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A DFT STUDY OF REORGANIZATION ENERGY OF SOME CHOSEN CARBAZOLE DERIVATIVES

Strong efforts toward finding an organic semiconductor with a molecule characterized by a low charge transfer energy applying quantum-chemical calculations are undertaken. Density Functional Theory (DFT) calculations made for carbazole (Cz) and three isomers of benzocarbazole, benzo (a) carbazole (BaCz), benzo (b) carbazole (BbCz) and benzo (c) carbazole (BcCz) proves the possibility of lacking the growth of reorganization energy despite the molecule dimensions enlargement. Benzo(b)carbazole molecules with high longitudinal dimension of the rigid skeleton $d = 9,05 \text{ \AA}$ posses the low value of reorganization energy for both hole and electron transport of 0,18 eV and 0,11 eV, respectively. We suggest that the reduction of reorganization energy may be related to the diminishing of intramolecular hydrogen interactions.

Keywords: reorganization energy, DFT calculations, benzocarbazoles, Marcus-Hush theory of electron transport.

1. INTRODUCTION

Nowadays, carbazole derivatives have attracted interests of semiconductors electronics and optoelectronics industry [1]. Carbazole ($C_{12}NH_9$) (here denoted as Cz) and its benzeno-derivatives ($C_{16}NH_{11}$) correspond to the rigid skeleton of aromatic hydrocarbons where the one double C=C bond is replaced by N-H [2]. The properties of Cz and benzocarbazoles favorable for applications in technology are related to the fact that their molecular structure is based on a rigid heteroaromatic skeleton. The results of DFT calculations presented in this

work are devoted to the impact of molecular structure of the three isomers of benzocarbazole: benzo(a)cabazole (BaCz), benzo(b)carbazole (BbCz) and for benzo(c)carbazole (BcCz) on the reorganization energy. The structure of studied molecules is known. Batra *et. al.* [3] in 1973 have reported results of the SCF-LCAO-MO calculations for the electronic structure of Cz molecule. The crystal structure of Cz has been redetermined lately by Gajda *et. al.* [4]. The molecule of Cz has crystallographically imposed mirror symmetry (C_{2v}). The benzocarbazole molecules are asymmetric.

Lack of the comparative calculations for reorganization energy of Cz and benzocarbazole isomers in the literature is observed. This work tries to fill this gap and shows such a calculations for the hole and electron reorganization energy for materials mentioned above.

2. DFT CALCULATIONS

The molecular quantum chemical calculations were performed using Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) with use of the Gaussian 09 program package [5]. All calculations on the studied compounds were done on cluster machines Blueocean in TUL (*Lodz University of Technology*) Computing & Information Services Center infrastructure.

The geometrical structures of all studied heteroacenes of this work in the ground state and in the -1 , $+1$, excited states, were realized at B3LYP/63-111++G(d,p) theory level [6,7]. Optimized geometries of isolated molecules (in the gas state) for Carbazole (Cz), benzo(a)cabazole (BaCz), benzo(b)carbazole (BbCz) and for benzo(c)carbazole (BcCz) are shown in Figs. 1 - 4, respectively.

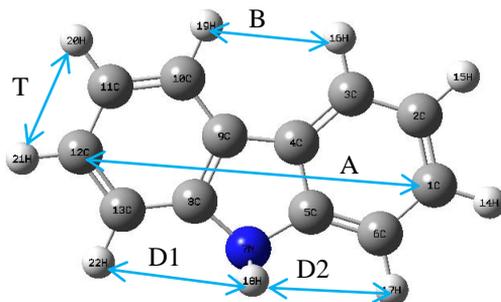


Fig. 1. Molecule of carbazole (Cz)

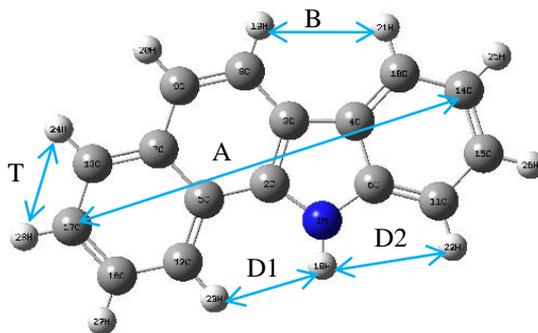


Fig. 2. Molecule of benzo(a)carbazole (BaCz)

