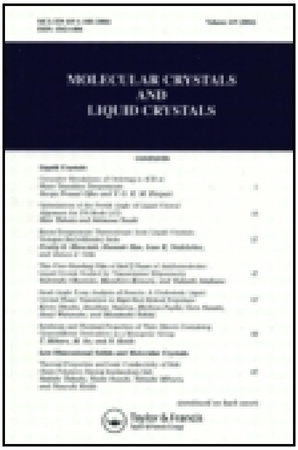

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Quantum Chemical Design of Multivariable Anisotropic Random-Walk Molecular Devices Based on Stilbene and Azo-Dyes

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Quantum chemical *ab initio* calculations and investigations of several organic photoelectron donor, electron acceptor molecules and their supermolecules connecting via the electron insulator bridges were performed using Hartree-Fock (HF) and density functional theory (DFT) methods. The optimized ground state geometry was as initial optimizing geometry in the first excited state using *ab initio* configuration interaction single-excitation (CIS) method. The results of single molecule and supermolecule calculations were used for the design and *ab initio* calculations of two-, three-, four- and six-variable anisotropic random-walk molecular devices based on stilbene and azo-dye molecules. Two kinds of logically AND controlled molecular random-walkers were designed.

Keywords: ab initio quantum chemistry; stilbene and azo-dye molecules; optimization in excited state; molecular random-walker; logically controlled random-walker

INTRODUCTION

The synthesis and construction of molecular devices based on light induced molecular motions are in the initial stage now. Prof. V. Balzani group in University of Bologna and coworkers are constructing light-fueled molecular-level machines: switches, plug/socket systems based on interlocked molecular compounds.[1-3] The light-driven monodirectional molecular rotors are investigating in Stratingh Institute, University of Groningen with collaboration of Tohoku University, Japan.[4] The phenomenon of anisotropy of photoinduced translation diffusion of azo-dyes was described recently.[5] In this article we extend the variety of random-walking molecules by the design of multivariable and logically controlled molecular devices composed of photoactive photodonor, photoacceptor moieties attached to stilbene or azo-dye molecules.

QUANTUM CHEMICAL CALCULATIONS METHODS

Quantum chemical *ab initio* HF[6] and density functional theory DFT[7] calculations with the Berny geometry optimization[8] were used in this paper to gain the structural and electronic structure information on single molecules and supermolecules which could potentially serve as molecular devices.

The optimization in ground state were performed using the DFT in the framework of Becke's three parameter hybrid method[9] and Perdew/Wang 91 gradient-corrected correlation functional[10] (B3PW91) model or HF method in the 6-31G,[11] 6-311G**,[12] cc-pVDZ, cc-pVTZ[13] basis sets using Gaussian 94, Revision E.2[14] package.

After full or partial geometry optimization in the ground state, the *ab initio* HF configuration interaction single-excitation (CIS)[15] method was used for the geometry optimization in the first excited state.

RESULTS OF SINGLE MOLECULE CALCULATIONS

Electron Donor Molecules

The quantum chemical geometry optimization of three photo electron donor molecules: carbazole (abbreviation of this molecule will be Cz and the formula is $C_{12}H_9N$), 1,4-phenylenediamine (PhDA, $C_6H_4(NH_2)_2$), N,N,N',N'-tetramethyl-1,4-phenylenediamine (TeMePhDA, $C_6H_4(N(CH_3)_2)_2$) was performed using the DFT B3PW91/cc-pVTZ model.

The singlet transitions of optimized Cz were calculated by ZINDO/S-CI method. The values of transition oscillator strengths (f) were obtained: 309.0 nm, f=0.015 arbitrary units; 260.8 nm, f=0.09; 232.6 nm, f=1.577; 227.7 nm, f=0.260; and 217.0 nm, f=0.506 that correlate with the experimental absorption spectrum.

Electron Acceptor Molecules

Several organic electron acceptor molecules: benzene (C_6H_6, Ph), 1,2,4,5-tetracyanobenzene (TCNB, $C_6H_2(CN)_4$), 7,7,8,8- tetracyanoquinodimethane (TCNQ, $C_8H_4(CN)_4$), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TeFTCNQ, $C_8F_4(CN)_4$), 4,5-dinitro-9-(dicyanomethylidene)fluorene (DN9(CN)2F, $C_{13}H_6C(CN)_2(NO_2)_2$) were optimized using B3PW91/cc-pVTZ model.

