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Computational Investigations about the Ground and Excited States' Properties of Trans-4-N,N-Dimethylamino-4'-Nitro-Stilbene (DNS) and Trans-4-N,N-Dimethyl-Amino-4'-Cyanostilbene (DCS) Derivatives

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Abstract

The ground and lowest-lying singlet excited state geometries and dipole moments of trans-4-N,N-dimethylamino-4'-nitro-stilbene (DNS) derivative and the trans-4-N,N-dimethyl-amino-4'-cyanostilbene (DCS) derivative are calculated at the B3LYP level of theory for the first time in this work. The vertical excitation energies and the fluorescence emission energies are obtained for the two species. The calculated results are compared with available experimental results and show good consistency. The molecular orbital analyses in these molecules have been performed. The comparison of the atomic charge distributions in the ground and excited states of both the DNS derivative and DCS derivative implies the intra molecular charge transfer (ICT) process during the excitation period.

Introduction

During the past several years, the field of electro optical organic and nonlinear optical material has received extensive attention [1-3] because of their possible application as fluorescence probes, electro optical switches and chemical sensors. Due to the electron donating and accepting groups on opposite sides, such material, which is connected by a highly delocalized electron system, is important for the nonlinear optical properties. Stilbene and donor–acceptor (DA)-substituted stilbenes are the molecules which have been used in photo physics and photochemistry [4-7]. More or less, the interest results from the complex mechanism relevant to bond twisting in these molecules. The torsional motion of the central C=C bond in trans-stilbene and its analogs are responsible for the trans-cis isomerization which does not proceed through conical intersection in the excited state potential energy surface [8]. It is known that twisting of the benzonitrilo (acceptor) and dimethylamino (donor) C-N bond in N,N-dimethylaminobenzonitrile (DMABN) could lead to a twisted intramolecular charge transfer (TICT) state, which is responsible for the dual fluorescence [9,10] or displays stokes-shifted fluorescence [11] in polar solvents. TICT-based dual fluorescent systems have been used as ratio metric fluorescent chemo sensors [12]. What is more, the TICT concept has inspired the design of donor-acceptor systems which have ultra large hyperpolarizability [13]. Twisting motion of the NO_2 group in nitro aromatics could result in the ultrafast fluorescence quenching [14] and facilitate internal conversion of the lowest singlet excited state. 4-dimethylamino-4'-cyanostilbene (DCS), is a typical stilbene which involves the process of photo induced intramolecular charge transfer (CT) in polar solvents [15-18]. Trans-4-(N,N-dimethylamino)-4'-nitrostilbene (DNS) is a nonlinear optical dye which contains potential torsional modes in the excited states [19]. Torsional motion about a specific bond in the excited state, such as the trans-cis photo isomerization of alkenes [20,21], is an important nonradiative decay channel for many π-conjugated systems.

The trans-4-N,N-dimethylamino-4'-nitrostilbene (DNS) derivative, as well as the DCS derivative which have been shown in Scheme 1, are used to generate antibodies which bind donor-acceptor-substituted stilbenes to afford strong blue to green fluorescent complexes [22].

