Comparative DFT studies of UV-vis and fluorescence spectra of diphenylamino-nitro-trans-stilbene

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ABSTRACT

DFT calculations have served as a critical tool to understand and design organic small molecules for many applications in the field of photoelectronics. Although many efforts have been made towards accurately describing UV-vis and fluorescence properties of organic small molecules, there are much needs to evaluate the accuracy of various functionals in description of electronic properties of organic small molecules. In this work, we make comparisons of ten functionals, i.e. B3LYP, HSEH1PBE, CAM-B3LYP, PBE, HCTH, LSDA, BVP86, B3PW91, MPW1PW91, ωB97XD, in the calculation of the energies of the frontier orbitals, UV-vis and fluorescence spectra of diphenylamino-nitro-trans-stilbene and with the experimental results. DFT calculations were carried out for both the ground and excited states and TD-DFT calculations were performed to obtain the UV-vis and fluorescence spectra. For the orbital energies, B3LYP and B3PW91 provide the best result with respect to the experiment. For UV-vis and fluorescence, CAM-B3LYP and MPW1PW91 results are closer to the experiments. Structural comparisons between the ground and excited states of the molecule were also made.

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1. Introduction

Organic small molecule (OSM) based materials have been widely used in solar cells[1-34] and sensing/imaging[35-70] technologies due to their facile functionalization and synthesis. Therefore, designing[71,72] and tuning organic small molecules[73,74] have been active research fields and studying OSMs[75-99] have attracted a lot of attentions. Among various characterization tools being used to study OSMs, DFT calculations have served as a critical tool to understand and design OSMs for applications in the technology of photoelectronics.

Although many efforts have been made towards accurately describing UV-vis and fluorescence properties of organic small molecules, there are much needs to evaluate the accuracy of various functionals in description of electronic properties of polar OSMs that have a donor-acceptor character. Although the energies of frontier orbitals, i.e. HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), UV-vis, and fluorescence spectra are important properties in the understanding and designing OSMs for many photoelectronic applications, accurate predictions are still difficult to achieve.

In this work, we examined eleven functionals, i.e. B3LYP[100,101], CAMB3LYP[102], HSEH1PBE[103,104], PBE[105], TPSS[106], HCTH[107] LSDA[108-110] wB97XD,[111] mPW1PW91,[112] B3PW91,[113] BPV86.[113-115] in their calculations of the energies of the frontier orbitals, UV-vis and fluorescence spectra of diphenylamino-nitro-trans-stilbene and compared them as well as with the experimental results. The choice of diphenylamino-nitro-trans-stilbene, also denoted often as benzenamine, 4[(1E)-2-(4-nitrophenyl)ethenyl]-N,N-diphenyl-(9Cl,ACl) or 4-[(1E)-2-(4-Nitrophenyl)ethenyl]-N,N-diphenylbenzenamine(ACI), as shown in Fig. 1 comes

from the fact that it is one of the most polar molecule among the seven molecules being studied in our work,[97] which allow the stringiest examination of the accuracy of the functionals. Structures of both ground state and excited state were calculated using these functionals. The TDDFT calculations of both ground and excited states were carried out to obtain VU-vis and fluorescence spectra.

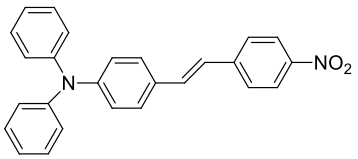


Figure 1. Structure of diphenylamino-nitro-trans-stilbene

2. Computational details

All calculations were performed using Gaussian09 software.[116] The solvent used is dichloromethane so that comparisons can be made with experiments. The solvent was treated using the polarized continuum model (PCM) for all calculations. Ground state geometry optimization of diphenylamino-nitro-trans-stilbene was performed using all eleven functionals. The excited geometry optimization was performed using TD-DFT calculations using eleven functionals. However, the optimization using TPSS was failed. The UV-vis and fluorescence spectra of the molecule was obtained using TD-DFT on the ground and excited state geometry, respectively.

Full geometry optimizations were performed without any constraints. Default convergence criteria were used in all calculations, which were also used previously in our DFT calculations:[117-123]The self-consistent field convergence was 10^{-8} a.u.; the gradient and energy

convergences were 10^{-4} and 10^{-5} a.u., respectively. Except for the excited state optimization of the molecule using TPSS functional, all geometry optimizations were carried out successfully.

3. Results and discussion

The results from DFT calculations of diphenylamino-nitro-trans-stilbene were summarized in Tables 1-15. In what follows, we first compare the electronic and optical properties obtained among the functionals and compare them with the experimental data. As shown in Table 1, the HOMO and LUMO energies of the molecule at the ground state and the excited state are very different among the functionals. In comparison to the experimental values, B3LYP and B3PW91 seems to be more accurate.

Table 1. The HOMO and LUMO energies of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground and the excited S_1 states

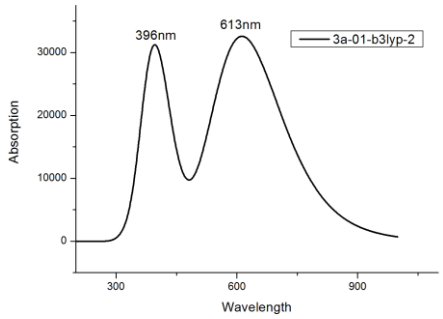
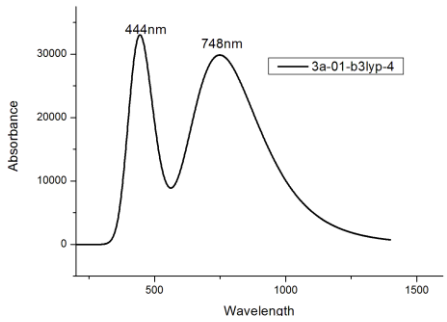
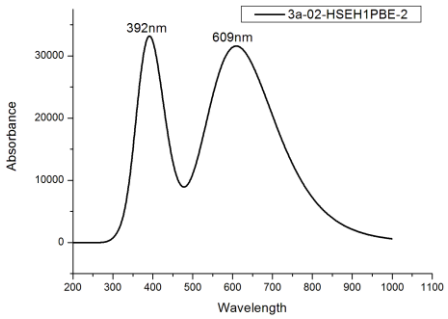
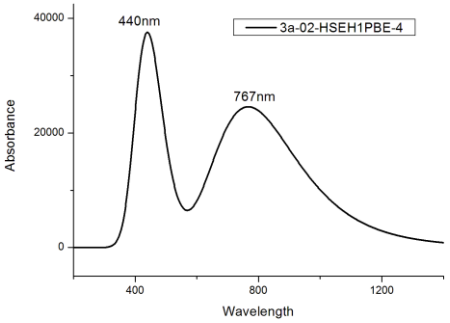
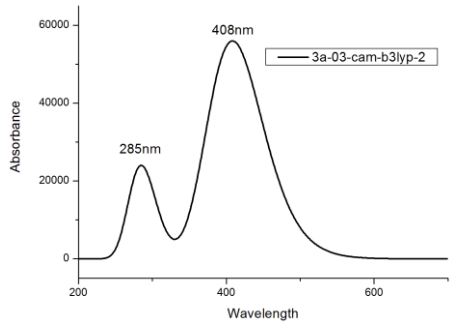
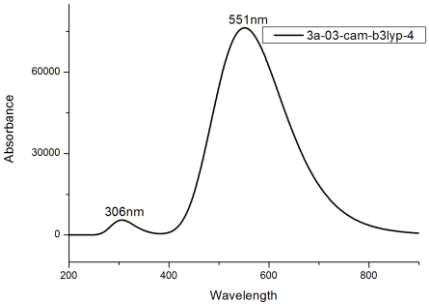
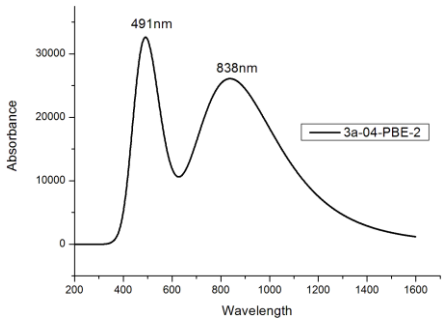
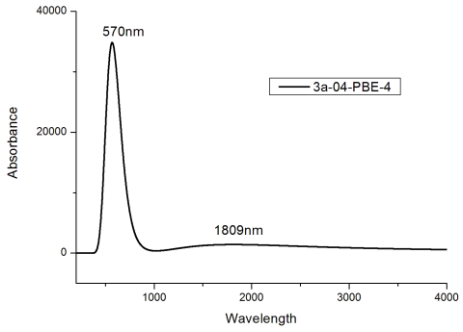
	Ground state			Excited S_1 state		
Functionals	HOMO /eV	LUMO /eV	Gap /eV	HOMO /eV	LUMO /eV	Gap /eV
1.B3LYP	-5.33	-3.08	2.25	-5.31	-3.38	1.93
2. HSEH1PBE	-5.16	-3.22	1.94	-5.14	-3.55	1.59
3. CAM-B3LYP	-6.52	-1.86	4.66	-6.35	-2.2	4.15
4. PBE	-4.78	-3.61	1.17	-4.69	-4.02	0.67
5. TPSS	-4.72	-3.52	1.2	--	--	--
6. HCTH	-4.91	-3.66	1.25	-4.83	-4.07	0.76
7. LSDA	-5.43	-4.26	1.17	-5.34	-4.67	0.67
8. BPV86	-4.86	-3.71	1.15	-4.77	-4.12	0.65
9. B3PW91	-5.39	-3.07	2.32	-5.36	-3.37	1.99
10. MPW1PW91	-5.53	-2.89	2.64	-5.5	-3.18	2.32
11. ωB97XD	-7.06	-1.25	5.81	-6.85	-1.61	5.24
Exp.*	-5.63	-3.51	2.12			