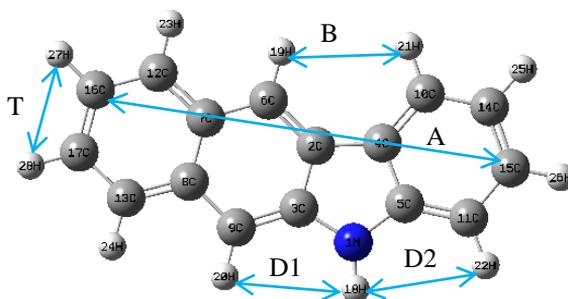


Fig. 3. Molecule of benzo(b)carbazole (BbCz)

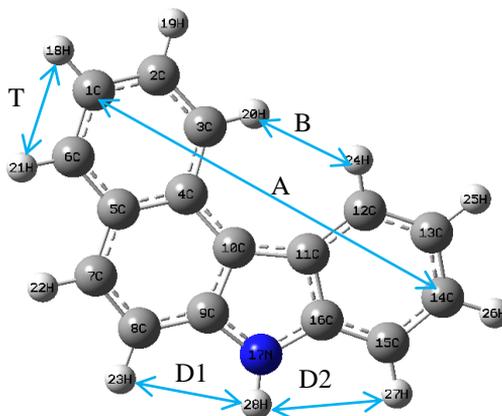


Fig. 4. Molecule of benzo(c)carbazole (BcCz)

Table 1
Calculated distances d between some characteristic atoms in the molecule of Cz, BaCz, BbCz, BcCz. The numbers and labels of atoms and types of distance as in Figs. 1-4 (all values are in Å).

Type of distance	Cz		BaCz		BbCz		BcCz	
		d		d		d		d
A	1C-12C	6.83	17C-14C	8.81	16C-15C	9.05	1C-14C	8.13
B	19H-16H	2.81	19H-21H	2.80	19H-21H	2.73	20H-24H	2.03
D1	22H-18H	2.80	23H-18H	2.34	20H-18H	2.80	23H-28H	2.75
D2	18H-17H	2.80	18H-22H	2.81	18H-22H	2.81	28H-27H	2.79
T	17H-21H	2.46	24H-20H	2.47	28H-27H	2.49	21H-18H	2.47

The calculated distances indicated in Table 1 are divided into four corresponding types A, B, D1 as well as D2 and T. Type A includes the maximum spacing of C atoms. The largest is for BbCz molecules and is of 9.05 Å. The value of the type B range indicates the possibility occurrence of intramolecular hydrogen interactions. We observe such interactions in the case of BcCz, where the distance to $d_{20\text{H}-24\text{H}}$ is much shorter than for the other compounds.

The difference between the values of D1 and D2 indicates the asymmetry of the hydrogen interactions in the vicinity of the N atom. The greatest value of such asymmetry is observed for BaCz. A very low value of $d_{23\text{H}-18\text{H}} = 2,34$ Å for BaCz indicates a strong intramolecular hydrogen interaction. The practically constant value of the type T distance between hydrogens for all benzocarbazole isomers indicates the value of the distance for the hydrogens of the benzene substituting carbazole slightly greater than the distance for the hydrogens of the benzene of unsubstituted carbazole.

3. RESULTS AND DISCUSSION

The DFT calculations, reported in Fig. 5, have revealed similar electronic spectra for studied compounds. The HOMO-LUMO values clearly indicate that the lowering of LUMO values and rise of HOMO values are connected with the elongation of the aromatic skeleton (see the distance type A in Table 1). If we compare the energy change of the HOMO and LUMO levels for all of the studied benzocarbazoles with respect to the corresponding energy levels of Cz, a much bigger decrease in the levels of LUMO is observed compared to such a change for the levels of HOMO. Thus, the energy gap E_g decreases in these carbazole derivatives comparing with the carbazole. A similar effect was observed in [8] for the Cz derivatives, however, it was thought to be related to the

delocalization at 9-N-position of carbazole connected with the presence of the lone pair of electrons on the amine nitrogen atom leading to reduction of the electron overlap in the Cz ring.