The free 1 and 2 complexes absorb with the wavelength maxima of 430 nm and 373 nm, respectively [23-25]. Both the derivatives' absorption spectra display no substructure. The steady-state fluorescence spectra of them are broad and composed of no substructure. To the best of our knowledge, computational investigations of the spectroscopic properties of the ground state and the excited state of these derivatives do not exist until now. The motivation of this work is to explore the nature of the ground and the excited states, to see whether our theoretical predictions could be comparable to available experimental results, to look for the mechanism of formation of the charge-transfer excited state. We will focus on the neutral molecule 1 and 2 and first look at calculations in which solvent effects are not included in the present work. Some work related with investigating the solvent effects which might influence the spectroscopic properties to some extents is ongoing. The most widely used method to study excited states of such kind of molecules is time-dependent density functional Theory (TDDFT)s.
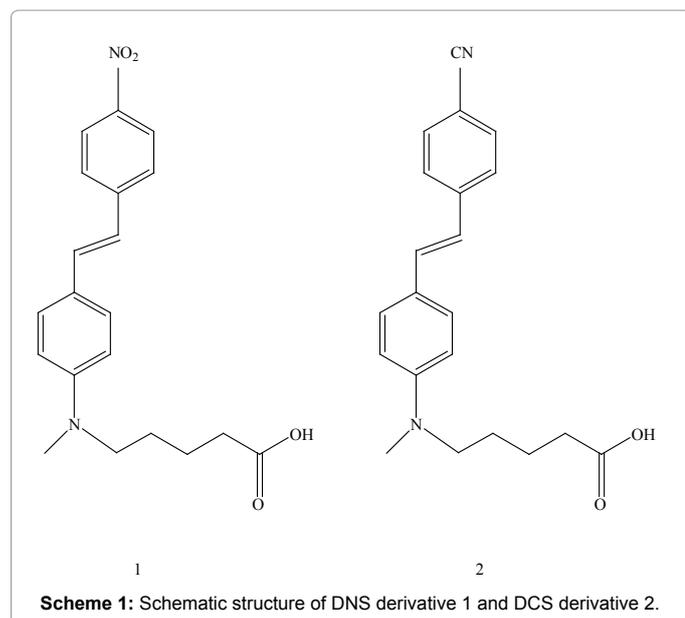
Computational details and theory

All predictions were made with the Gaussian 09 program package [26]. The density functional theory at the B3LYP level of theory [27-30] and the 6-311G** basis set was performed to calculate the ground-state structures and dipole moments of DNS derivative and the DCS derivative. As has been known, CIS method has been used successfully in the structure optimization of the excited state [31,32]. Since the CIS method makes use of a HF state's orbitals in a CI procedure to deal with the higher roots and incorporated only parts of the electronic correlation effects, the excitation energies obtained by the CIS calculations are often overestimated [33]. In this work, we

Scheme 1: Schematic structure of DNS derivative 1 and DCS derivative 2.

rectify the flaw of the CIS method by using the time-dependent DFT (TDDFT) [34-36] method to investigate the excited state properties. The TDDFT calculations are applied to the lowest-lying excited state equilibrium geometry and other excited state properties including the dipole moments, excitation energies to the lower three excited states as well as emission energies from the lowest three excited states. The emission resulted from the excited state geometries, which are the same as the ground state geometry. In this work, we have also calculated the Mulliken charges of all the atoms [37-40] in order to study the charge change between the ground and excited states. The changes of atomic charges can provide sufficient proof for the charge transfer (CT) study.

Results and Discussion

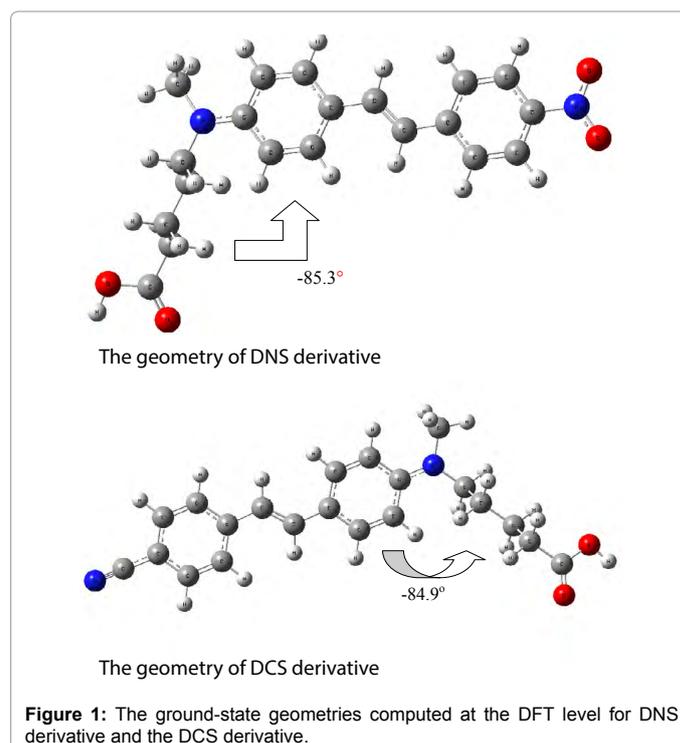### Ground and lowest-lying singlet excited state geometries of DNS derivative and the DCS derivative

