

Modelling of electron transfer in DMABI dimer by quantum chemistry approach

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This work is devoted to a quantum-chemical study of electron transfer (ET) processes in several DMABI (N,N-dimethylamino benzylidene indan-1,3-dione) dimers according to X-ray data of α -modification crystal. ET is evaluated by the Marcus theory and the Fermi golden rule in the framework of one-particle electronic state of a pending molecule. Visualization of the energetic parameters and topology of intermolecular ET allows creating the reaction model from its first principles.

Key words: ordered molecular aggregates, dimer, DMABI, intermolecular electron transfer, electronic states, Fermi golden rule

INTRODUCTION

Electron transfer (ET) reactions in ordered molecular aggregates contain a significant part of chemical physics. Estimation of electronic charge redistribution between charge donor and charge acceptor allow us to create the basic dynamical model for analyzing absorption spectra. However, only the quantum chemical approach presents the possibility to operate in quantitative terms within the molecular electron framework.

This work was aimed to study condensed media properties of a famous model system – the organic semiconductor N,N-dimethylamino benzylidene indan-1,3-dione (DMABI) which was briefly studied in last decade by our group. Molecular absorption and fluorescence dynamics, studied experimentally [1, 2] and theoretically [3], vibration dynamics [4], the TICT reaction mechanism proposed for a single molecule model [5], the self-trapped exciton model using the Toyozawa approach proposed for a crystalline derivative [6–8] explain the complicated phenomenological interpretations of different properties. However, many experimental problems remain unsolved [9, 10] due to the difficult nature

of the molecular crystal which expresses both the crystalline and the molecular behaviour [11]. In this case, it is necessary to estimate additional aspects such as intermolecular interactions in the closest package of molecular derivatives.

We have used the quantum chemistry program *NUVOLA* [12] for a theoretical study of electron transfer reactions by the perturbation theory methods [13]. Within the framework of electron donor–acceptor moieties, two molecules represent the donor–acceptor pair.

The ET process was estimated from the electronic overlap of two corresponding electronic states which belong to different molecules. This estimation was performed using the one-particle approach as a transition between the LUMO (and higher) states of the mentioned dimer molecules. The process takes place in case of the equal energy value of the corresponding electronic states only.

OBJECT OF INVESTIGATION

N,N-dimethylamino benzylidene indan-1,3-dione (DMABI) belongs to the class of polar organic salts (see Fig. 1). Two chromophoric fragments – indandione and parabenzene – are connected through the [=C–] bridge. Due to a large value of the dipole moment in the ground state (up

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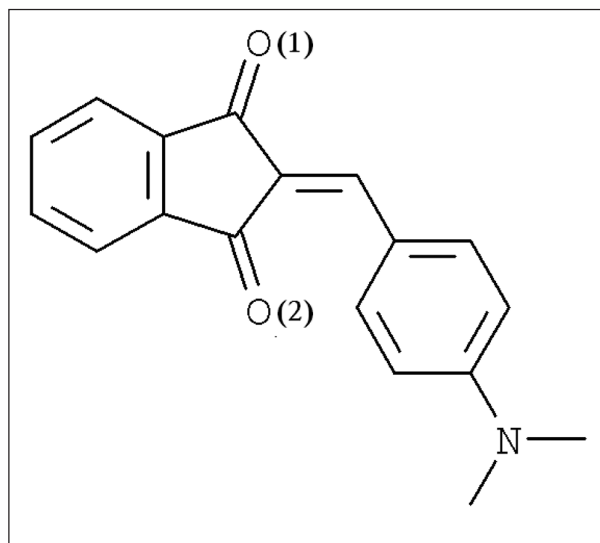


Fig. 1. N,N-dimethylamino benzylidene indan-1,3-dione (DMABI) monomer

to 2.3 D), the mentioned derivative could form several molecular monocrystals which exhibit molecular as well as condensed media properties. Three crystallographic modifications are known from exact X-ray measurements [14–16]. We have used DMABI crystallographic data presented in [14, 17]. Figure 2 represents a stack containing four DMABI molecules extracted from a crystallographic α -modification. This stack contains an obvious double DMABI-dimer pair {DMABI- j , k }, $j, k \in [1..4]$ according to a scheme shown in Fig. 2, which expresses the coupling behaviour in all overlapping points. Three pending dimer structures – DMABI-21, DMABI-23 and DMABI-24 – were formulated as the initial model structures for following simulations as part of the stack presented above.