* data taken from Ref. [98].

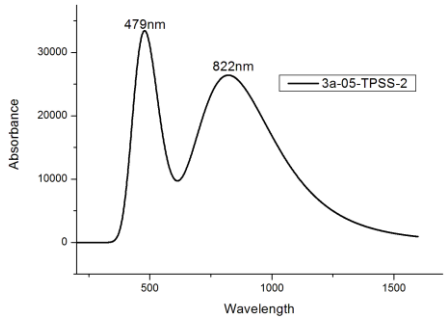
The calculated UV-vis spectra and the fluorescence spectra are summarized in Table 2.The experimental data of UV-vis and fluorescence spectra of the molecule in dichloromethane are

436 nm and 702 nm, respectively. Compared to the experimental values, the CAM-B3LYP and MPW1PW91 results are closer. However, the DFT results shown here indicate that further functionals are needed to describe the optical properties of polar OSMs.

Table 2. The UV-vis and fluorescence spectra of diphenylamino-nitro-trans-stilbene in dichloromethane

Functionals	UV-vis spectra	Fluorescence spectra
1.B3LYP		
2. HSEH1PBE		
3. CAM-B3LYP		
4. PBE		

5. TPSS*



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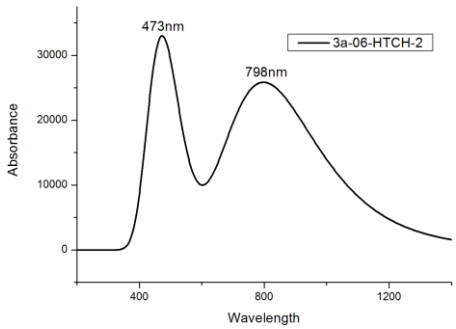
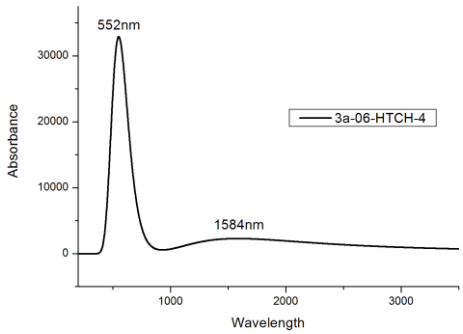
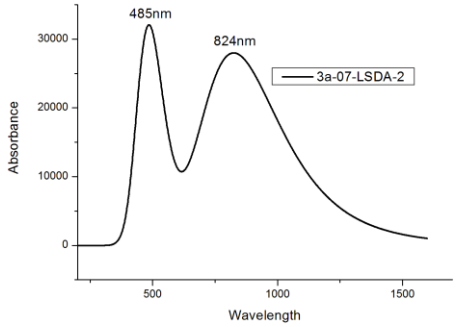
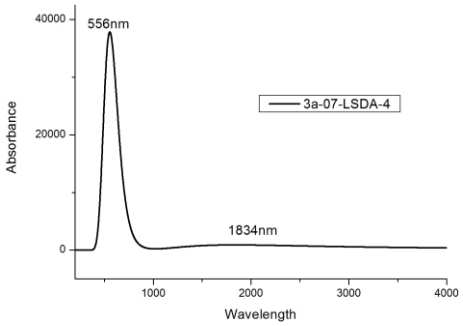
6. HCTH





7. LSDA





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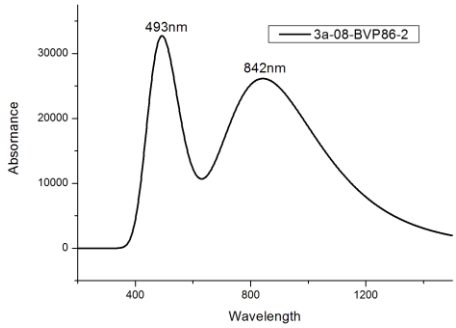
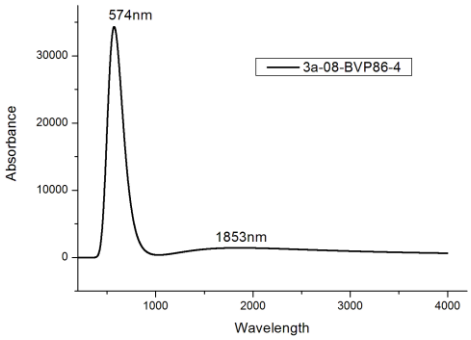
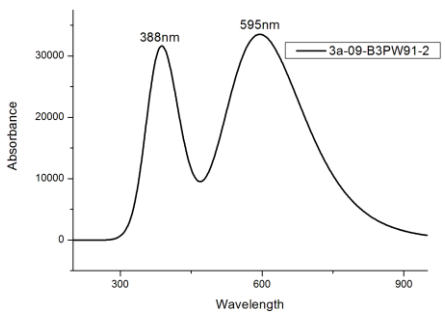
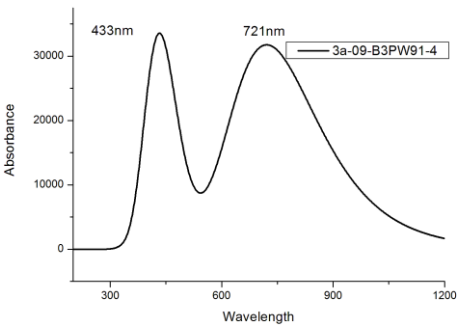