No restrictions on symmetries were imposed on the initial structures before optimizing the stationary points of these molecules. The ground-state geometries computed at the DFT level for DNS derivative and the DCS derivative are plotted in Figure 1 for atom labeling. The optimized structural parameters of the ground and lowest-lying singlet excited states of DNS derivative and the DCS derivative calculated at B3LYP density functional method have been listed in Table 1 of the Supporting Information which are in accordance with the atom numbering scheme shown in these figures. The optimized equilibrium geometries of the lowest-lying singlet excited states of DNS derivative and the DCS derivative are plotted in Figure 2 and the Supporting Information has also listed the geometric parameters of these optimized structures. It should be noted that the ground-state geometries were used for geometry optimization of the first singlet excited state, namely, the lowest-lying singlet excited state**. Comparing the optimized geometrical parameters of the first singlet excited state (S_1) with the corresponding ground state (S_0), the dihedral angle between dimethylamino derivative and nitrostilbene in the ground state of DNS derivative is -85.3° while the dihedral angle between dimethylamino derivative and nitrostilbene in the first excited state of DNS derivative is -91.2°. Notably, all the functional groups in the DNS derivative are in the same plane for the ground state. However, in the lowest-lying singlet excited state of DNS derivative, the dihedral angle

between C=C double bond and the plane of the nitro-phenyl group is found to be -90.6° which is twisted from the ground state geometry. As for the ground state and the lowest-lying singlet excited state of the DCS derivative, the dihedral angle between C=C double bond and the plane of the aromatic ring is found to be 0°. That is to say, there are no twisted geometries for these electronic states. The dihedral angle between dimethylamino derivative and cyanostilbene in the ground state of DCS derivative is -84.9°, what is more, the dihedral angle between dimethylamino derivative and nitrostilbene in the first excited state of DCS derivative is -88.8°.

Furthermore, a frequency analysis was performed on all DFT structures to confirm that all the frequencies are real for the computed stable structures. It is found that all the vibrational modes have real frequencies, which indicate that all the optimized geometries are true minima. In addition, the total energies of the ground and lowest-lying singlet excited states of the DNS derivative and the DCS derivative are given in Table 1. It could be found that the energies of the lowest excited state of these molecules are higher than the counterparts of the ground state.