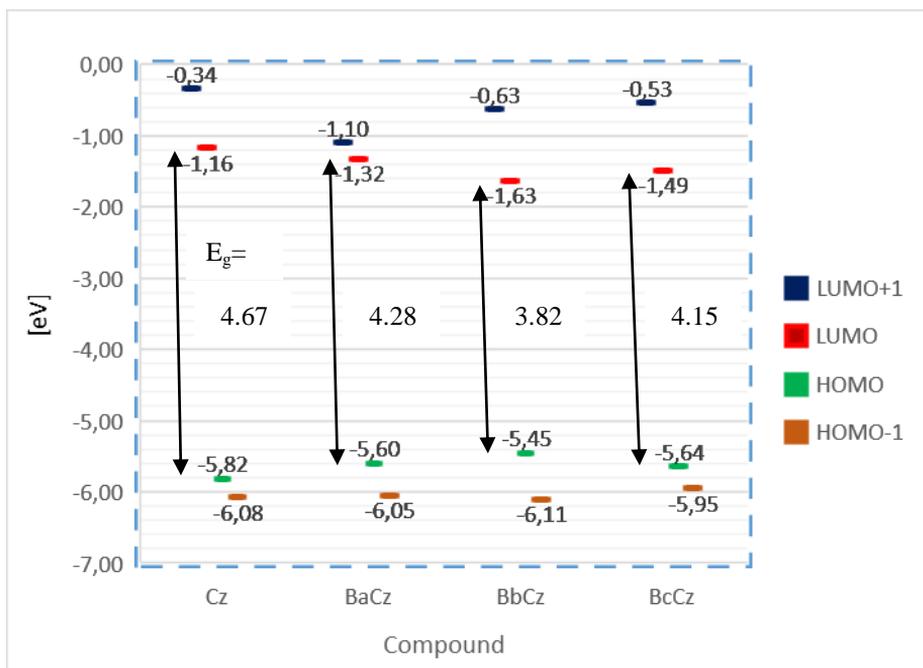


Fig. 5. Calculated energy level of LUMO+1, LUMO, HOMO, HOMO-1, and Energy gap value (E_g) for Cz, BaCz, BbCz and BcCz at the B3LYP/6-311G(d,p) theory level

3.1. Reorganization energy

In organic materials the charge transport can be described by a hopping model in which charge carriers jump between adjacent molecules. Theoretical approach is based on the Marcus electron transfer theory [9,10,11]. The overall rate constant for the charge transfer is proportional to $\exp[-\lambda/4kT]$ (k - Boltzmann's constant, T - temperature). The quantity λ , the reorganization energy of the molecule affects critically the charge transfer process. The calculations of reorganization energy were made with use the schema represented by Mallocci *et. al.* [12,13].

The reorganization energy for hole transport (λ_h) can be computed via the “four point method” as a sum of the two contributions, $\lambda_1 + \lambda_2$ that are defined as:

$$\lambda_1 = E_0(M^+) - E_0(M^*) \quad (1)$$

$$\lambda_2 = E_I(M^*) - E_I(M^+) \quad (2)$$

where $E_0(M^*)$ and $E_0(M^+)$ are the energies of the neutral molecule at the cation geometry and at the optimal ground-state geometry, respectively, $E_I(M^*)$ and $E_I(M^+)$ represent the energy of the charged state in the neutral and optimal cation geometry, respectively. Similarly, the reorganization energy for electron transfer is a sum of the two contributions, $\lambda_3 + \lambda_4$ that are defined as:

$$\lambda_3 = E_0(M^-) - E_0(M^*) \quad (3)$$

$$\lambda_4 = E_I(M^*) - E_I(M^-) \quad (4)$$

where $E_0(M^*)$ and $E_0(M^-)$ are the energies of the neutral molecule at the anion geometry and at the optimal ground-state geometry, respectively, $E_I(M^*)$ and $E_I(M^-)$ represent the energy of the charged state in the neutral and optimal anion geometry, respectively. The calculated reorganization energies for hole and electron obtained as the results of above calculated model for studied molecules are listed in Table 2.

Calculations of λ_1 , λ_2 , λ_3 and λ_4 needs knowledge of the values of Ionization Potential and Electronic Affinity.

In order to evaluate the Ionization Potential (I_p) and Electronic Affinity (E_A), all compounds in cationic and anionic geometry were fully optimized.

In order to obtain I_{p_v} values, the total energies of the ionic states of studied molecules were calculated, using the optimized geometry of the neutral system. The total energy of the neutral was subtracted from the energy of the radical cation (or anion) of the studied molecule obtained at the geometry of neutral [12,13]:

$$I_{p_v} = E_0(M^*) - E_I(M^*) \quad (5)$$

In order to obtain E_{A_v} values, the total energies of the ionic states of studied molecules were calculated, using the equilibrium geometry of the ionic state. The total energy of the radical cation (or anion) of the studied molecule obtained at the equilibrium geometry was subtracted from the energy of the neutral molecule [12,13]

$$I_{Pv} = E_0(M^*) - E_I(M^*) \quad (6)$$

For all of the benzocarbazoles comparing with the Cz, the I_{Pv} and E_{Av} values decreased. The calculated I_{Pv} values are in good agreement with calculated values in literature. For Cz experimental value of I_{Pv} 7.67 eV [2] and calculated by taking the difference of total energies for the neutral molecule and the positive ion was found to be 8.6 eV [3], but when used Koopmans' theorem instead which ignores relaxation effects the value was 9.4 eV [5] and 8.11 eV [2]. For benzocarbazole isomers the values of I_{Pv} are in good agreement with measured and calculated [2] values for BaCz 7.32 eV and 7.70 eV, for BbCz 7.22 eV and 7.63 eV, for BcCz 7.35 eV and 7.77 eV respectively.