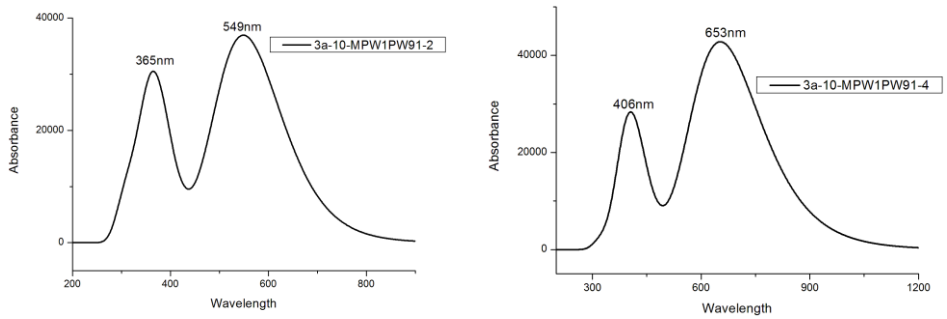


9. B3PW91

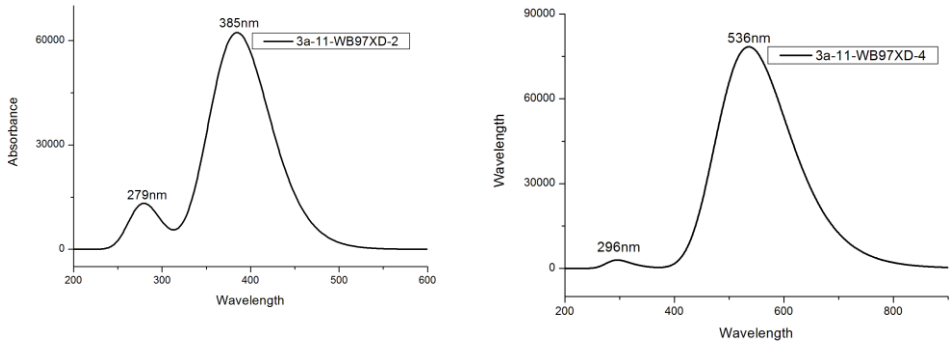




10. MPW1PW91



11. ωB97XD



Although there are great needs in the development of functionals, the DFT results are still useful in inspiring further explorations in the synthesis of organic small molecules, which involves dehydrogenation[124-127] and C-C bond cleavage and/or coupling[128-132] during catalytic reactions.[133-158] The usefulness of DFT studies often comes from the relative changes of the electronic and optical properties after functionalization of a molecule, which were predicted more accurately. Another aspect of DFT results are the elucidation of geometry parameters. In Fig. 2, we show four angles between various phenyl groups. The calculated dihedral angles of the molecule at the ground and the excited state are summarized in Table 3 and the pictures of the structures in Table 4.

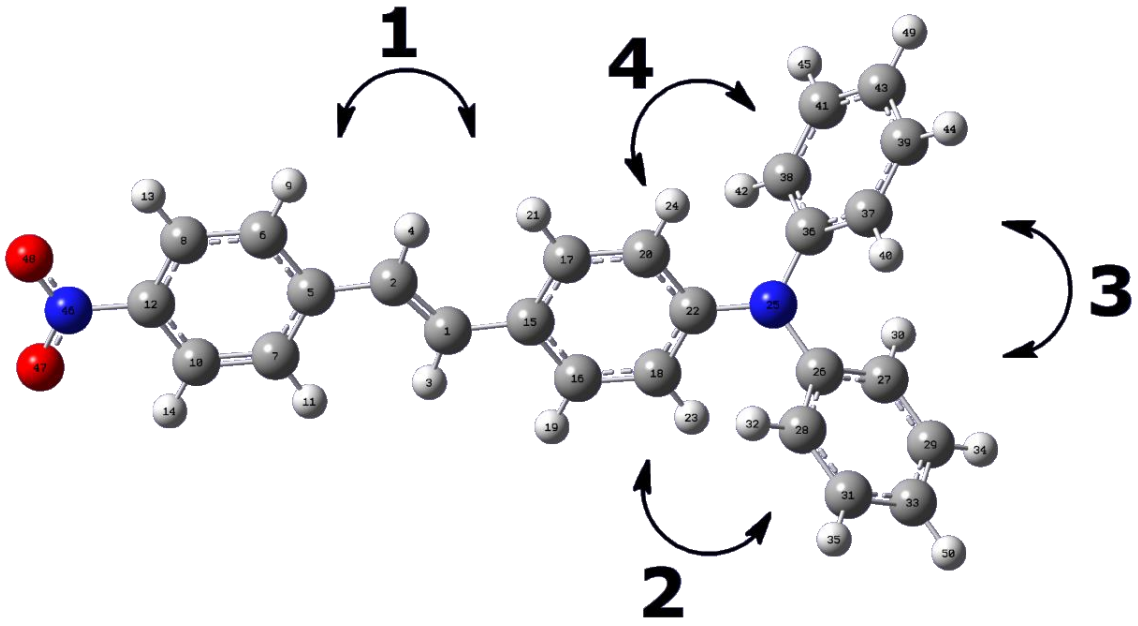
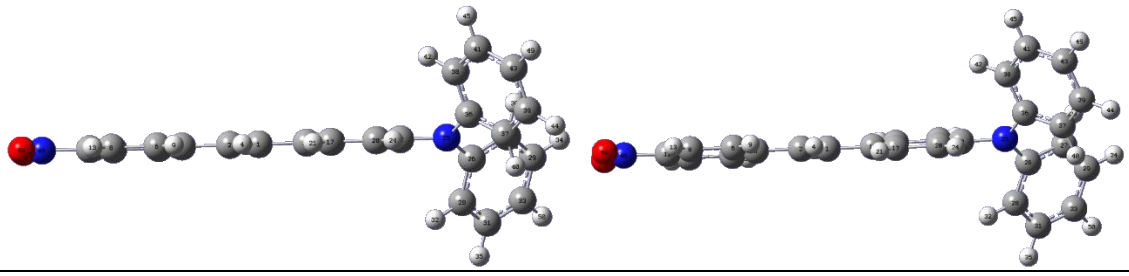
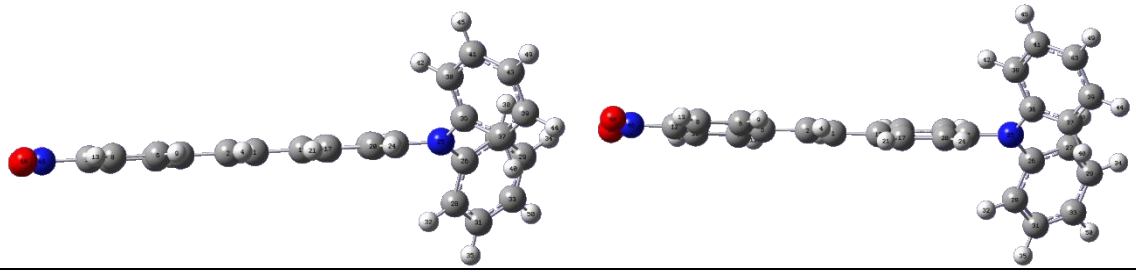
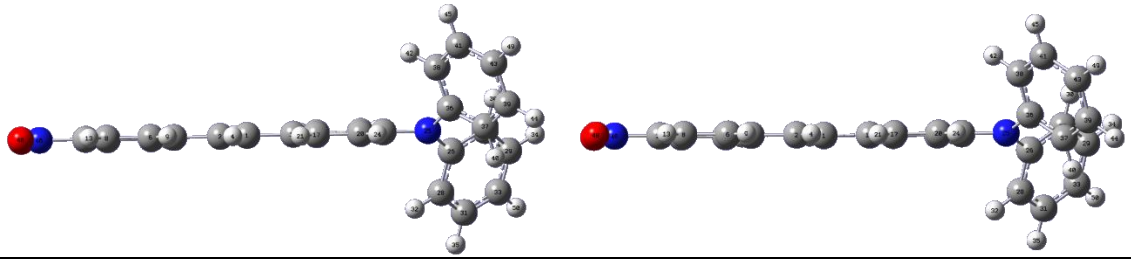


Figure 2. Four angles of diphenylamino-nitro-trans-stilbene: **1**-between phenyl C5-C6-C8-C12-C10-C7 and phenyl C15-C16-C18-C22-C20-C17; **2**-between phenyl C15-C16-C18-C22-C20-C17 and phenyl C26-C27-C29-C33-C31-C28; **3**-between phenyl C26-C27-C29-C33-C31-C28 and phenyl C36-C37-C39-C43-C41-C38; **4** -between phenyl C36-C37-C39-C43-C41-C38 and phenyl C15-C16-C18-C22-C20-C17;

Table 3. The four angles (in degree) shown in Fig. 2 of diphenylamino-nitro-trans-stilbene in dicholmethane

Functioanls	ground state				excited S_1 state			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
1.B3LYP	1.47	68.4	76.2	68.31	9.80	69.27	64.97	69.02
2. HSEH1PBE	2.40	65.73	73.63	66.21	13.55	69.71	60.37	69.34
3. CAM-B3LYP	2.49	68.31	74.78	68.46	0.62	65.22	79.73	65.29
4. PBE	1.64	65.22	73.80	65.58	16.51	80.59	52.94	80.13
5. TPSS*	2.56	64.88	73.37	64.72	----	----	----	----
6. HCTH	7.20	70.88	80.53	68.70	29.71	85.09	58.42	81.49
7. LSDA	0.93	60.25	68.09	60.93	7.89	78.70	48.10	78.07
8. BPV86	1.32	65.62	74.40	66.09	20.45	80.81	53.09	80.21
9. B3PW91	2.59	66.89	74.75	67.11	9.45	68.32	64.21	67.95
10. MPW1PW91	4.00	66.66	74.28	66.81	5.72	65.87	66.80	65.91
11. ωB97XD	7.45	70.28	75.28	66.31	4.65	67.20	80.29	63.85

Table 4. Molecular structures of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground (left) and excited S_1 (right) states obtained from different functionals.