The vertical excitation energies and the fluorescence emission energies

The optimized geometries of the ground state have been used to compute the vertical excitation energies (VEE) of the DNS derivative and the DCS derivative by means of TD-B3LYP calculations in the gas phase. For comparison, the results of experimental observation for the DNS derivative and the DCS derivative are also included. All the results are listed in Table 2. It could be seen that the vertical excitation energy of DNS derivative has the value of 2.61 eV. The excited state (S_1) has the highest oscillator strength (0.81) and its excitation energy of 474 nm matches very well with the experimental absorption spectra which show an absorption maximum of 430 nm. Accordingly, the vertical excitation energy of DCS derivative has the value of 3.07 eV.
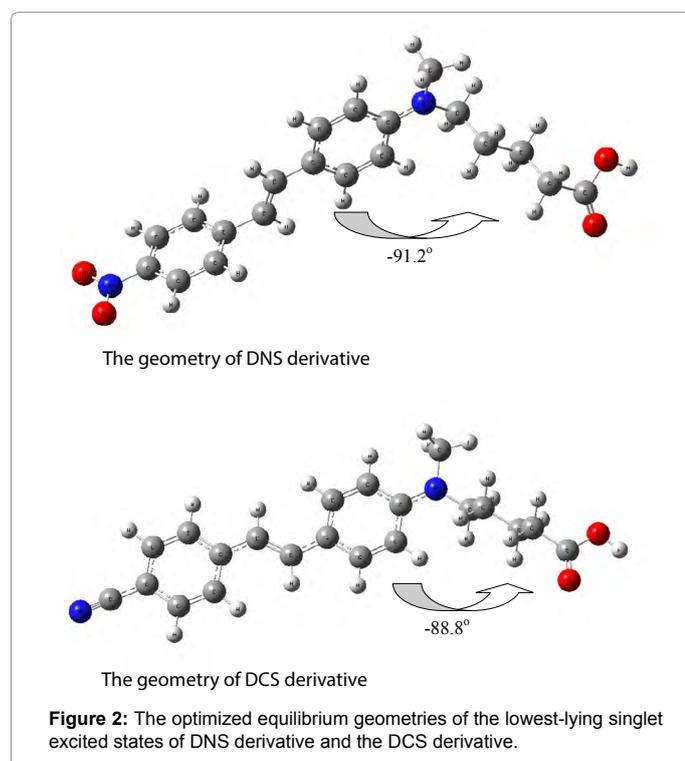

The geometry of DNS derivative

The geometry of DCS derivative

Figure 1: The ground-state geometries computed at the DFT level for DNS derivative and the DCS derivative.

	DNS derivative	DCS derivative
Ground state	-1186.00	-1073.71
Excited state	-1185.98	-1073.62

Table 1: The energies (in Hartree) of the ground and lowest-lying singlet excited states of the DNS derivative and the DCS derivative

DNS derivative	Vertical excitation energy	Oscillator strength	Exp [22] (absorption)	Fluorescence emission energy
S_1	474 nm (2.61 ev)	0.81	430 nm	631nm (1.97 ev)
S_2	334 nm (3.71 ev)	0.4211		384nm (3.23 ev)
S_3	331 nm (3.74 ev)	0.0000		315nm (3.93 ev)
DCS derivative	Vertical excitation energy	Oscillator strength	Exp [22] (absorption)	Fluorescence emission energy
S_1	403 nm (3.07 ev)	1.18	373 nm	427 nm (2.90 ev)
S_2	313 nm (3.96 ev)	0.02		319 nm (3.89 ev)
S_3	305 nm (4.07 ev)	0.01		311 nm (3.98 ev)

Table 2: The vertical excitation energies and fluorescence emission energies of the DNS derivative and the DCS derivative.

Figure 2: The optimized equilibrium geometries of the lowest-lying singlet excited states of DNS derivative and the DCS derivative.

The excited state (S_1) has the highest oscillator strength (1.18) and its excitation energy of 403 nm matches very well with the experimental absorption spectra which show an absorption maximum of 373 nm.

By means of calculations, we will now start to characterize the emission energies. Fluorescence emission energies of the DNS derivative and the DCS derivative are also listed in Table 2. The states relevant for the emission are the three lowest excited states. Since the geometries of these excited states are the same as the ground state geometry according to the Frank-Condon's rule, the ground state geometry could be used for calculating the emission energies. There is no experimental emission energy for the DNS derivative, while the experimental emission energy for the DCS derivative is 574 nm [41,42]. When compared with the available experimental information of fluorescence emission energy, our calculated results are not in good agreement with the experimental results, which might be due to the
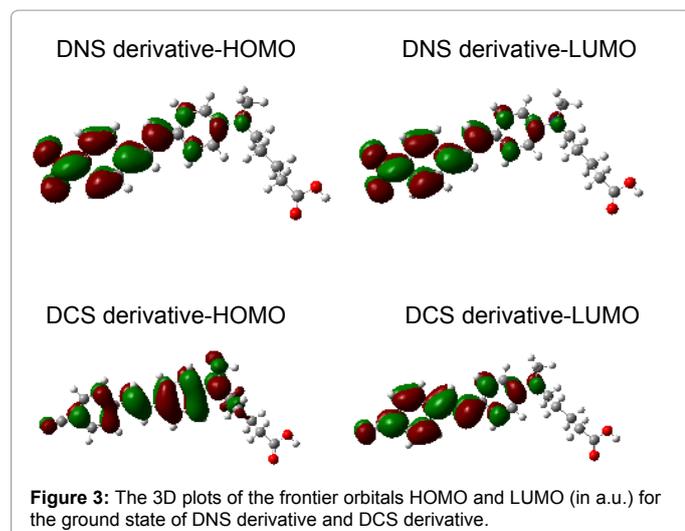
problem of choosing the appropriate functional and basis sets for the title molecules.