The DMABI-21 dimer represents an alternated derivative in which monomers are separated by a short contact (~ 3.8 Å) and four π -conjugated fragments of different MS are placed “face-to-face”. The DMABI-24 dimer represents a shifted derivative in which monomers are separated by a short contact (~ 3.8 Å), but only two π -conjugated fragments are in “face-to-face” orientation. The DMABI-23 dimer represents an alternated derivative in which monomers are separated by a long distance (> 7 Å).

THEORETICAL BACKGROUND

The ET process was estimated according to the basic models of quantum chemistry theory. Specifically, the Fermi golden rule (Eq. 1) and Marcus’ theory [18] were used for evaluating the ET parameters. The dynamical ET process between the two molecular systems, MS-1 and MS-2, is defined by the rate W (dimension – events per second, s^{-1} or Hz):

$$W = \frac{2\pi}{\hbar} S_{\alpha\beta}^2 \delta(E_\alpha - E_\beta), \quad (1)$$

where α and β represent electronic states of separate molecular systems, MS-1 and MS-2, respectively. The interaction between these systems could be expressed via the intermolecular electronic coupling $S_{\alpha\beta}$ parameter:

$$S_{\alpha\beta} = \langle \alpha | \hat{V} | \beta \rangle, \quad (2)$$

where \hat{V} represents a Hamiltonian of intermolecular interaction.

The $\delta(x)$ function expresses the strongest resonant condition (band halfwidth converges to zero). For ET process

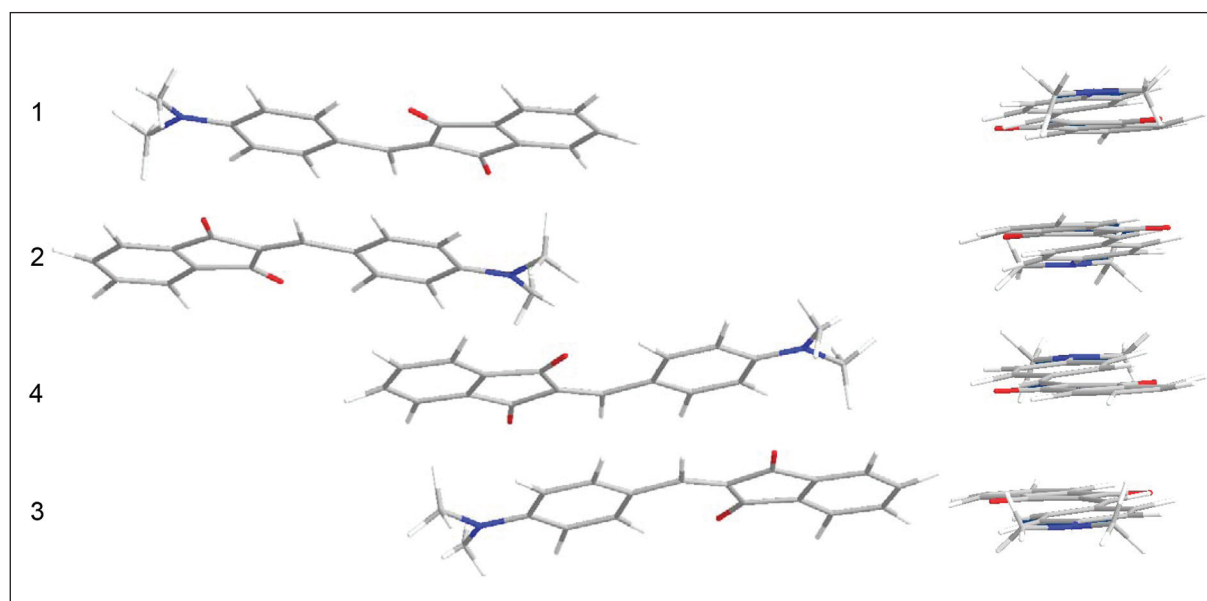


Fig. 2. Four-membered stack of DMABI molecules in the crystallographic α -modification according to Ref. [14]. XZ (left) and YZ (right) projections. Molecules are numbered in a row (1–2–3–4) for indexing purposes

simulation purposes, we have replaced this expression by a gaussian-shaped function containing the halfwidth σ parameter which allows us to control the resonant conditions according to Marcus' theory:

$$\delta(E_\alpha - E_\beta) \Rightarrow \frac{1}{2\pi\sigma} \exp\left(-\left(\frac{E_\alpha - E_\beta}{2\sigma}\right)^2\right). \quad (3)$$