1-B3LYP

2-HSEH1PBE

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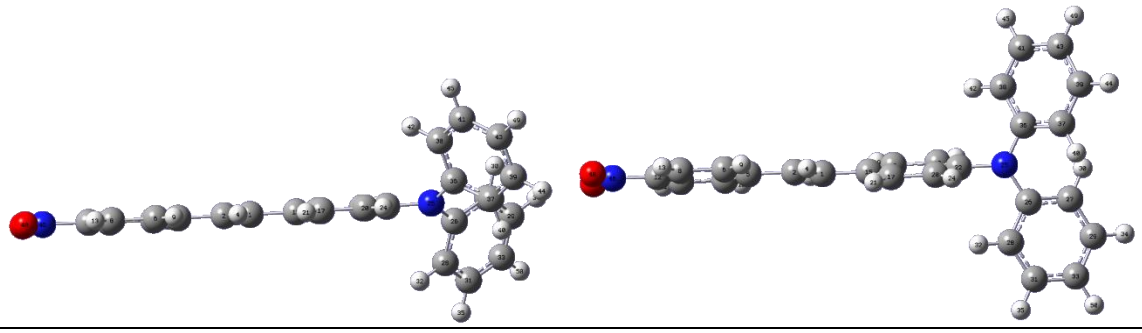
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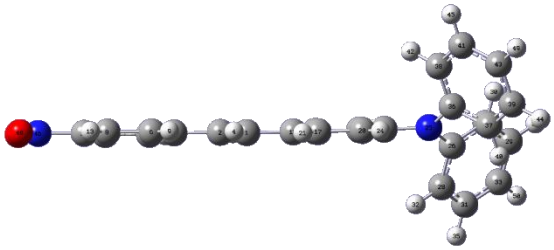
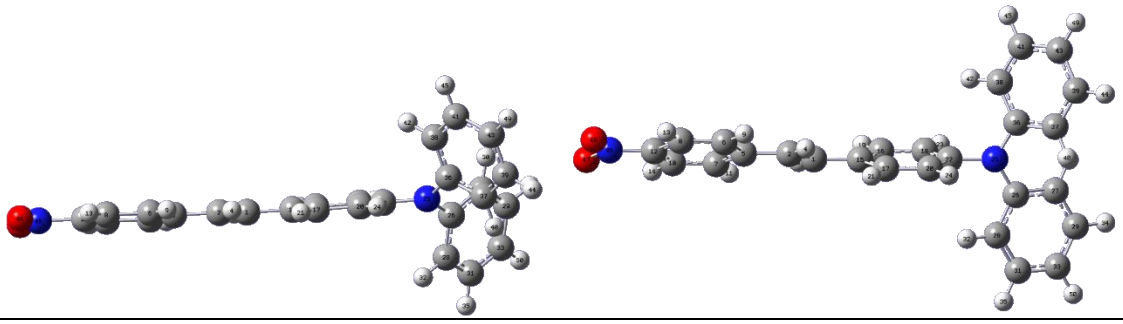
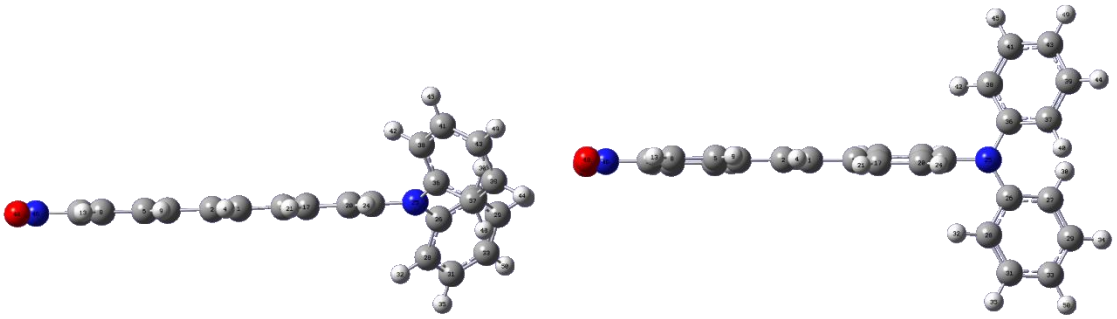
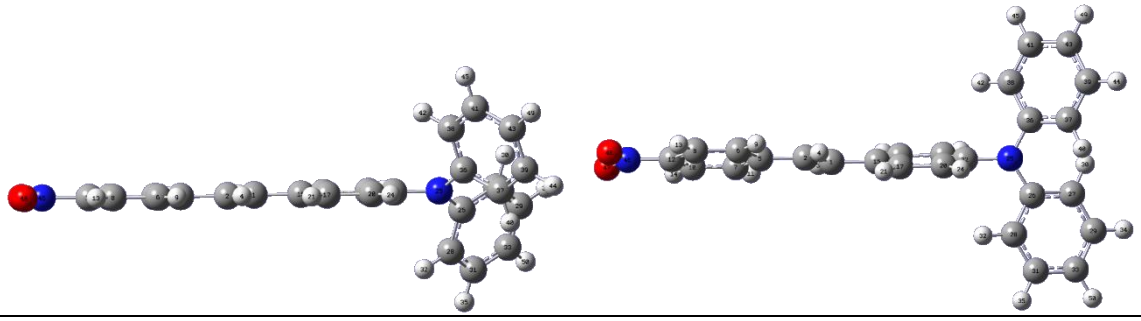

5-TPSS



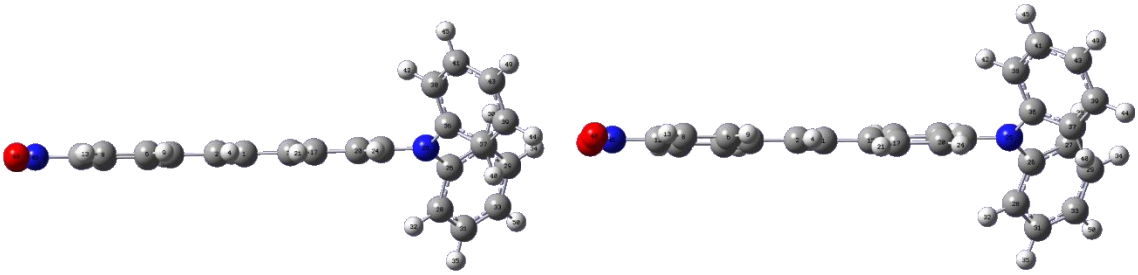
6-HCTH



7-LSDA



8-BPV86



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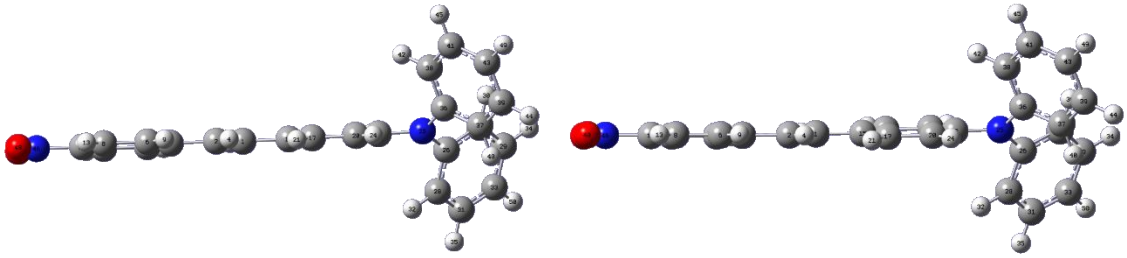
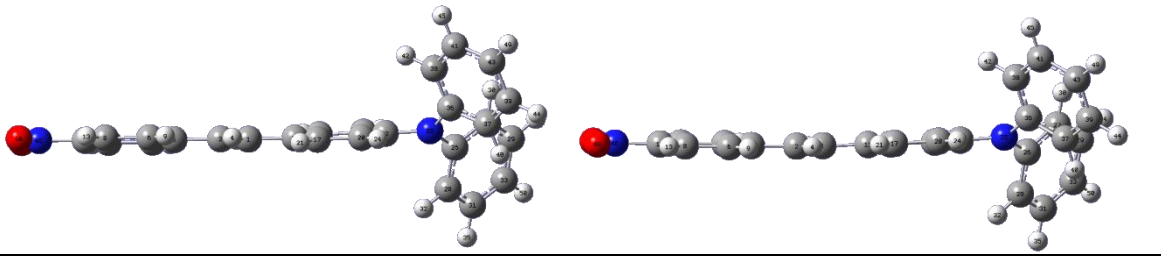


10-MPW1PW91



11-ωB97XD

As shown in Tables 3 and 4, there are differences in the predicted values among the functionals. Understandably, these differences will affect the electronic and optical properties being calculated. We do note that the structures at the ground and excited states are the local minima. Dynamics simulation[159-162] will be necessary to understand the changes of the structures at room temperature due to vibrational and rotational motions of the molecule and the impact of the structural changes on the electronic and optical properties. In addition to the four dihedral angles, the other geometry parameters, such as bond lengths, torsion angles, and other dihedral angles of the molecule at the ground and excited states are summarized in Tables 5-16.