For the design of charge transfer supramolecules-dyads electron donors are connected via the electron insulator bridges with electron acceptor molecules. We compare HOMO values which correlate with ionisation potential and LUMO values that correlate with electron affinity. For example, our calculations shows that TCNQ (LUMO lower) is better electron acceptor than TCNB and PhDA (HOMO higher) is better electron donor than Cz.

Stilbene Molecule

The planes of phenyl rings are totally by 13.36 degrees twisted in optimized *trans* - stilbene ground state: each phenyl ring is twisted by 6.68 degrees relatively to -HC=CH- bridge to opposite sides. Geometry optimization of the *trans* - stilbene molecule in the first excited state using *ab initio* CIS-HF method in the 6-311G and STO-3G basis sets shows that it becomes planar. In the first excited state the *trans*-stilbene molecule becomes in 0.11 Angstroms (Å) shorter because two angles C-C-C in left and right sides of the -HC=CH- bridge become smaller. The excitation process in organic photoactive molecules is very fast (picoseconds) and relaxation is due to the vibrations and dissipation of the excitation energy on surface. In the first excited state the planar *trans*-stilbene molecule should move on the surface during relaxation process due to the twisting of phenyl rings relatively -HC=CH- bridge by 13.36 degrees. The other kind of movement of relaxed *trans*-stilbene molecule is related with enlargement of two angles -C-C-C- near -HC=CH- bridge.

The values of overlapping population (OP)[16] in the single bonds C-C near the -HC=CH- bridge of ground state *trans*-stilbene optimized by B3PW91\6-311G** are equal to 0.828 and OP value on bridge -HC=CH- is equal to 1.192. During the optimization by CIS-RHF/STO-3G in first excited state the OPs on bonds C-C become larger: 0.882 and on C=C becomes smaller: 1.050 but this does not allow free rotate along bridge C=C bond. That correlates with experiments[17] claiming what fluorescence yield, i.e. *trans-cis* transition in stilbene depends on temperature (in low temperatures it is approximately equal to 1).

The geometry optimization of the *cis*-stilbene molecule in the ground state was performed applying the DFT B3PW91\6-311G** model. According to the computations the dihedral angle between bridge and near bridge atoms: C - C=C - C is equal to 6.7 degrees, and phenyl rings are twisted approximately by 37 degrees relatively to the C - C=C - C bridge plane (rotations are around C - C bonds). The total energy of the *cis* - stilbene is in 0.19 eV = 4.5 kcal/mol higher than in the *trans* - stilbene.

The first singlet excited state of the *cis* conformation was investigated applying CIS - RHF\STO-3G geometry optimization. At the beginning of optimization procedure the dihedral angle between the atoms C - C=C - C increases, while angle between phenyl ring and the -C=C- bridge decreases (geometry was going towards *trans*-stilbene conformation). Although the geometry optimization convergence was not achieved due to oscillations between two total energy minima and in these two geometries the tetrahedral angles between phenyl rings and the -C=C- bridge become not the same. It means that the symmetry in first excited *cis*-stilbene molecule is broken. Therefore it is possible crossing between the first excited state and the double-excited state and free returning to the *trans*-stilbene conformation. That correlates with above-mentioned experiment[17] claiming that fluorescence yield, i.e. *cis-trans* transition in stilbene does not depend on temperature.

Disperse Orange 3 (DO3) molecule

We have investigated DO3 azo-dye molecule $NH_2\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}NO_2$ (see Figure 1) because it is more simple for quantum chemical simulations in comparison with Disperse Red 1 molecule that was investigated in GCO-CEA-Saclay.[5] The ground state geometry optimization was performed using B3PW91\6-311** model. The angles C(3)-N(8)=N(15) and C(16)-N(15)=N(8) of optimized molecule are respectively 114.08 and 115.51 degrees.

In the DO3 molecule the intramolecular hydrogen bonds between the bridge nitrogen atoms and phenyl closest hydrogen atoms exist (not underlined PO values in Figure 1). These hydrogen bonds keep molecule almost in one plane: only 0.015 and 0.005 degrees are between the ring planes and the -N=N- bridge.

