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Arvydas Tamulis [a] & Liudmila Bazhan [b]

[a] Institute of Theoretical Physics and Astronomy of the Lithuanian Academy of Sciences, A. Goštauto 12, Vilnius, 2600, The Republic of Lithuania

[b] PolytechniK Institute of Nizhnii Novgorod, Nizhnii Novgorod, USSR

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ELECTRONIC STRUCTURE OF THE SUPERMOLECULES AND SUPRAMOLECULES CONSTRUCTED FROM CARBAZOLE AND ACCEPTOR MOLECULES

ARVYDAS TAMULIS
Institute of Theoretical Physics and Astronomy of the Lithuanian Academy of Sciences, A.Goštauto 12, Vilnius, 2600, The Republic of Lithuania

LIUDMILA BAZHAN
Polytechnik Institute of Nizhnii Novgorod, Nizhnii Novgorod, USSR

Abstract Quantum chemical investigations of the electronic structure of the design carbazole (Cz) containing supermolecules, supramolecules, single charge donor and acceptor molecules were performed in the framework of the semiempirical neglect of differential overlap (MNDO) method. The data obtained show that it is a small charge redistribution in Cz-$(CH_2)_4$-1,2,4,5-tetracyanobenzene (TCNB) and Cz::TCNB. These designed derivatives are potential molecular photodiodes. The sequence of the stability of the Cz containing supramolecules is found. The modeling of the photoinduced charge separation in Cz, TCNB, 2,4,7-trinitro-9-diciano-fluorene (TN9$(CN)_2$F) and 2,4,5,7-tetranitro-9-diciano-fluorene (TeN9$(CN)_2$F) molecules was done.

1. INTRODUCTION

The investigations of the photogeneration and photosensibilization in the chaotic carbazolyl containing photoconductors[1-3] and the studies of electron transfer in supermolecules and supramolecules[4] led us to design and theoretical investigation of supermolecules: Cz-σ(or π)-bridge-acceptors and supramolecules: Cz:acceptors[5,6]. These design derivatives can be synthesized and used as the molecular photo-rectifiers, as the basic elements of the molecular computers and the other molecular nanoelectronics devices.

Quantum chemical calculations of the design Cz containing supermolecules, supramolecules were performed in the framework of MNDO[7] method in this work.The MNDO method was also used for the investigation of monomers: donors, acceptors, insulators and its single charge ions. The data

obtained[5,6] show that ionization potential (I_K) of the electron donor-Cz is - 8.25 eV and electron affinities (A_K) of the electron acceptors: 2,4,7-trinitro-9-fluorenone (TNF), 2,4,5,7-tetranitro-9-fluorenone (TeNF), $TN9(CN)_2F$, $TeN9(CN)_2F$, 7,7,8,8/tetracianoquinodimethane (TCNQ) are: -2.84, -3.26, -3.09, -3.53, -2.82 eV respectively. The experimental values of Cz, TNF and TeNF were refered[1,2]. In additional to these data A_K of TCNB was obtained: -2.09 eV. The conformational state, when the $-NO_2$ fragment in the fourth position is perpendicular to plane of the whole molecule, is more stable for TNF and $TN9(CN)_2F^-$ molecules (the total energies of these conformational states are lower 0.77 eV and 0.47 eV respectively).

The alkanes are insulators[8]. The ionization potential of C_2H_6 is -12.70 eV, I_K of C_3H_8 is -12.41 eV, I_K of C_5H_{12} is -12.07 eV.

The values of I_K and A_K are presented by using Koopman's approximation (the index K it means).

2.ELECTRONIC STRUCTURE OF THE SUPERMOLECULE Cz-$(CH_2)_4$-TCNB

There were designed and calculated Cz containing supermolecule: 1) carbazole-$(CH_2)_4$-TCNB. There were assumed that the alkane groups bridge most probable join with N atom in Cz and with C atom in TCNB ring (see Fig.1). All the values in Figures 1,2 and 3 must be multiplied by 10^{-3}.