In addition, dipole moments of the ground state geometries of the DNS derivative and the DCS derivative are 11.26 Debye and 10.53 Debye, respectively. The corresponding excited state dipole moments for the two molecules are calculated to be 10.48 Debye and 11.34 Debye, respectively. It could be concluded that there are no substantial changes in the dipole moments of the two molecules when they are excited.

HOMO and LUMO analyses

It is well-known that analysis of molecular orbitals (MOs) can provide insight into the nature of the excited states [43]. The most important molecular orbitals in molecules are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [44]. The frontier orbital gap could help characterize the microscopic phenomenon within the molecule. The HOMO is the orbital which primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. The 3D plots of the frontier orbitals HOMO and LUMO (in a.u.) for the ground state of DNS derivative and DCS derivative are shown in Figure 3. The positive phase is red and the negative one is green. It can be seen from the figure that the HOMO is distributed in nitrostilbene and N-CH_3 moiety. The LUMO in DNS derivative is found to spread over the nitrostilbene and N-CH_3 moiety. All the HOMO and LUMO have nodes. The nodes in each HOMO and LUMO are placed symmetrically. It can be seen from the figure that the HOMO is distributed in cyanostilbene and the CH_2-N-CH_3 moiety. The LUMO in DCS derivative is found to spread over the cyanostilbene and the N-CH_3 moiety. As for the excited states, it can be seen from Figure 4 that both the HOMO and LUMO of DNS derivative are distributed in nitrostilbene and N-CH_3 moiety. All the HOMO and LUMO have nodes. The nodes in each HOMO and LUMO are placed symmetrically. It could also be seen from the figure that the HOMO is distributed in cyanostilbene and the CH_2-N-CH_3 moiety in the first excited state of DCS derivative. The LUMO in DCS derivative is found to be located at the cyanostilbene and the N-CH_3 moiety.
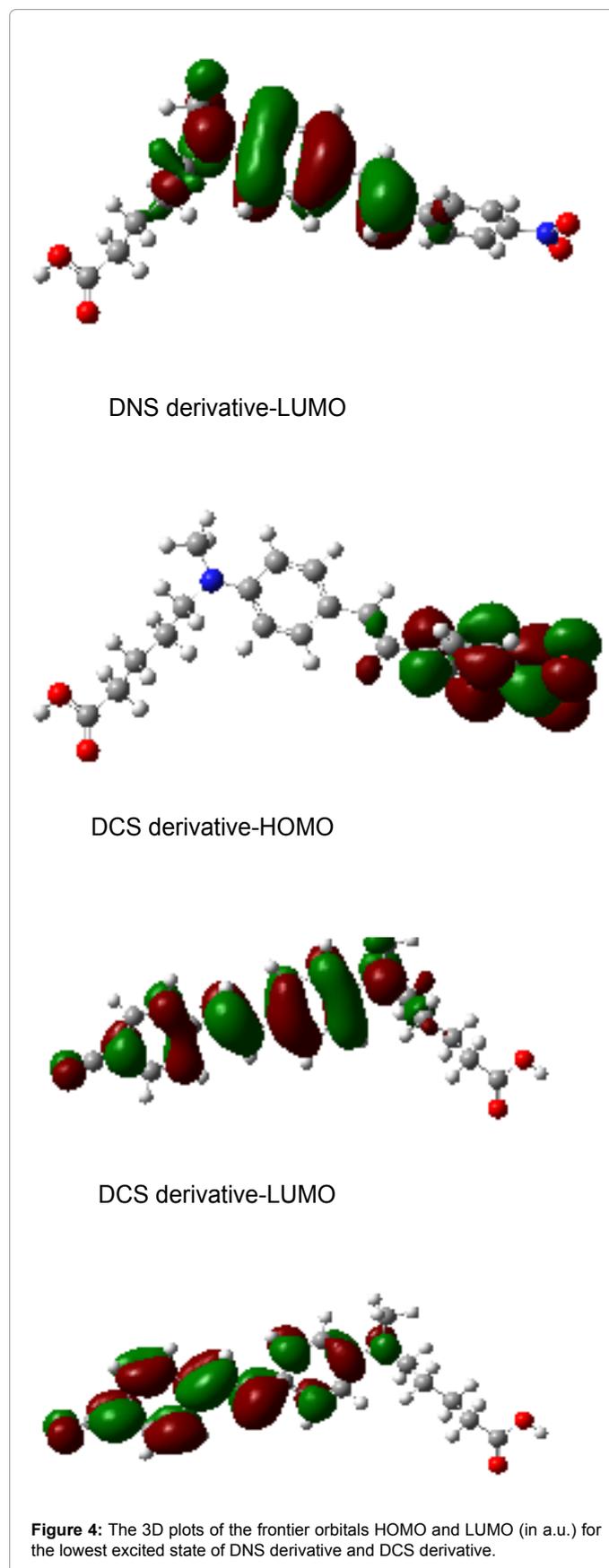
The energy gap of HOMO–LUMO could explain the eventual charge transfer interaction within the molecule. The energy values of HOMO and LUMO levels for the ground state of DNS derivative are computed to be -0.1979 a.u. and -0.0914 a.u. respectively, and