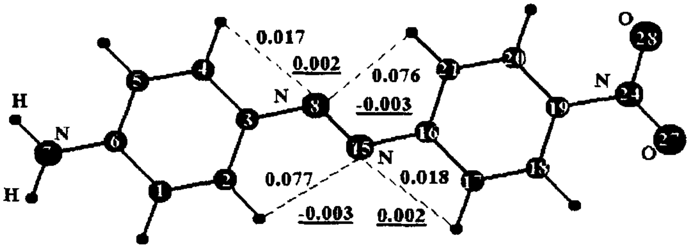

FIGURE 1 Geometry optimization of the DO3 azo-dye molecule performed in the ground state using B3PW91/6-311G** and in the first excited state using CIS-RHF\STO-3G results in a planar structure. In the first excited state the intramolecular hydrogen bond OP values are presented before the optimization and underlined are the ones after optimization.

We have optimized azo-dye molecule in the first excited state by using CIS-HF\STO-3G. The results show that angles C(3)-N(8)=N(15) and C(16)-N(15)=N(8) change respectively from 115.5 to 123.5 and from 114.1 to 121.9 degrees. Due to the increasing of the angles, the excited molecule becomes longer by 0.202 Å. During excitation two intramolecular hydrogen bondings (see underlined PO values in Figure 1) are broken and other two reduced while the molecule remains in one plane. The relaxation process will lead to a reduction of C-N=N angles and in such a way the DO3 molecule is able to move on the surface.

DESIGN OF MOLECULAR RANDOM-WALKERS

Two-variable anisotropic random-walk stilbene-based molecular motor devices are designed from carbazole (Cz), 1,4-phenylenediamine (PhDA), stilbene and TCNQ molecules joined with -C_2H_2- (or by more flexible -N=N-) fragment bridges. This random-walk molecular device should be excited by two different wavelengths that correspond approximately to the wavelengths of single Cz and PhDA molecules investigated by CNDO\S-CI and ZINDO-CI methods. After excitation this supermolecule should be deformed in two different ways due to the two different ways of excitation and further to the two different ways of electron tunneling to the acceptor fragment TCNQ. During the relaxation process this supermolecule should dissipate the energy by moving on the surface in two different ways.

Another kind of two-variable random-walk stilbene-based devices are designed based on one electron-donor fragment and two electron-acceptor fragments Cz-C_2H_2-C_6H_4-CH=CH-C_6H_3(-C_2H_2-TCNQ)(-NO_2). The same device was designed replacing the bridge -C_2H_2- to one that it is more flexible: - N=N-. In this case we have: Cz-N=N-C_6H_4-CH=CH-C_6H_3(-C_2H_2-TCNQ) (- NO_2); Cz-N=N-C_6H_4-CH=CH-C_6H_3(-N=N-TCNQ)(-NO_2).

Several two-variable random-walk molecular motors were designed based on DO3 azo-dye calculation results: (Cz-C_2H_2-)(NH_2-)C_6H_3-N=N-C_6H_4-NO_2; (PhDA-C_2H_2-)(NH_2-)C_6H_3-N=N-C_6H_4-NO_2; NH_2-C_6H_4-N=N-C_6H_3(-NO_2) (-C_2H_2-TCNQ); NH_2-C_6H_3-N=N-C_6H_3(-NO_2)(-C_2H_2-TCNB). Replacing the bridge -C_2H_2- by more flexible -N=N- we have: (Cz-N=N-)(NH_2-)C_6H_3-N=N-C_6H_4-NO_2; (PhDA-N=N-)(NH_2-)C_6H_3-N=N-C_6H_4-NO_2; NH_2-C_6H_4-N=N-C_6H_3(-NO_2)(-N=N-TCNQ); NH_2-C_6H_4-N=N-C_6H_3(-NO_2)(-N=N-TCNB).