There is a small charge redistribution in the ground state of the supermolecules constructed of Cz, various alkane or alkene chains and TCNB (see Fig.1) or TNF[6], TCNQ[6] molecules. The MNDO calculation data obtained show that ionization potential of 1 supermolecule is -8.29 eV, electron affinity: -2.10 eV and dipole moment d=0.69 Deb. These data and data in the references 5,6 show that the donor-acceptor properties of supermolecules slightly depend on: 1) the number of alkane or alkene groups in the bridges,

2) the presence of π bonds, and 3) the various conformations in the bridges.

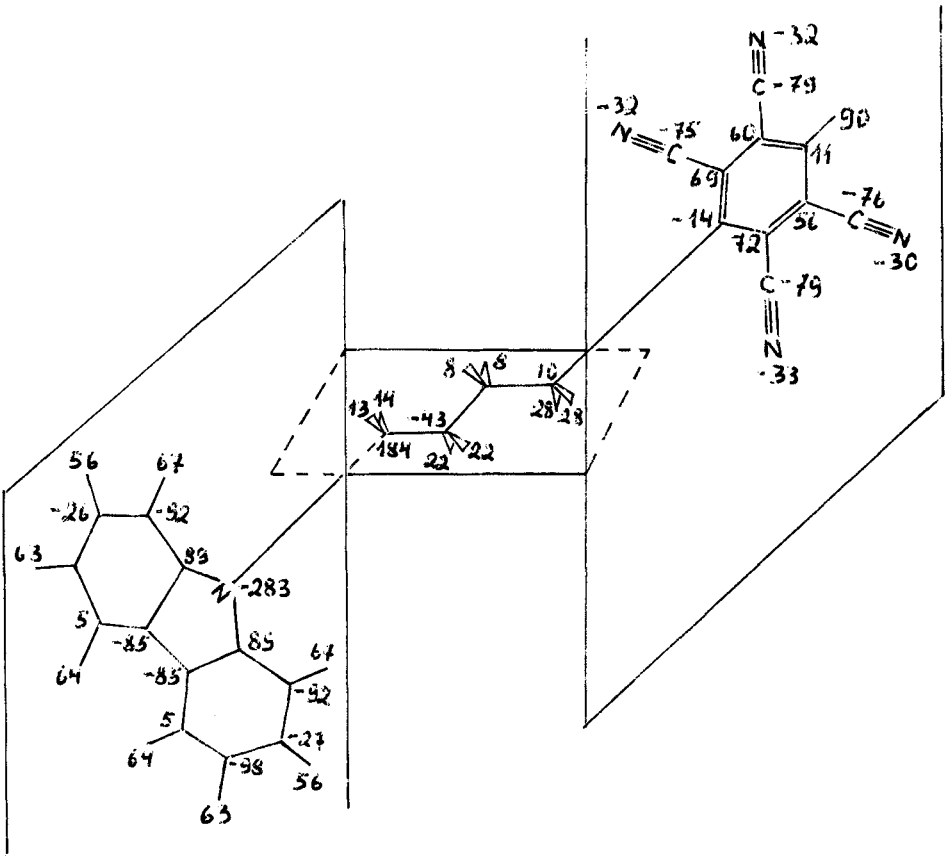

FIGURE 1. Charges on the atoms in the supermolecule Cz-$(CH_2)_4$-TCNB

The calculations data show that Cz containing supermolecules can be considered as systems with isolated electron donor and electron acceptor parts. Therefore these systems are potential molecular photodiodes, because we can expect only photoinduced charge separation.

We suppose that it is possible to join fatty acid fragments with 20 or 22 $-CH_2$ links to 3rd and 6th carbon atoms in the Cz fragment of 1 supermolecule and build Langmuir-Blodgett films.

3. THE MODELING OF THE PHOTOINDUCED CHARGE SEPARATION IN THE SUPRAMOLECULES

The supramolecules self assembly of Cz and TCNB (see Fig.2) or $TN9(CN)_2F$[6], TNF[6], TeNF[6], TCNQ[6] molecules were investigated.

