron states of free molecules

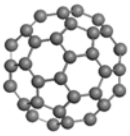
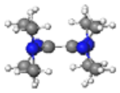
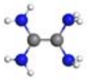
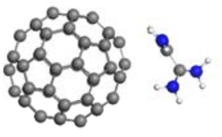
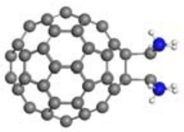
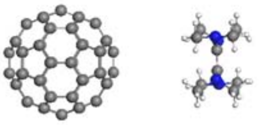
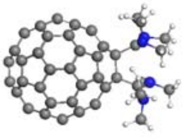
: Calculated quantities (AM1), singlet	 **Fullerene** *C_{60}*		 *DMMA* *C_3NH_7*		 **TDAE** *$C_{10}N_4H_{24}$*		 *TAE* *$C_2N_4H_8$*		 *COANP* *$C_{13}H_{19}N_3O_2$*	
	RHF	**UHF**	**RHF**	**UHF**	**RHF**	**UHF**	**RHF**	**UHF**	**RHF**	**UHF**
Heat of formation, *ΔH, kcal/mol*	972.70	955.56	49.96	40.15	53.36	53.31	13.14	12.91	9.42	9.42
Ionization potential, *I, eV*	9.64	9.86	7.13	7.98	8.70	8.69	8.02	7.51	9.32	9.32
Electron affinity, *ε, eV*	2.95	2.66	-1.06	-1.94	-0.90	-0.96	-1.29	-1.75	0.94	0.94
Dipole moment, *Db*	0.0	0.01	2.16	1.29	0.01	0.04	0.75	0.02	7.95	7.95
Squared spin, (S**2)	0.0	4.92	0.0	0.75	0.0	0.09	0.0	0.43	0.0	0.0
Symmetry	I_h	I_h	C_s	C_s	C_i	C_s	C_2	D_2	C_1	C_1
Radicalization energy, E_{rad}, *kcal/mol*	17.14		9.81		0.05		0.23		0.00	

Table 4. Characteristics of electron states of D-A complexes C_{60}+TAE and C_{60}+ TDAE

Calculated quantities(AM1), singlet	 C_{60}-TAE				 *C_{60}+TDAE*			
	R_{st}>0.20 nm		R_{st}=0.17 nm		R_{st}>0.20 nm		R_{st}=0.17 nm	
	RHF	UHF	RHF	UHF	RHF	UHF	RHF	UHF
Heat of formation, *ΔH, kcal/mol*	<985.76>[1]	<968.36>	967.10	945.34	1025.97	1008.66	1039.98	1017.08
Coupling energy, E_{coupl}, *kcal/mol*	<-0.09>	<-0.11>	-98.82	-83.39	-0.09	-0.21	-81.05	-75.03
Difference energy, ΔE_{tot}, *kcal/mol*	17.40		21.76		17.31		22.90	
Charge energy, E_{chg}, *kcal/mol*	0.00		-		0.00		-	

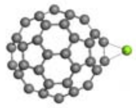
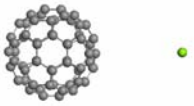
Squared spin, (S**2)	0.0	5.16	0.0	5.48	0.0	5.02	0.0	6.54
Ionization potential, *I, eV*	8.02	8.20	9.25	9.57	8.70	8.69	8.83	7.96
Electron affinity, *ε, eV*	2.94	1.84	2.80	2.44	2.95	2.67	2.71	2.33
Dipole moment, *Db*	0.79	1.44	3.93	3.65	0.05	0.05	4.99	4.84
Symmetry	C_1	C_1	C_2	C_2	C_1	C_1	C_2	C_1
Partner charge, C_{60}/*XXX, am.eд.*[2]	0.0/0.0	0.0/0.0	- 0.138/0.133	- 0.136/0.134	0.00/0.00	0.00/0.00	- 0.26/0.26	- 0.03/0.03
Partner composition of HOMO, C_{60}/*XXX*, %	0.0/100	0.0/100	98.6/1.4	7.2/92.8	0.0/100	0.0/100	17.3/82.5	0.0/100
Partner composition of LUMO, C_{60}/*XXX*, %	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0	100/0.0

---

[1] Data in < > correspond to R_{fin}=0.37nm. TAE structure is well similar to that of free molecule.

[2] Notation C_{60}/*XXX* means that the data divided by slash from the next rows should be related to the relevant partners, i.e. to C_{60} and the second partner *XXX*, respectively.

Table 6. Characteristics of electron states of D-A complexes C_{60}+2Li и C_{60}+ Mg

Calculated quantities(PM3), singlet	 *C_{60}-2Li*[1]		 *C_{60}- Mg*[2]				C_{60}	
	R_{st}=0.323 nm		R_{st}=0.183 nm		R_{st}=0.480 nm			
	RHF	UHF	RHF	UHF	RHF	UHF	RHF	UHF
Heat of formation, *ΔH, kcal/mol*	840.76	804.37	868.52	853.38	871.77	830.42	811.02	798.45
Coupling energy, E_{coupl} *, kcal/mol*	-36.54	-60.36	+22.5	+19.93	+25.75	-3.03		
Difference energy, ΔE_{tot}*, kcal/mol*	36.39		15.14		41.35		12.57	
Charge energy, E_{chg} *, kcal/mol*	-		-		0.00			
Squared spin, (S**2)	0.0	5.44	0.00	4.81	0.0	5.03	0.0	4.29
Ionization potential, *I, eV*	5.72	7.13	8.47	8.71	7.27	8.17	9.48	9.67
Electron affinity, *ε, eV*	2.21	1.76	2.57	2.37	2.88	2.65	2.89	2.65
Dipole moment, *Db*	3.11	0.26	7.08	6.91	0.04	0.00	0.00	0.00
Symmetry	C_{2h}	C_1	C_{2v}	C_2	C_1	C_1	I_h	D_{3d}
Partner charge, C_{60}/*XXX, am.eд.*	- 1.13/+1.13	- 1.13/+1.13	-0.44/+0.44	- 0.45/+0.45	0.0/0.0	0.0/0.0		
Partner composition of HOMO, C_{60}/*XXX*, %	99.2/0.8	98.6/1.4	74.1/25.9	70.8/29.2	0.0/100.0	0.0/100.0		
Partner composition of LUMO, C_{60}/*XXX*, %	97.9/2.1	88.4/11.6	99.4/0.6	8.5/91.5	100.0/0.0	100.0/0.0		

---

[1] Calculated data for 2Li, singlet: *ΔH*=66.28 *kcal/mol*; IP=5.39 *eV*; EA=1.09 *eV*; (S**2)=0.00.

[2] Calculated data for Mg, singlet:*ΔH*=35.00 *kcal/mol*; IP=7.93 *eV*; EA=1.13 *eV*; (S**2)=0.00.