DNS derivative-HOMO   DNS derivative-LUMO

DCS derivative-HOMO   DCS derivative-LUMO

Figure 3: The 3D plots of the frontier orbitals HOMO and LUMO (in a.u.) for the ground state of DNS derivative and DCS derivative.

the energy difference is 0.1065 a.u. When the molecule excites, the HOMO and LUMO energy difference decreases to 0.0864 a.u. The high energy of HOMO means that it is easy for HOMO to donate electrons whereas the low energy of LUMO means that it is easy for LUMO to accept electrons. Since the energy gap between the LUMO and HOMO has decreased in the excited state, it is easier for the electrons of the HOMO to be excited. The energy values of HOMO and LUMO levels for the ground state of DCS derivative are computed to be -0.1952 a.u. and -0.0736 a.u., respectively, and the energy difference is 0.1216 a.u. When the molecule excites, the HOMO and LUMO energy difference decreases to 0.1112 a.u. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [45,46]. The low values of frontier molecular orbital gap in the excited states indicate that both the molecules are more reactive and less stable.

The atomic charge distributions

The Mulliken atomic charges are displayed in Table 3. The charge distribution of DNS derivative shows that all the hydrogen atoms are positive, whereas nearly all the carbon atoms are negatively charged. These are the cases no matter in the ground state or the first excited state. The oxygen atoms have negative charges. The charge distribution of DCS derivative shows that all the hydrogen atoms are positive in the ground state whereas nearly all the hydrogen atoms are positive