Table 5. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from B3LYP

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.36	--	--	1.36	--	--
3	H	1	2		1.09	118.7	--	1.09	119.4	--
4	H	2	1	3	1.09	119.1	-179.6	1.09	118.6	-178.3
5	C	2	1	3	1.46	126.4	0.1	1.46	127.4	0.9
6	C	5	2	1	1.42	118.5	-179	1.41	119	-175.9
7	C	5	2	1	1.42	123.8	0.9	1.42	123.6	4
8	C	6	5	2	1.39	121.7	179.8	1.39	122	179.5
9	H	6	5	2	1.09	119.1	0	1.09	119.1	-0.2
10	C	7	5	2	1.39	121.3	-179.7	1.39	121.5	-179.5
11	H	7	5	2	1.08	120.3	0.3	1.09	120.1	0.7
12	C	8	6	5	1.4	118.8	0	1.41	119.4	0.1
13	H	8	6	5	1.08	121.1	-179.8	1.08	121.2	-179.8
14	H	10	7	5	1.08	120.9	-179.9	1.08	121	-179.8
15	C	1	2	5	1.46	127.1	180	1.46	126	180
16	C	15	1	2	1.41	119.1	-179.5	1.41	118.8	-174.2
17	C	15	1	2	1.41	124	0.5	1.42	123.8	5.8
18	C	16	15	1	1.39	122	179.7	1.39	121.8	179.6
19	H	16	15	1	1.09	119.2	0.6	1.09	119.2	0.6
20	C	17	15	1	1.39	121.5	179.9	1.39	121.4	-179.4
21	H	17	15	1	1.09	120.2	0.9	1.08	120.2	1.6
22	C	18	16	15	1.41	120.5	0.4	1.41	119.8	0
23	H	18	16	15	1.08	119.7	-179.1	1.08	120.2	-178.4
24	H	20	17	15	1.08	119.5	-179.1	1.08	120	-178.7
25	N	22	18	16	1.41	121.2	179.9	1.42	120.3	-179.7
26	C	25	22	18	1.43	120.7	-32.9	1.41	119.6	-44.1
27	C	26	25	22	1.4	120.2	133.9	1.41	120.2	141.7
28	C	26	25	22	1.4	120.5	-46.8	1.41	120	-37.5
29	C	27	26	25	1.4	120.2	179	1.39	119.7	-179.5
30	H	27	26	25	1.09	119.6	-0.8	1.08	119.8	-1.3
31	C	28	26	25	1.4	120.2	-179.6	1.39	119.7	179.8
32	H	28	26	25	1.09	119.6	0.1	1.08	119.8	-1.8
33	C	29	27	26	1.4	120.5	0.7	1.4	120.4	-0.2
34	H	29	27	26	1.09	119.4	-179.9	1.09	119.4	179
35	H	31	28	26	1.09	119.4	179.9	1.09	119.4	179
36	C	25	22	18	1.43	120.4	146.1	1.41	119.7	135.7
37	C	36	25	22	1.4	120.2	134	1.41	120.2	141.9
38	C	36	25	22	1.4	120.5	-46.5	1.41	120	-37.3
39	C	37	36	25	1.4	120.2	179.2	1.39	119.7	-179.4
40	H	37	36	25	1.09	119.6	-0.6	1.08	119.8	-1.3
41	C	38	36	25	1.4	120.2	-179.9	1.39	119.7	179.7
42	H	38	36	25	1.09	119.6	0	1.08	119.8	-1.8
43	C	39	37	36	1.4	120.5	0.7	1.4	120.4	-0.2
44	H	39	37	36	1.09	119.4	180	1.09	119.4	179
45	H	41	38	36	1.09	119.4	179.9	1.09	119.4	179
46	N	12	8	6	1.45	119.4	-179.8	1.41	120.2	-179.7
47	O	46	12	8	1.24	118.5	180	1.28	119.1	-179.5

48	O	46	12	8	1.24	118.5	0	1.28	119.1	0.4
49	H	43	39	37	1.09	120.3	179.7	1.09	120.1	-179.7
50	H	33	29	27	1.09	120.3	179.7	1.09	120.1	-179.7

Table 6. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from HSEH1PBE

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.35	--	--	1.35	--	--
3	H	1	2		1.09	118.8	--	1.09	119.5	--
4	H	2	1	3	1.09	119.2	-179.4	1.09	118.6	-177.8
5	C	2	1	3	1.45	126.2	0.1	1.46	127.2	1.3
6	C	5	2	1	1.41	118.4	-178.9	1.41	119	-175.2
7	C	5	2	1	1.41	123.7	0.9	1.41	123.5	4.6
8	C	6	5	2	1.38	121.7	179.7	1.39	121.9	179.4
9	H	6	5	2	1.09	119.1	-0.1	1.09	119	-0.2
10	C	7	5	2	1.38	121.2	-179.6	1.38	121.5	-179.4
11	H	7	5	2	1.08	120.3	0.3	1.09	120.1	0.8
12	C	8	6	5	1.39	118.8	0	1.41	119.4	0.1
13	H	8	6	5	1.08	121.3	-179.8	1.08	121.4	-179.8
14	H	10	7	5	1.08	121.1	180	1.08	121.2	-179.8
15	C	1	2	5	1.45	126.9	179.8	1.46	125.8	179.9
16	C	15	1	2	1.41	119.1	-178.5	1.41	118.8	-171.1
17	C	15	1	2	1.41	123.9	1.3	1.41	123.6	8.9
18	C	16	15	1	1.39	122	179.4	1.39	121.7	179.4
19	H	16	15	1	1.09	119.1	0.4	1.09	119.2	0.3
20	C	17	15	1	1.38	121.5	-179.7	1.39	121.3	-179.3
21	H	17	15	1	1.09	120.2	1.2	1.08	120.2	1.7
22	C	18	16	15	1.4	120.4	0.4	1.4	119.6	0.2
23	H	18	16	15	1.09	119.8	-179	1.09	120.4	-178.5
24	H	20	17	15	1.09	119.7	-179.2	1.09	120.2	-178.8
25	N	22	18	16	1.4	121.2	-179.8	1.42	120.1	-179.7
26	C	25	22	18	1.42	120.8	-31.6	1.4	119.3	-47.4
27	C	26	25	22	1.4	120.1	135.6	1.41	120.3	144.4
28	C	26	25	22	1.4	120.5	-45.1	1.41	119.8	-34.4
29	C	27	26	25	1.39	120.2	179	1.39	119.7	-179.4
30	H	27	26	25	1.09	119.5	-0.8	1.08	119.8	-1.6
31	C	28	26	25	1.39	120.1	-179.6	1.39	119.7	179.7
32	H	28	26	25	1.09	119.6	0.2	1.08	119.7	-2
33	C	29	27	26	1.39	120.5	0.7	1.4	120.4	0
34	H	29	27	26	1.09	119.4	-179.9	1.09	119.4	178.9
35	H	31	28	26	1.09	119.4	179.9	1.09	119.4	178.9
36	C	25	22	18	1.42	120.3	146.7	1.4	119.3	132.4
37	C	36	25	22	1.4	120.2	135.7	1.41	120.3	144.7
38	C	36	25	22	1.4	120.4	-44.9	1.41	119.8	-34
39	C	37	36	25	1.39	120.1	179.2	1.39	119.7	-179.4
40	H	37	36	25	1.09	119.5	-0.6	1.08	119.8	-1.6
41	C	38	36	25	1.39	120.1	-179.8	1.39	119.7	179.7
42	H	38	36	25	1.09	119.6	0	1.08	119.7	-2
43	C	39	37	36	1.4	120.5	0.8	1.4	120.4	0.1