The molecules Cz, TCNB, TCNQ, TNF, TeNF and $TN9(CN)_2F$ in the supramolecules: Cz::TCNB, Cz::TNF, Cz::TeNF, Cz::$TN9(CN)_2F$, and Cz::TCNQ were oriented in the parallel planes. The maximum of the attraction energy of

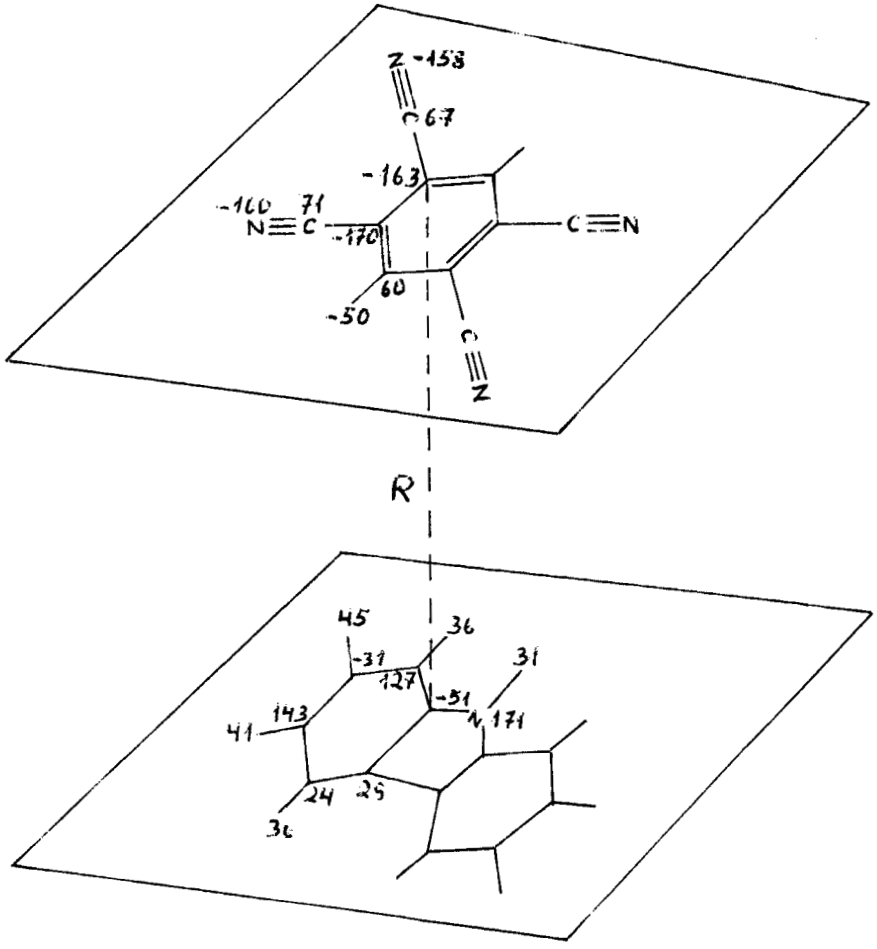

FIGURE 2. Supramolecule Cz::TCNB. The additional electron hole distribution on the Cz molecule and additional electron distribution on the TCNB molecule.

the oriented electrostatic forces for the Cz::TCNB supramolecule is E=0.535 kcal/mol when the distance R=5.2Å. The I_K=-8.44 eV, and A_K=-2.01 eV for this complex, dipole moment d=0.97 Deb. The row of the supramolecules stability given from the attraction energy calculations is following: Cz::TeNF > Cz::TNF > Cz::TCNB > Cz::TN9$(CN)_2$F > Cz::TCNQ.

It is a very small charge redistribution in the ground state of all these supramolecules. Therefore these systems are potential molecular photodiodes.

The calculations of positive charged Cz and negative charged acceptor molecules were performed. The additional electron hole is localized on the negative charged atoms of the neutral Cz molecule while the additional electron is localized on the ≡C-C≡N fragments of the TCNB molecule (see Fig.2) and on the $-C(CN)_2$ and $-NO_2$ fragments of the TN9$(CN)_2$F molecule (see Fig.3). We expect that these local charge distribution regions are present during the photoinduced charge separation in the Cz containing supermolecules and supramolecules.