According to the Fermi golden rule definition, the electronic states α and β of separate molecular systems, MS-1 and MS-2, respectively, must be of one-particle state type. We have generated molecular orbitals (MO) in the framework of atomic orbitals (AO). *Ab initio*, the Hartree-Fock (HF) method allows expressing MO in a "pure" one-particle-state manner. However, this exact assumption is not fully suitable for spectrometric tasks such as the definition and simulation of the bathochromic shift of absorbance spectrum. For practical needs, we decided to use another, less precise method as a first assumption. We have used the pseudo-one-particle state assumption when MO were generated using the semi-empirical ZINDO but not the classical *ab-initio* HF method.

Mainly semi-empirical calculation methods [19] are applied for quantum molecular process simulations. Then the theoretical results are compared with experimental data in order to understand the physical nature of the process.

In our case, theoretical and experimental absorbance spectra were compared with quite a high accuracy. Consequently, the semi-empirical method ZINDO [20] (Zerner intermediate neglect of differential overlap, suitable for UV / VIS absorbance spectra simulations) was selected. The ZINDO method is suitable also for IT process description (in comparison with the traditional *ab-initio* HF or electron correlation MP2 methods) due to the specification of our task which could be expressed as follows. It is necessary to estimate the population of the electronic system of an electron-donor molecule in a strongly fixed region – between {LUMO} and {LUMO + n } states, $n < 10$. The population of higher states ($n > 10$) is beyond our interest.

The simulations were done employing the *Gaussian03* program package [21] (MO in the framework of AO, one-par-

ticle state density matrix). Routine calculations were carried out using the *ZINDO* (*nstate* = 10, *singlets*) task.

MAIN ELECTRONIC TRANSITIONS IN THE MOLECULES

The intermolecular ET process was evaluated for three different DMABI-21, DMABI-23 and DMABI-24 dimers. This process could be conditionally divided into two parts: i) electronic excitation of MS-1 from HOMO (and lower) into LUMO (and higher) and excited state population; ii) a significant overlap of resonant MO populated and vacant in LUMO (and higher) between MS-1 and MS-2, respectively. The electronic excitation of MS-1 could be done using several experimental techniques, such as particle injection, excitation by UV-VIS light, etc. The overlap of resonant MO represents the behaviour of resonance ET.

Each MS was described using a model of MO in the framework of separated AO. For all three dimers, three main types of electronic transitions ($S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$) were analyzed and pictured in the form of schematic Jablonski diagrams. Figure 3 and Table represent the electronic transitions in the first molecule, MS-1, after excitation. The spectroscopic transition $S_0 \rightarrow S_n$ could be characterized using two parameters: energy E and oscillator strength f . However, spectroscopic transition comprises several one-particle transitions (HOMO- N_1) \rightarrow (LUMO + N_2) with a corresponding weight coefficient k (the total number of MO is equal to the sum of N_1 and N_2). The first three electronic transitions were analyzed in previous works (1–3, 5). According to the tasks of geometry simulation of a single molecule, several conformers were established.

A twisted conformer (polar solution environment, twisting about the [=C–] bridge), representing molecular absorption in the red region characterized by $S_0 \rightarrow S_1$, partially allowed transition of $n \rightarrow \pi^*$ type (charge redistribution from indandione carbonyl to parabenzene ring).

However, a plain conformer (extracted from crystallographic stacks, all monomers of the mentioned DMABI dimmers), representing molecular absorption in the blue region, characterized by $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ forbidden transition of $n \rightarrow \pi^*$ type (charge redistribution from indandione carbonyl

Table. Calculated electronic transition parameters of first molecule in DMABI-21 dimer Gaussian-03, ZINDO, singlets only