Table 2
Calculated adiabatic ionization potential (I_p) and electron affinity (E_A), reorganization energies for hole (λ_h) and electron (λ_e), difference between λ_h and λ_e ($\Delta\lambda$), at the B3LYP/6-311G(d,p) level (all values are in eV)

compound	I_{Pv}	E_{Av}	λ_h	λ_e	$\Delta\lambda$
Cz	7.48	0.39	0.27 ¹	0.10 ¹	0.16
BaCz	7.10	0.12	0.25 ¹	0.14 ¹	0.11
BbCz	6.93	0.21	0.18 ¹	0.11 ¹	0.09
BcCz	7.14	0.05	0.26 ¹	0.16 ¹	0.10

¹Koopmans' theorem [14].

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Benzo(b)carbazole molecule with the largest longitudinal skeleton size (measured as the greatest distance between the centers of carbon atoms in the molecule, *i.e.* as distance type A given in Table 1 and in Figs. 1-4) $d = 9.05 \text{ \AA}$ is characterized by the lowest reorganization energy for hole conductivity $\lambda_h = 0.18 \text{ eV}$. This energy is reduced by 33% compared to Cz ($\lambda_h = 0.27 \text{ eV}$). BbCz is characterized with the lowest reorganization energy among benzocarbazole isomers for electronic conductivity $\lambda_e = 0.11 \text{ eV}$. This value is slightly higher than for Cz ($\lambda_e = 0.10 \text{ eV}$). The analysis of the distances between

the selected characteristic hydrogen atoms (as the distance type B, D1, D2 and T) given in Table 1 and in Figs. 1-4) leads to assume that the reduction of the reorganization energy observed for BbCz is related to the reduction of intramolecular interactions between characteristic hydrogen atoms adjacent to each other.

4. CONCLUSIONS

1. Increasing the strength of internal hydrogen interactions leads to increase of the reorganization energy.
2. Despite of the increase in the size of the molecular skeleton, the linear BbCz system favors the reduction of the reorganization energy compared to the unsubstituted Cz. It is probably related to the reduction of the strength of internal hydrogen interactions favour.
3. The extension of the Cz molecule's skeleton length by one benzene ring favours the reduction of the reorganization energy. This property can be used to improve the hole and electron transporting material.

4. ACKNOWLEDGEMENTS

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OBLICZENIA DFT ENERGII REORGANIZACJI DLA WYBRANYCH POCHODNYCH KARBAZOLU

Streszczenie

W artykule przedstawiono wyniki obliczeń kwantowo-mechanicznych mających na celu poszukiwanie cząsteczki organicznego półprzewodnika charakteryzującego się niską energią transferu ładunku. Obliczenia z wykorzystaniem teorii funkcjonału gęstości (DFT) zostały wykonane dla karbazolu (Cz) i trzech izomerów benzokarbazolu, benzo(a)karbazolu (BaCz), benzo(b)karbazolu (BbCz) i benzo(c)karbazolu (BcCz) dowodzą, że można uniknąć wzrostu energii reorganizacji cząsteczki tak dla przewodnictwa dziurowego jak i dla przewodnictwa elektronowego pomimo zwiększenia rozmiarów przestrzennych szkieletu aromatycznego cząsteczki. Cząsteczki benzo(b)karbazolu o największym rozmiarze podłużnym szkieletu $d = 9,05 \text{ \AA}$ charakteryzują się najniższą energią reorganizacji dla przewodnictwa dziur $\lambda_h = 0,18 \text{ eV}$ oraz najniższą wśród izomerów benzokarbazolu energią reorganizacji dla przewodnictwa elektronowego $\lambda_e = 0,11 \text{ eV}$. Analiza odległości pomiędzy wybranymi charakterystycznymi atomami wodoru pozwala przypuszczać, że zmniejszenie energii reorganizacji obserwowane dla benzo(b)karbazolu jest związane ze zmniejszaniem wewnątrzcząsteczkowych oddziaływań pomiędzy sąsiadującymi atomami wodoru.