except hydrogen atom 3 and 4. What is more, all the oxygen atoms have negative charges. The atomic charges for optimized geometries of the ground state and the first excited state of DNS derivative and DCS derivative have also been analyzed in this work. The atomic charge distributions of DNS derivative and DCS derivative are shown in Figure 5. In order to describe the change of atomic charges obviously, we divided molecular structures into several parts and summed the atomic charge of each unit. DNS derivative was divided into four parts, nitro-benzene unit, H-C=C-H unit, methyl amino-benzene unit and derivative unit. The sum of atomic charges of nitro-benzene unit in the ground state is calculated to be -0.055778, which changes to -0.114433 in the lowest excited state. However, the sum of the derivative part displays an opposite tendency of change, which changed from 0.129097 in the ground state to 0.174263 in the lowest excited state. All of this demonstrated the charge transfer from the left part to the right part of the molecule. Therefore, it indicates strongly that the excited state of DNS derivative is an intramolecular charge transfer (ICT) state as a whole.
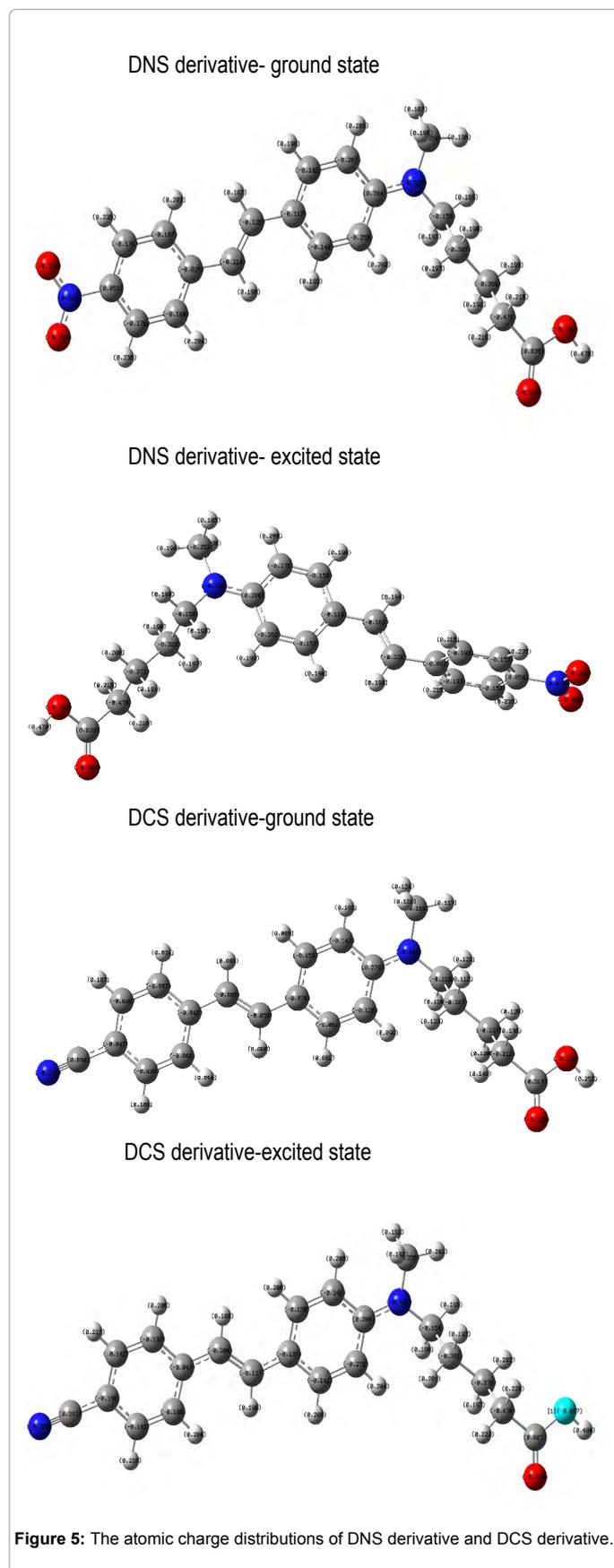

DNS derivative-LUMO

DCS derivative-HOMO

DCS derivative-LUMO

Figure 4: The 3D plots of the frontier orbitals HOMO and LUMO (in a.u.) for the lowest excited state of DNS derivative and DCS derivative.

DNS derivative- ground state

DNS derivative- excited state

DCS derivative-ground state

DCS derivative-excited state

Figure 5: The atomic charge distributions of DNS derivative and DCS derivative.