Electronic transition	Energy E , eV	Osc. strength, f	MO character	Coefficient k	Transition dipole moment D			CT type
					X_a	Y	Z	
$S_0 \rightarrow S_1$	2.7489	0.0044	HOMO-6 \rightarrow LUMO	0.31795	-0.2490	-0.0531	0.0124	From indandione carbonyl >C=O(1) to parabenzene ring, $n \rightarrow \pi^*$
			HOMO-4 \rightarrow LUMO	0.29327				
			HOMO-4 \rightarrow LUMO + 1	0.36494				
$S_0 \rightarrow S_2$	2.8671	0.0002	HOMO-6 \rightarrow LUMO + 1	0.36826	-0.0498	0.0084	-0.0180	From indandione carbonyl >C=O(2) to parabenzene ring, $n \rightarrow \pi^*$
			HOMO-4 \rightarrow LUMO	0.27196				
			HOMO-4 \rightarrow LUMO + 1	-0.22706				
$S_0 \rightarrow S_3$	3.1929	1.0178	HOMO \rightarrow LUMO	0.67317	3.6063	0.0297	-0.0721	From indandione pentaring to parabenzene ring, $\pi \rightarrow \pi^*$

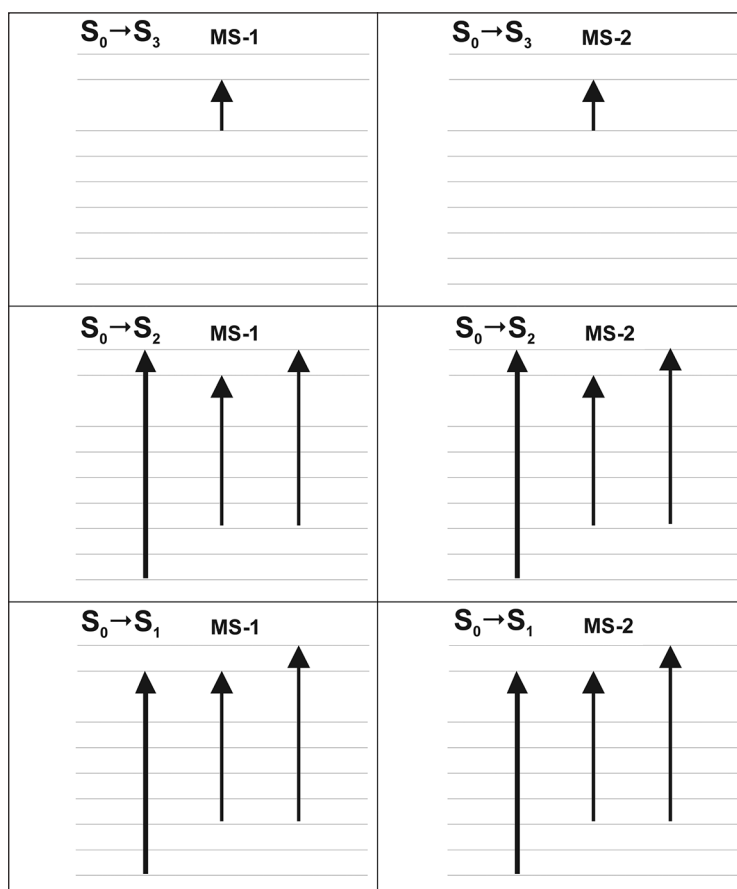


Fig. 3. One-particle state distribution and corresponding electronic transitions near HOMO–LUMO region of DMABI-21 structure (first, MS-1, and second, MS-2, molecules).

S_1 , S_2 , S_3 states are of spectrometric interest. Arrows indicate the strongest transitions between HOMO (and lower) and LUMO (and higher) levels. HOMO–LUMO levels are separated by gap

to parabenzenzene ring) and $S_0 \rightarrow S_3$, allowed transition of $\pi \rightarrow \pi^*$ type (charge redistribution from indandione pentaring to parabenzenzene ring).

According to Fig. 3, there are two one-particle states (number 53, [LUMO] and number 54, [LUMO + 1]) which

could be populated by excitation of spectroscopic states S_1 , S_2 , S_3 . Figure 4 represents the simulated UV/visible absorbance spectrum of MS-1. The main ET events occur after excitation of the electronic band of 3.2 eV (according to the simulated spectrum).