44	H	39	37	36	1.09	119.4	180	1.09	119.4	178.9
45	H	41	38	36	1.09	119.4	179.9	1.09	119.5	178.9
46	N	12	8	6	1.44	119.3	-179.8	1.41	120.2	-179.7
47	O	46	12	8	1.23	118.3	179.8	1.27	119	-179.6
48	O	46	12	8	1.23	118.3	0	1.27	118.9	0.3
49	H	43	39	37	1.09	120.3	179.6	1.09	120	179.9
50	H	33	29	27	1.09	120.3	179.7	1.09	120	180

Table 7. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from cam-B3LYP

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.34	--	--	1.4	--	--
3	H	1	2		1.09	119	--	1.09	118.6	--
4	H	2	1	3	1.09	119.4	-179.5	1.09	118	180
5	C	2	1	3	1.46	126.1	0.1	1.41	126.6	0
6	C	5	2	1	1.4	118.4	-178.3	1.43	119.3	-179.6
7	C	5	2	1	1.41	123.5	1.6	1.43	123.7	0.2
8	C	6	5	2	1.38	121.6	179.8	1.37	122	179.9
9	H	6	5	2	1.09	119.3	0	1.09	118.6	0
10	C	7	5	2	1.38	121.2	-179.7	1.37	121.4	-179.8
11	H	7	5	2	1.08	120.4	0.3	1.08	119.9	0.1
12	C	8	6	5	1.39	118.6	0.1	1.41	120	0
13	H	8	6	5	1.08	121.2	-179.8	1.08	121.4	-179.9
14	H	10	7	5	1.08	121	-179.9	1.08	121.1	180
15	C	1	2	5	1.46	126.9	180	1.41	125.6	179.9
16	C	15	1	2	1.4	119	-179.2	1.43	119.4	-179.4
17	C	15	1	2	1.4	123.7	0.8	1.43	124.2	0.4
18	C	16	15	1	1.39	121.8	179.6	1.37	122.3	-179.8
19	H	16	15	1	1.09	119.2	0.4	1.09	118.5	1.2
20	C	17	15	1	1.38	121.4	179.8	1.37	121.7	-179.5
21	H	17	15	1	1.08	120.3	0.7	1.08	119.9	1.5
22	C	18	16	15	1.4	120.4	0.6	1.42	121	-0.3
23	H	18	16	15	1.08	119.8	-179.1	1.08	119.9	-178.6
24	H	20	17	15	1.08	119.6	-179.1	1.08	119.6	-178.7
25	N	22	18	16	1.41	121.1	179.7	1.37	120.9	180
26	C	25	22	18	1.42	120.5	-34.5	1.43	121.2	154.7
27	C	26	25	22	1.4	120.3	134.7	1.4	119.7	131.7
28	C	26	25	22	1.4	120.5	-45.8	1.4	120.1	-49.4
29	C	27	26	25	1.39	120.2	179.1	1.39	119.7	179.1
30	H	27	26	25	1.08	119.5	-0.6	1.08	119.8	-1
31	C	28	26	25	1.39	120.2	-179.8	1.39	119.7	-179.3
32	H	28	26	25	1.08	119.5	0.1	1.08	119.8	0
33	C	29	27	26	1.39	120.5	0.8	1.39	120.3	0.4
34	H	29	27	26	1.09	119.4	-179.8	1.08	119.5	179.7
35	H	31	28	26	1.09	119.4	-179.9	1.08	119.5	179.7
36	C	25	22	18	1.42	120.3	144.1	1.43	121.1	-25.2
37	C	36	25	22	1.4	120.2	135.4	1.4	119.7	131.1
38	C	36	25	22	1.4	120.5	-45	1.4	120	-49.9
39	C	37	36	25	1.39	120.2	179.3	1.39	119.7	179.2

40	H	37	36	25	1.08	119.5	-0.5	1.08	119.8	-1
41	C	38	36	25	1.39	120.2	179.9	1.39	119.7	-179.4
42	H	38	36	25	1.08	119.6	0	1.08	119.8	-0.1
43	C	39	37	36	1.39	120.5	0.8	1.39	120.3	0.4
44	H	39	37	36	1.09	119.4	-179.8	1.08	119.5	179.7
45	H	41	38	36	1.09	119.4	-179.9	1.08	119.5	179.7
46	N	12	8	6	1.45	119.2	-179.9	1.4	119.9	179.9
47	O	46	12	8	1.23	118.4	-179.8	1.26	119.4	0.1
48	O	46	12	8	1.23	118.4	0.1	1.26	119.1	-179.8
49	H	43	39	37	1.08	120.3	179.6	1.08	120.1	179.8
50	H	33	29	27	1.08	120.3	179.6	1.08	120.1	179.8

Table 8. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from PBE

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.37	--	--	1.36	--	--
3	H	1	2		1.1	118.6	--	1.1	119.4	--
4	H	2	1	3	1.1	118.9	-179.6	1.1	118.4	-177.5
5	C	2	1	3	1.45	126.4	0	1.47	127.6	1.8
6	C	5	2	1	1.42	118.6	-179.3	1.42	119	-176.7
7	C	5	2	1	1.43	123.9	0.5	1.42	123.8	3.4
8	C	6	5	2	1.39	121.8	179.7	1.4	122	179.9
9	H	6	5	2	1.09	119	-0.1	1.1	119	0
10	C	7	5	2	1.39	121.4	-179.6	1.39	121.6	-179.7
11	H	7	5	2	1.09	120.2	0.3	1.09	120	0.4
12	C	8	6	5	1.41	118.9	0	1.41	119.5	0
13	H	8	6	5	1.09	121.3	-179.8	1.09	121.5	-179.9
14	H	10	7	5	1.09	121.1	180	1.09	121.2	-179.9
15	C	1	2	5	1.45	127.1	179.8	1.47	125.9	-179.7
16	C	15	1	2	1.42	119.1	-178.9	1.42	119.1	-167.1
17	C	15	1	2	1.42	124	0.9	1.42	123.5	13.2
18	C	16	15	1	1.39	122.1	179.5	1.4	121.8	179.4
19	H	16	15	1	1.1	119	0.5	1.09	119.2	-0.7
20	C	17	15	1	1.39	121.6	-179.5	1.4	121.4	-179.4
21	H	17	15	1	1.09	120.1	1.4	1.09	120.2	0.7
22	C	18	16	15	1.42	120.4	0.1	1.4	119.1	0.5
23	H	18	16	15	1.09	119.9	-179	1.09	120.7	179.8
24	H	20	17	15	1.09	119.7	-179.1	1.09	120.5	179.6
25	N	22	18	16	1.41	121.2	-179.6	1.46	119.7	-179.9
26	C	25	22	18	1.43	120.9	-30.5	1.41	119	-86.7
27	C	26	25	22	1.41	120	135.6	1.42	120.2	150.8
28	C	26	25	22	1.41	120.5	-45.3	1.42	120	-25.9
29	C	27	26	25	1.4	120.1	178.9	1.4	119.8	-178.7
30	H	27	26	25	1.09	119.6	-0.9	1.09	119.9	-2.1
31	C	28	26	25	1.4	120	-179.4	1.39	119.6	179.5
32	H	28	26	25	1.09	119.6	0.2	1.09	120	-1.7
33	C	29	27	26	1.41	120.5	0.6	1.41	120.4	0.1
34	H	29	27	26	1.09	119.4	179.9	1.09	119.4	178.8
35	H	31	28	26	1.09	119.3	179.8	1.09	119.3	178.6