Three-variable anisotropic random-walk stilbene-based molecular motors are designed in two ways. Cz, PhDA, TeMePhDA, stilbene and TCNQ molecules joined with the -C_2H_2- fragment bridges: (Cz-C_2H_2-)(PhDA-C_2H_2-) (TeMePhDA-C_2H_2-)C_6H_2-CH=CH-C_6H_4-C_2H_2-TCNQ or in another manner: Cz-C_2H_2-C_6H_4-CH=CH-C_6H_2(-C_2H_2-TCNQ)(-C_2H_2-TCNB)(-NO_2); Cz-N=N-C_6H_4-CH=CH-C_6H_2(-N=N-TCNQ)(-N=N-TCNB)(-NO_2); Cz-C_2H_2-C_6H_4-CH=CH-C_6H_2(-N=N-TCNQ)(-C_2H_2-TCNB)(-NO_2); Cz-C_2H_2-C_6H_4-

CH=CH-C_6H_2(-C_2H_2-TCNQ)(-N=N-TCNB)(-NO_2).

Several three-variable random-walk motors were designed based on DO3 azo-dye calculation results: (Cz-C_2H_2-)(PhDA-C_2H_2-)(NH_2-)C_6H_2-N=N-C_6H_4-NO_2; (Cz-N=N-)(PhDA-C_2H_2-)(NH_2-)C_6H_2-N=N-C_6H_4-NO_2; (Cz-C_2H_2-)(-NH_2)(TeMePhDA-)C_2H_2-C_6H_2-N=N-C_6H_4-NO_2; (Cz-N=N-) (- NH_2)(TeMePhDA-)C_2H_2-C_6H_2-N=N-C_6H_4-NO_2; (Cz-N=N-)(PhDA-N=N -) (NH_2-)C_6H_2-N=N-C_6H_4-NO_2; (Cz-N=N-)(TeMePhDA-N=N-) (NH_2-)C_6H_2-N=N-C_6H_4-NO_2; NH_2-C_6H_4-N=N-C_6H_2(-C_2H_2-TCNQ)(- C_2H_2-TCNB)(-NO_2); NH_2-C_6H_4-N=N-C_6H_2(-C_2H_2-TCNQ) (- C_2H_2-TCNB)(-NO_2); NH_2-C_6H_4-N=N-C_6H_2(-N=N-TCNQ)(-C_2H_2-TCNB)(-NO_2); NH_2-C_6H_4-N=N-C_6H_2(-N=N-TCNQ)(-N=N-TCNB)(-NO_2).

Four-variable anisotropic random-walk stilbene-based molecular motor devices were designed attaching Cz and PhDA molecules via the -C_2H_2- or - N=N- fragment bridges to the left side of stilbene molecule and TCNQ and TCNB molecules joining via the -C_2H_2- or -N=N- fragment bridges to the right side of stilbene. Six-variable stilbene based molecular random-walkers are designed joining Cz, PhDA, TeMePhDA molecules via the -C_2H_2- (or -N=N-) fragment bridges to left side of stilbene molecule and TCNQ and TCNB molecules joining via the -C_2H_2- (or -N=N-) fragment bridges to right side of stilbene or in such a way: (Cz-C_2H_2-)(PhDA-C_2H_2-)C_6H_3-CH=CH-C_6H_2(- C_2H_2-TCNQ)(-C_2H_2-TCNB)(-NO_2); (Cz-N=N-)(PhDA-)C_2H_2-C_6H_3-CH=CH-C_6H_2(-C_2H_2-TCNQ)(-C_2H_2-TCNB)(-NO_2); (Cz-N=N-) (PhDA-N=N-)C_6H_3-CH=CH-C_6H_2(-C_2H_2-TCNQ)(-C_2H_2-TCNB)(-NO_2); (Cz-N=N-)(PhDA-N=N-)C_6H_3-CH=CH-C_6H_2(-N=N-TCNQ)(-C_2H_2-TCNB) (-NO_2); (Cz-N=N-)(PhDA-N=N-)C_6H_3-CH=CH-C_6H_2(-N=N-TCNQ)(-N=N-TCNB)(-NO_2).

Four-variable random-walk motors were designed based on the DO3 azo-dye calculation results: (Cz-C_2H_2-)(NH_2-)C_6H_3-N=N-C_6H_3-(C_2H_2-TCNQ) (- NO_2). Six-variable random-walk motors are designed as: (Cz-C_2H_2-) (PhDA-C_2H_2-)(NH_2-)C_6H_2-N=N-C_6H_3(-C_2H_2-TCNQ)(-NO_2)and (Cz-C_2H_2-)(NH_2-)C_6H_3-N=N-C_6H_2(-C_2H_2-TCNQ)(-C_2H_2-TCNB)(-NO_2). Were designed all possible four- and six-variable random-walkers analogs replacing

- C_2H_2 - bridge to the more flexible one: -N=N-.