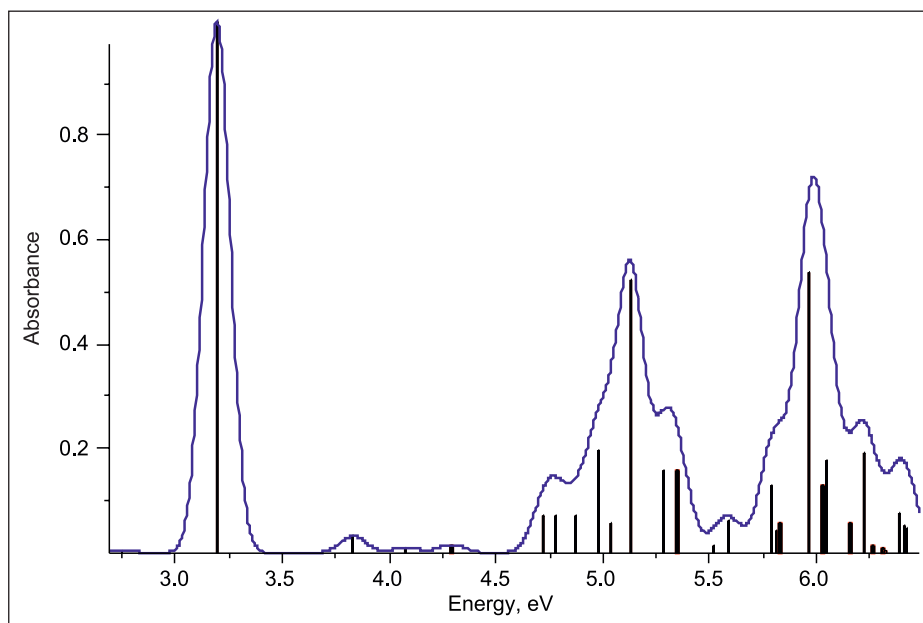


Fig. 4. Simulated MS-1 absorption spectrum of DMABI-21 dimer. ZINDO transitions (vertical lines) and corresponding gaussian-shaped bands, bandwidth 500 cm^{-1} . $S_0 \rightarrow S_3$ represents allowed transition at 3.2 eV

INTERMOLECULAR DISTRIBUTION OF ELECTRON TRANSFER RATIO

Figure 5 presents the spectral distribution of the ET ratio for the mentioned structures (DMABI-21, DMABI-23, DMABI-24). ET processes start from states 53 [LUMO] and 54 [LUMO + 1]. Only the dimers that contain neighbouring

molecules separated by a short distance (up to 4 Å) express an effective ET process (ET ratio up to 10^{11} Hz, DMABI-21, DMABI-24). When the intermolecular distance is long (up to 7 Å, DMABI-23), the ET process is less effective (ratio up to 1000 Hz).

Figures 6 and 7 represent a 2D map of intermolecular ET ratio distribution in an atomic framework simulated

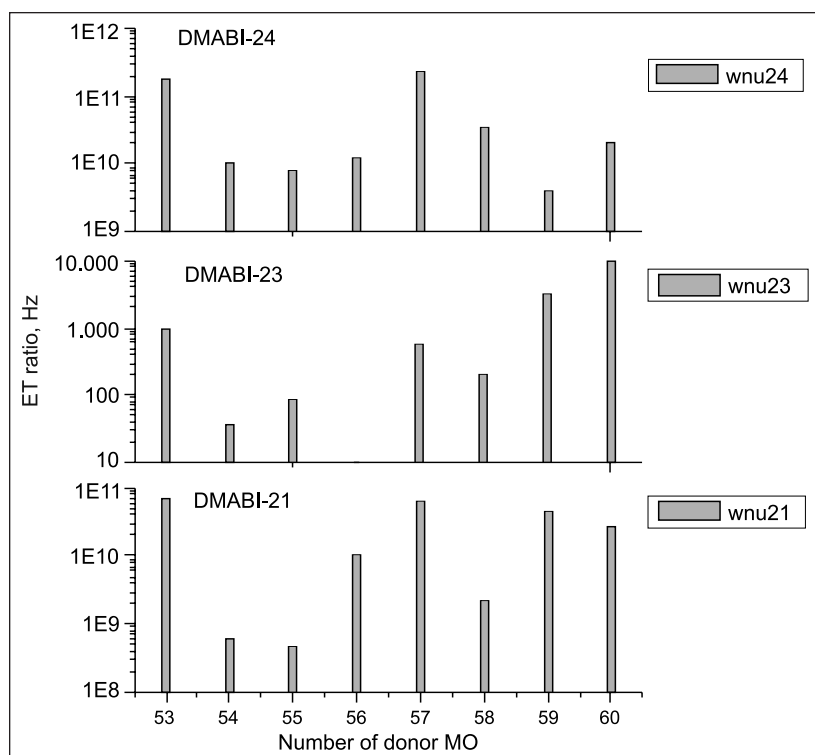


Fig. 5. Spectral dependence of ET ratio (calculated using Eq. 1) on MO number of donor molecule DMABI