36	C	25	22	18	1.43	120.4	148.1	1.41	118.5	94
37	C	36	25	22	1.41	120.1	135.5	1.42	120.1	146.5
38	C	36	25	22	1.41	120.4	-45.3	1.42	120	-29.9
39	C	37	36	25	1.4	120	179.2	1.4	119.7	-178.3
40	H	37	36	25	1.09	119.5	-0.8	1.09	119.9	-1.6
41	C	38	36	25	1.4	120	-179.7	1.39	119.6	179.1
42	H	38	36	25	1.09	119.6	0	1.09	120	-2.1
43	C	39	37	36	1.41	120.5	0.8	1.41	120.3	0.1
44	H	39	37	36	1.09	119.4	179.9	1.09	119.4	178.7
45	H	41	38	36	1.09	119.4	179.8	1.09	119.3	178.6
46	N	12	8	6	1.45	119.5	-179.8	1.43	120.2	-179.8
47	O	46	12	8	1.25	118.4	179.8	1.29	118.9	179.8
48	O	46	12	8	1.25	118.4	0	1.29	118.7	-0.1
49	H	43	39	37	1.09	120.3	179.6	1.09	120.1	179.8
50	H	33	29	27	1.09	120.3	179.8	1.09	120.1	179.9

Table 9. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from TPSS

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--			
2	C	1			1.37	--	--			
3	H	1	2		1.09	118.7	--			
4	H	2	1	3	1.09	119	-179.4			
5	C	2	1	3	1.45	126.3	0			
6	C	5	2	1	1.42	118.5	-179.1			
7	C	5	2	1	1.42	123.9	0.7			
8	C	6	5	2	1.39	121.8	179.6			
9	H	6	5	2	1.09	119	-0.2			
10	C	7	5	2	1.39	121.3	-179.5			
11	H	7	5	2	1.09	120.2	0.4			
12	C	8	6	5	1.41	118.8	0			
13	H	8	6	5	1.09	121.4	-179.8			
14	H	10	7	5	1.09	121.2	179.9			
15	C	1	2	5	1.45	127	179.6			
16	C	15	1	2	1.42	119.1	-178.2			
17	C	15	1	2	1.42	124	1.5			
18	C	16	15	1	1.39	122.1	179.1			
19	H	16	15	1	1.09	119	0.3			
20	C	17	15	1	1.39	121.6	-179.3			
21	H	17	15	1	1.09	120.2	1.6			
22	C	18	16	15	1.42	120.3	0.3			
23	H	18	16	15	1.09	119.9	-178.8			
24	H	20	17	15	1.09	119.7	-179.1			
25	N	22	18	16	1.41	121.2	-179.4			
26	C	25	22	18	1.43	121	-29.7			
27	C	26	25	22	1.41	119.9	135.4			
28	C	26	25	22	1.41	120.5	-45.5			
29	C	27	26	25	1.4	120	178.8			
30	H	27	26	25	1.09	119.6	-1			
31	C	28	26	25	1.4	119.9	-179.4			

32	H	28	26	25	1.09	119.7	0.2
33	C	29	27	26	1.4	120.5	0.6
34	H	29	27	26	1.09	119.4	179.9
35	H	31	28	26	1.09	119.3	179.8
36	C	25	22	18	1.43	120.4	148.2
37	C	36	25	22	1.41	120	136.1
38	C	36	25	22	1.41	120.3	-44.6
39	C	37	36	25	1.4	120	179.1
40	H	37	36	25	1.09	119.6	-0.8
41	C	38	36	25	1.4	120	-179.7
42	H	38	36	25	1.09	119.7	0
43	C	39	37	36	1.4	120.5	0.8
44	H	39	37	36	1.09	119.4	179.9
45	H	41	38	36	1.09	119.4	179.9
46	N	12	8	6	1.45	119.4	-179.8
47	O	46	12	8	1.26	118.5	179.8
48	O	46	12	8	1.26	118.5	0
49	H	43	39	37	1.09	120.3	179.6
50	H	33	29	27	1.09	120.3	179.7

Table 10. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from HCTH

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.36	--	--	1.35	--	--
3	H	1	2		1.09	118.4	--	1.09	119.3	--
4	H	2	1	3	1.09	118.7	-178.5	1.09	118.1	-176
5	C	2	1	3	1.45	127	0.5	1.46	128	2.7
6	C	5	2	1	1.42	118.6	-177	1.41	119.2	-172.1
7	C	5	2	1	1.42	124.3	2.8	1.41	124	8.2
8	C	6	5	2	1.39	122	179.6	1.39	122.2	179.7
9	H	6	5	2	1.09	119.1	-0.2	1.09	119.1	0
10	C	7	5	2	1.38	121.5	-179.5	1.39	121.8	-179.7
11	H	7	5	2	1.09	120.4	0.6	1.09	120.1	0.7
12	C	8	6	5	1.4	119.2	0.2	1.41	119.8	0.2
13	H	8	6	5	1.08	120.8	-179.7	1.08	120.8	-179.7
14	H	10	7	5	1.08	120.5	-179.9	1.08	120.6	-179.7
15	C	1	2	5	1.45	127.6	179.6	1.47	126.1	-179.5
16	C	15	1	2	1.41	119.1	-175.5	1.41	119.2	-158.8
17	C	15	1	2	1.41	124.4	4.2	1.41	123.5	21.8
18	C	16	15	1	1.39	122.3	178.8	1.39	121.8	179.5
19	H	16	15	1	1.09	119.1	0.1	1.09	119.4	-0.4
20	C	17	15	1	1.38	121.8	-179	1.39	121.5	-179.5
21	H	17	15	1	1.09	120.3	2.2	1.09	120.2	1.1
22	C	18	16	15	1.41	120.6	0.4	1.39	119.3	0.6
23	H	18	16	15	1.09	119.4	-178.6	1.09	120.4	179.9
24	H	20	17	15	1.09	119.2	-179	1.09	120.2	-179.9
25	N	22	18	16	1.4	121.4	-179.4	1.45	119.8	179.9
26	C	25	22	18	1.42	120.9	-30.6	1.39	119.4	-82
27	C	26	25	22	1.4	120.2	129.5	1.42	120.3	151.4

28	C	26	25	22	1.4	120.5	-51.4	1.42	120.5	-25.5
29	C	27	26	25	1.39	120.2	178.8	1.39	120	-178.4
30	H	27	26	25	1.09	119.7	-1.1	1.08	120	-1.6
31	C	28	26	25	1.39	120.2	-179.3	1.39	119.9	179.2
32	H	28	26	25	1.09	119.7	0.2	1.08	120.2	-2.2
33	C	29	27	26	1.4	120.5	0.5	1.4	120.4	0
34	H	29	27	26	1.09	119.4	179.9	1.09	119.3	178.6
35	H	31	28	26	1.09	119.4	179.8	1.09	119.3	178.7
36	C	25	22	18	1.42	120.7	147.6	1.41	118.3	99
37	C	36	25	22	1.4	120.2	132.3	1.41	119.9	140.1
38	C	36	25	22	1.4	120.5	-48.5	1.41	120.4	-36.7
39	C	37	36	25	1.39	120.2	179	1.39	119.9	-178
40	H	37	36	25	1.09	119.7	-1	1.08	120	-0.9
41	C	38	36	25	1.39	120.2	-179.6	1.39	119.7	178.9
42	H	38	36	25	1.09	119.7	0	1.08	120.2	-2.4
43	C	39	37	36	1.4	120.5	0.6	1.4	120.4	-0.1
44	H	39	37	36	1.09	119.4	179.9	1.09	119.3	178.7
45	H	41	38	36	1.09	119.4	179.8	1.09	119.3	178.6
46	N	12	8	6	1.45	119.7	-179.8	1.42	120.5	180
47	O	46	12	8	1.24	118.4	-179.5	1.27	118.9	-179.9
48	O	46	12	8	1.24	118.4	0.4	1.27	118.8	0
49	H	43	39	37	1.09	120.3	179.7	1.09	120.1	180
50	H	33	29	27	1.09	120.3	179.8	1.09	120.1	179.9