Atom No (1)	Atomic charge (G)	Atom No (1)	Atomic charge (E)
1C	-0.067	1C	-0.055
2C	-0.071	2C	-0.084
5C	-0.075	5C	-0.077
6C	-0.071	6C	-0.078
7C	-0.047	7C	-0.061
8C	-0.037	8C	-0.145
10C	-0.051	10C	-0.124
12C	0.011	12C	0.280
15C	-0.076	15C	-0.042
16C	-0.067	16C	-0.089
17C	-0.046	17C	-0.065
18C	0.025	18C	-0.046
20C	-0.045	20C	-0.052
22C	0.106	22C	0.119
25N	0.048	25N	0.168
26N	-0.360	26N	-0.462
27O	-0.217	27O	-0.279
28O	-0.217	28O	-0.279
29C	-0.066	29C	-0.115
30C	-0.226	30C	-0.187
33C	-0.223	33C	-0.237
36C	-0.217	36C	-0.213
41C	0.339	41C	0.317
42O	-0.381	42O	-0.326
43O	-0.329	43O	-0.328
45C	-0.196	45C	-0.164
Atom No (2)	**Atomic charge (G)**	**Atom No (2)**	**Atomic charge (E)**
1C	-0.057	1C	0.034
2C	-0.084	2C	0.100
5C	-0.077	5C	0.638
6C	-0.080	6C	-0.060
7C	-0.063	7C	-0.655
8C	-0.132	8C	0.105
10C	-0.130	10C	-0.453
12C	0.261	12C	-0.484
15C	-0.039	15C	1.028
16C	-0.085	16C	-0.029
17C	-0.067	17C	-0.822
18C	-0.028	18C	-0.312
20C	-0.030	20C	-0.615
22C	-0.047	22C	1.973
25N	-0.466	25N	0.267
26C	-0.030	26C	-0.606
27C	-0.253	27C	0.102
30C	-0.230	30C	-0.065
33C	-0.215	33C	-0.517
38C	0.315	38C	-0.181
39O	-0.325	39O	-0.248
40O	-0.320	40O	-0.150
42C	0.030	42C	-1.793
43N	-0.224	43N	-0.174
44C	-0.176	44C	-0.371

Table 3: The Mulliken charge distribution of the ground state (G) and the lowest excited state (E) of DNS derivative (1) and DCS derivative (2).

Correspondingly, DCS derivative was divided into four parts, cyano-benzene unit, H-C=C-H unit, methylamino-benzene unit and derivative unit. The sum of atomic charges of methylamino-benzene unit in the ground state is calculated to be -0.137221, which changes to 0.108464 in the lowest excited state. However, the sum of similar phenomenon happened to the derivative part changes from 0.19065 in the ground state to -0.041502 in the lowest excited state. Since the methylamino-benzene unit and the derivative part display the opposite trend in the charge distribution, we could conclude that there exists the charge transfer from the derivative unit to methylamino-benzene unit. Because the derivative unit and the methylamino-benzene unit locate at the same part of the molecule, we have to assume that the excited state of DCS derivative is a locally intramolecular charge transfer (ICT) state.

Conclusion

We investigate the spectroscopic properties of the ground state and the excited state of trans-4-N,N-dimethylamino-4'-nitrostilbene (DNS) derivative, as well as 4-dimethylamino-4'-cyanostilbene (DCS) derivative in this work. Based on the ground state geometries, the vertical excitation energies of the two molecules are computed. The calculated results show good consistency with available experimental information. The excited state geometries of the two molecules are also calculated which form the basis of obtaining the fluorescence emission energies of the two molecules. Furthermore, the frontier molecular orbitals and the atomic charge distributions of DNS derivative and DCS derivative have also been analyzed. It has been found that the DNS derivative is an intramolecular charge transfer (ICT) state as a whole while DCS derivative is a locally intramolecular charge transfer (ICT) state.

Acknowledgments

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