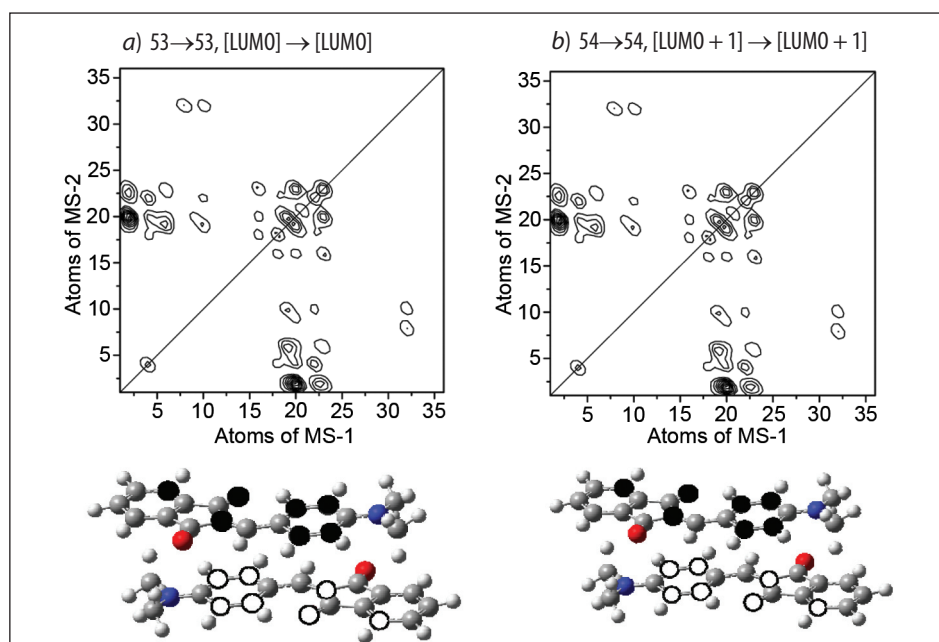


Fig. 6. 2D map of intermolecular ET ratio distribution (top) and corresponding intermolecular electron transition (bottom) simulated for a) [LUMO] \rightarrow [LUMO] and b) [LUMO + 1] \rightarrow [LUMO + 1] ET processes. DMABI-21 structure. Electron-donor atoms are coloured in white, and electron-acceptor atoms in black

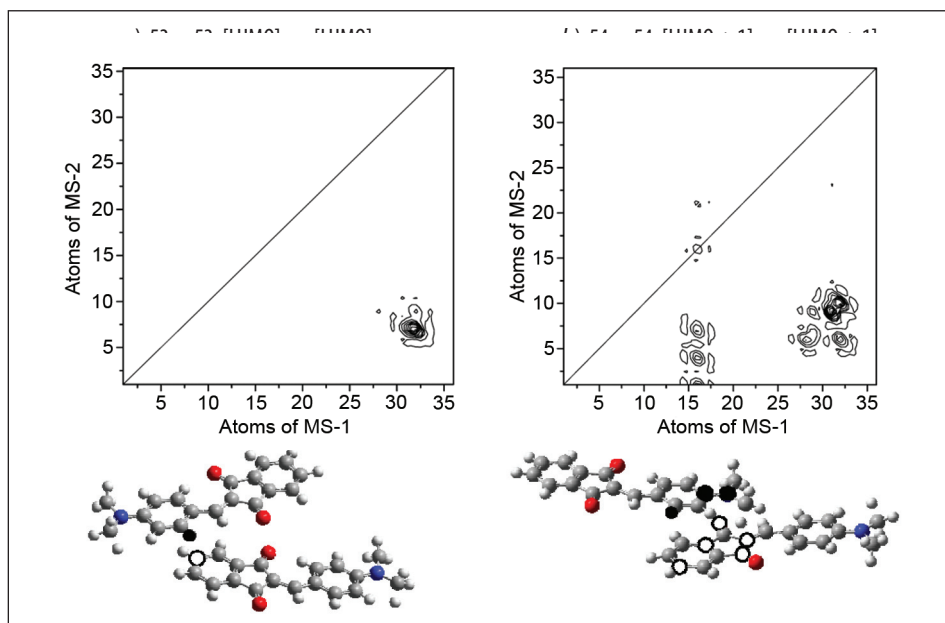


Fig. 7. 2D map of intermolecular ET ratio distribution (top) and corresponding intermolecular electron transition (bottom) simulated for a) [LUMO] → [LUMO] and b) [LUMO + 1] → [LUMO + 1] ET processes. DMABI-23 structure (left) and DMABI-24 structure (right). Electron-donor atoms are coloured in white and electron-acceptor atoms in black

for different ET processes: [LUMO] → [LUMO] and [LUMO + 1] → [LUMO + 1]. All the three structures (DMABI-21, DMABI-23, DMABI-24) are characterized for ET purposes.