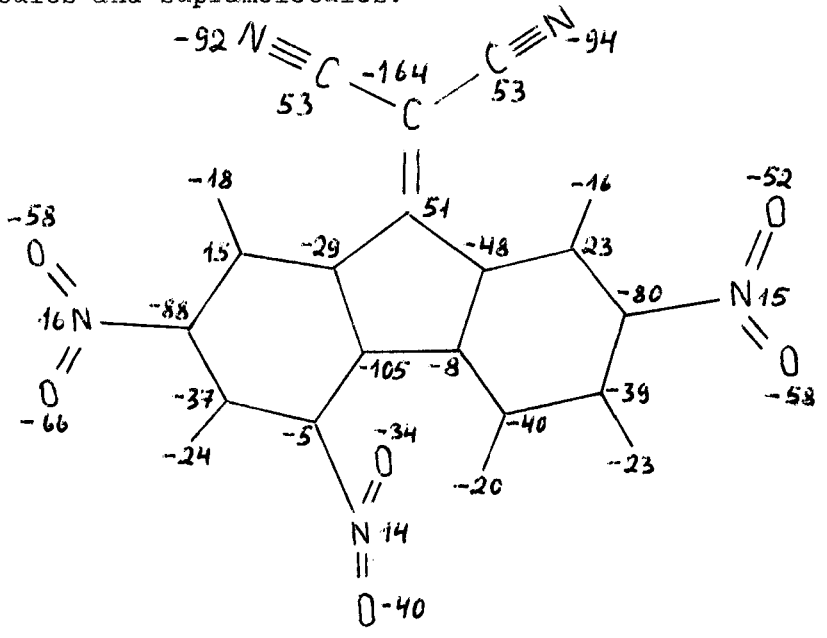

FIGURE 3. The additional electron distribution on the TN9(CN_2)F molecule.

REFERENCES

1. A.Tamulis, Š.Kudžmauskas,"Investigations of Electronic Structure of Carbazole, 2,4,7-Trinitro-9-Fluorenone, 2, 4,5,7-Tetranitro-9-Fluorenone Molecules and its Single Charge Ions by Using the NDO Methods", Deposited in the Lithuanian Research Institute for Scientific and Technical Information, 2659, Vilnius, Kalvarijų 3, The Republic of Lithuania, No 1908 LI, 1987.07.11., 28 pages (in Russian).
2. Š.Kudžmauskas, G.Vektaris, A.Tamulis, V.Liuolia, V.Gaidelis, A.Undzėnas "The Modeling of the Processes of the Photogeneration, Photosensibilization and Charge Carrier Transport in the Carbazolyl Containing Photoconductors", Deposited in Soviet Union Research Institute for Scientific and Technical Information, Moscow, Inventor No 02890037345. 1988.12.12, 50 pages (in Russian).
3. A.Tamulis, A.Undzėnas, L.Bažan, "The Electronic Processes in Carbazolyl Containing Polymers Sensitized by Pyrylium and Rhodamine 6G", Proc. of the 2nd International Symposium "Organic Materials for Non-Linear Optics", University of Oxford, UK, 4-6 September, 1990 (in press).
4. J.-M.Lehn,"Supramolecular chemistry-scope and perspectives. Molecules, supermolecules, and molecular devices", (Nobel lecture), Angewandte Chemie, 27,89(1988).
5. A.Tamulis, S.Janušonis, L.Bažan, Makromol.Chem.Macromol Symp., 46, 181 (1991).
6. A.Tamulis, L.Bazhan,"Charge Photogeneration in Carbazole Containing Compounds and Valency Bands of Oligomers", Proceedings of the 29th Europhysics Conference on Macromolecular Physics", Alexisbad (Germany), September 9-14, 1991, 6 pages (in press).
7. M.J.S.Dewar, W.Thiel, J.Amer.Chem.Soc., 99, 4899(1977).
8. A.Tamulis, Š.Kudžmauskas, Soviet Physics Collection (Litovskii Fizicheskii Sbornik/Lietuvos Fizikos Rinkinys), Allerton Press Inc., 29, 15 (1989).