Two-variable logically controlled random-walker is designed from photoelectron donor Cz molecule which is joined via bridge -C_2H_2- to another electron donor fragment -Phenyl-NO_2. These above derivatives are connected via -C_2H_2- or (-N=N-) bridges to photoelectron acceptor molecule 4,5-dinitro-9-(dicyanomethylidene)-fluorene (DN9$(CN)_2$F, $C_{13}H_6C(CN)_2(NO_2)_2$) and finally via -N=N- bridge to electron acceptor fragment -Ph-NO_2.

If the molecule Cz or fragment -Ph-NH_2 is excited by light, electron jumps on good electron acceptor molecule DN9$(CN)_2$F and remains here for some relaxation time. Only in the case if Cz and the fragment -Ph-NH_2 are excited, one electron should stay on DN9$(CN)_2$F and another electron should jump further to the fragment -Ph-NO_2. Second electron passing the -N=N- bridge will change the geometry of the supermolecule. After the dissipation of excited energy on the surface the supermolecule will return to its ground state geometry moving on the surface. Movement of such a random-walker is possible only if Cz and -Ph-NH_2 are excited therefore we call it logically AND controlling molecular random-walker.

Another kind of two variable logically controlled random-walker is designed from photoelectron donors Cz-C_2H_2-, PhDA-C_2H_2- and -Ph-NH_2 (left side of Figure 2) connected via the -C_2H_2- (or -N=N-) bridge to the photoelectron acceptor molecule DN9$(CN)_2$F and finally via the -N=N- bridge to the electron acceptor fragment -Ph-NO_2 (right side of Figure 2).

If the molecule Cz or PhDA, or fragment -Ph-NH_2 are excited by light, electron jumps on the good electron acceptor molecule DN9$(CN)_2$F and remains here for some relaxation time. Only in the case if Cz and fragment -Ph-NH_2 (or Cz and PhDA, or PhDA and -Ph-NH_2) are excited, one electron should stay on DN9$(CN)_2$F and another electron should jump further to the fragment -Ph-NO_2. Second electron passing the -N=N- bridge will change the geometry of the supermolecule. After the dissipation of excited energy on the surface the supermolecule will return to its ground state geometry moving on the surface.

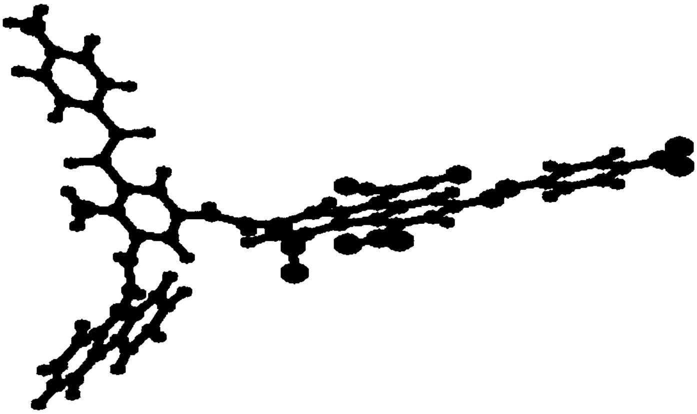

FIGURE 2 Three different ways logically AND controlled random-walker.

Movement of such a random-walker it is possible only if Cz and -Ph-NH_2 (or Cz and PhDA, or PhDA and -Ph-NH_2) are excited, therefore this device it should be three different ways logically AND controlled molecular random-walker.

All the above mentioned designed supermolecules (molecular random-walkers) were calculated in ground state by HF\6-311G** or DFT B3PW91\6-311G** methods and results show right electronic structure.

CONCLUSIONS

1. *Ab initio* quantum chemical optimization of the stilbene and the DO3 azo-dye molecules indicates on two different mechanisms of movement during excitation process. The stilbene molecule moves mainly by twisting of phenyl rings relatively -C=C- bridge and DO3 moves by increasing of angles <C-N=N- near bridge.
2. *Ab initio* quantum chemical investigations of ground and excited state of photoactive single molecules, stilbene and DO3 azo-dye allowed to design multivariable random-walk molecular devices and logically controlled random-walkers.

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