DISCUSSION

The molecular stack of DMABI (see Fig. 2) represents dimers of different geometry. This circumstance denotes different parameters of intermolecular interaction in case when the monomer structure is practically identical in all dimers. The electronic overlap factor depends on several parameters, such as distance, orientation angle etc.

The DMABI-21 dimer represents an alternated derivative in which monomers are separated by a short contact (~ 3.8 Å) and four fragments of different MS are placed “face-to-face”. Figure 6 shows the strongest electronic overlap and intermolecular charge redistribution between the electron donor pentaring and parabenzenes and the corresponding fragments of the electron acceptor. The ET maps of [LUMO] → [LUMO] and [LUMO + 1] → [LUMO + 1] transitions are practically identical. No significant differences were found using the HF/6-311G simulation routine.

The DMABI-23 dimer represents an alternated derivative in which monomers are separated by a twice longer distance (>7 Å). Figure 7a shows a weak electronic overlap of [LUMO] → [LUMO] transition and intermolecular charge redistribution between the electron donor indandione benzene and the electron acceptor parabenzenes. This fact shows that the ZINDO routine is acceptable for modelling the electronic properties of structures separated by a distance of up

to 5 Å. The STO-3G basis used in the ZINDO routine could not represent long-range intermolecular interactions.

The DMABI-24 dimer represents a shifted derivative in which monomers are separated by a short contact (3.8 Å) but only two fragments are in “face-to-face” orientation. Figure 7b shows quite a strong electronic overlap and intermolecular charge redistribution between the electron donor indandione and the electron acceptor amino benzene.

According to the initial presumption of the ET process, the MS-1 system must be electronically excited: it must be populated in a range from [LUMO + 1] up to [LUMO + N_2] state. In this case, both excitation pathways are possible (through the forbidden transition $S_0 \rightarrow S_1$ or the allowed transition $S_0 \rightarrow S_3$, etc). Following the relaxation processes (charge exchange between donor and acceptor) allows us to conclude that two types of ET are significant: i) delocalized in the DMABI-21 dimer from a whole molecule to a whole molecule along the long axes; ii) localized in the DMABI-24 dimer from indandione to amino benzene.

The simulation confirmed the previous idea of intermolecular ET well known from crystallographic references [14].

MAIN RESULTS AND CONCLUSIONS

To sum up, it should be mentioned that intermolecular ET transfer processes occurring in three various types of dimers from the α -modified crystallographic DMABI structure were briefly analyzed by quantum molecular theory methods. The ZINDO approximation method was applied for theoretical simulations of ET. The main results are discussed and presented in this particular work in the form of electronic

transition diagrams, tables of physical transition parameters, calculated absorbance spectra and three-dimensional intermolecular ET maps. The obtained theoretical results corroborate earlier presumptions on the topic. Two types of ET were established and visualized.

Received 20 December 2010

Accepted 15 February 2011

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ELEKTRONO PERNAŠOS DMABI DIMERE MODELIAVIMAS KVANTINĖS MOLEKULIŲ TEORIJOS ARTINIŲ

Santrauka

Šis darbas skirtas tarpmolekulinės elektrono pernašos (EP) tarp DMABI (N,N-dimethylamino benzylidene indan-1,3-dione) dimero molekulių teoriniam modeliavimui kvantcheminiais metodais, kai dimero struktūra pasirenkama kaip α kristalografinės modifikacijos gardelės dalis (Rentgeno struktūrinės analizės duomenys). EP vyksmo sparta įvertinta pagal Markus teoriją naudojant Fermi auksinę taisyklę viendalelinių elektroninių būsenų artiniu. Tarpmolekulinio EP vyksmo energetinių parametrų ir topologijos vizualizacija leidžia kurti fotocheminės reakcijos eigos modelį.