Table 11. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from LSDA

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.36	--	--	1.35	--	--
3	H	1	2		1.1	118.7	--	1.1	119.2	--
4	H	2	1	3	1.1	119	-179.7	1.1	118.6	-178.6
5	C	2	1	3	1.44	125.9	0	1.44	127.1	1.1
6	C	5	2	1	1.41	118.7	-179.8	1.41	119.3	-177.7
7	C	5	2	1	1.41	123.4	0	1.41	123.1	2.5
8	C	6	5	2	1.38	121.6	179.7	1.38	121.9	-179.9
9	H	6	5	2	1.1	118.7	-0.1	1.1	118.7	0.1
10	C	7	5	2	1.38	121.2	-179.6	1.38	121.4	180
11	H	7	5	2	1.1	119.9	0.2	1.1	119.6	0.2
12	C	8	6	5	1.39	118.7	0	1.4	119.3	0.1
13	H	8	6	5	1.09	122.1	-179.9	1.09	122.3	-179.9
14	H	10	7	5	1.09	121.9	179.9	1.09	122.2	-179.8
15	C	1	2	5	1.43	126.6	179.8	1.45	125.8	-179.3
16	C	15	1	2	1.41	119.3	-179.2	1.4	119.1	-174.9
17	C	15	1	2	1.41	123.5	0.7	1.4	123.3	5.2
18	C	16	15	1	1.38	121.9	179.7	1.39	121.7	-179.9
19	H	16	15	1	1.1	118.7	0.6	1.1	118.9	-0.3
20	C	17	15	1	1.38	121.4	-179.4	1.39	121.3	179.8
21	H	17	15	1	1.1	119.9	1.3	1.1	119.9	-0.1
22	C	18	16	15	1.4	120.2	-0.1	1.39	119	0.3
23	H	18	16	15	1.1	120.2	-179.2	1.1	120.9	179.4

24	H	20	17	15	1.1	120.1	-179.3	1.1	120.8	179.6
25	N	22	18	16	1.39	121.1	-179.5	1.43	119.7	179.6
26	C	25	22	18	1.41	120.9	-28.6	1.39	118.7	-89.9
27	C	26	25	22	1.4	119.9	139.6	1.41	120.4	153.4
28	C	26	25	22	1.4	120.5	-41.2	1.41	119.6	-23.4
29	C	27	26	25	1.39	120	179.2	1.38	119.6	-179.2
30	H	27	26	25	1.1	119.3	-0.7	1.09	119.8	-2.9
31	C	28	26	25	1.39	120	-179.5	1.38	119.5	-179.9
32	H	28	26	25	1.1	119.4	0	1.09	119.6	-1.2
33	C	29	27	26	1.39	120.5	0.4	1.39	120.3	0.3
34	H	29	27	26	1.1	119.4	179.8	1.09	119.4	178.7
35	H	31	28	26	1.1	119.3	179.7	1.09	119.4	178.5
36	C	25	22	18	1.41	120.4	150.1	1.39	118.5	90.9
37	C	36	25	22	1.4	120	139.1	1.41	120.2	149.3
38	C	36	25	22	1.4	120.4	-41.6	1.4	119.6	-27.2
39	C	37	36	25	1.39	120	179.4	1.38	119.6	-178.7
40	H	37	36	25	1.1	119.2	-0.5	1.09	119.7	-2.5
41	C	38	36	25	1.39	120	-179.7	1.38	119.5	179.6
42	H	38	36	25	1.1	119.4	-0.1	1.09	119.6	-1.5
43	C	39	37	36	1.39	120.5	0.5	1.39	120.3	0.2
44	H	39	37	36	1.1	119.4	179.8	1.09	119.4	178.7
45	H	41	38	36	1.1	119.4	179.8	1.09	119.4	178.5
46	N	12	8	6	1.43	119.3	-179.8	1.4	120.1	179.9
47	O	46	12	8	1.24	118.3	179.7	1.27	118.8	179.9
48	O	46	12	8	1.24	118.3	-0.1	1.27	118.7	0
49	H	43	39	37	1.1	120.3	179.7	1.09	120	179.8
50	H	33	29	27	1.1	120.3	179.9	1.09	120	179.8

Table 12. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from BPV86

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.37	--	--	1.36	--	--
3	H	1	2		1.1	118.6	--	1.1	119.5	--
4	H	2	1	3	1.1	118.9	-179.6	1.1	118.3	-177
5	C	2	1	3	1.45	126.4	0	1.47	127.6	2.2
6	C	5	2	1	1.43	118.6	-179.3	1.42	119	-175.5
7	C	5	2	1	1.43	123.9	0.5	1.42	123.7	4.8
8	C	6	5	2	1.39	121.8	179.7	1.4	122	-179.8
9	H	6	5	2	1.09	119	-0.1	1.1	119	0.1
10	C	7	5	2	1.39	121.4	-179.6	1.4	121.6	179.9
11	H	7	5	2	1.09	120.2	0.3	1.09	120	0.3
12	C	8	6	5	1.41	118.9	0	1.41	119.5	0.1
13	H	8	6	5	1.09	121.3	-179.8	1.09	121.4	-179.9
14	H	10	7	5	1.09	121.1	180	1.09	121.2	-179.8
15	C	1	2	5	1.45	127.1	179.9	1.47	125.8	-179.3
16	C	15	1	2	1.42	119.1	-179.2	1.42	119.1	-164.7
17	C	15	1	2	1.42	124	0.7	1.42	123.3	15.7
18	C	16	15	1	1.39	122	179.6	1.4	121.7	179.4
19	H	16	15	1	1.1	119	0.6	1.09	119.3	-0.6

20	C	17	15	1	1.39	121.6	-179.7	1.4	121.4	-179.4
21	H	17	15	1	1.09	120.1	1.2	1.09	120.1	0.9
22	C	18	16	15	1.42	120.4	0.2	1.4	119.1	0.5
23	H	18	16	15	1.09	119.9	-179	1.09	120.6	179.8
24	H	20	17	15	1.09	119.7	-179.1	1.09	120.5	179.6
25	N	22	18	16	1.41	121.2	-179.7	1.46	119.6	179.9
26	C	25	22	18	1.43	120.9	-30.8	1.41	119	-86.4
27	C	26	25	22	1.41	120	135.3	1.42	120.2	150.8
28	C	26	25	22	1.41	120.5	-45.6	1.42	120	-25.9
29	C	27	26	25	1.4	120.1	178.9	1.4	119.8	-178.7
30	H	27	26	25	1.09	119.6	-1	1.09	119.9	-2
31	C	28	26	25	1.4	120	-179.4	1.39	119.6	179.5
32	H	28	26	25	1.09	119.6	0.1	1.09	120	-1.7
33	C	29	27	26	1.41	120.5	0.6	1.41	120.4	0.1
34	H	29	27	26	1.09	119.4	179.9	1.09	119.4	178.8
35	H	31	28	26	1.09	119.3	179.8	1.09	119.3	178.6
36	C	25	22	18	1.43	120.5	148	1.41	118.6	94.2
37	C	36	25	22	1.41	120.1	135	1.42	120	146.4
38	C	36	25	22	1.41	120.4	-45.7	1.42	120	-30
39	C	37	36	25	1.4	120	179.2	1.4	119.7	-178.3
40	H	37	36	25	1.09	119.5	-0.8	1.09	119.9	-1.6
41	C	38	36	25	1.4	120	-179.8	1.4	119.6	179
42	H	38	36	25	1.09	119.6	-0.1	1.09	120	-2.1
43	C	39	37	36	1.41	120.5	0.8	1.41	120.3	0.1
44	H	39	37	36	1.09	119.4	179.9	1.09	119.4	178.7
45	H	41	38	36	1.09	119.4	179.8	1.09	119.3	178.6
46	N	12	8	6	1.45	119.5	-179.8	1.43	120.2	179.8
47	O	46	12	8	1.26	118.5	179.9	1.29	118.9	-179.8
48	O	46	12	8	1.26	118.5	0	1.29	118.8	0
49	H	43	39	37	1.09	120.3	179.6	1.09	120.1	179.8
50	H	33	29	27	1.09	120.3	179.7	1.09	120.1	179.9

Table 13. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from B3PW91

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.36	--	--	1.36	--	--
3	H	1	2		1.09	118.8	--	1.09	119.4	--
4	H	2	1	3	1.09	119.1	-179.4	1.09	118.5	-178.3
5	C	2	1	3	1.45	126.3	0.1	1.46	127.4	0.9
6	C	5	2	1	1.41	118.4	-178.8	1.41	119	-176.2
7	C	5	2	1	1.41	123.8	1	1.41	123.6	3.6
8	C	6	5	2	1.39	121.7	179.7	1.39	122	179.5
9	H	6	5	2	1.09	119.2	-0.1	1.09	119.1	-0.2
10	C	7	5	2	1.38	121.3	-179.6	1.38	121.5	-179.4
11	H	7	5	2	1.08	120.3	0.3	1.09	120.1	0.7
12	C	8	6	5	1.4	118.8	0	1.41	119.4	0.1
13	H	8	6	5	1.08	121.2	-179.8	1.08	121.3	-179.8
14	H	10	7	5	1.08	121	180	1.08	121.1	-179.8
15	C	1	2	5	1.45	127	179.8	1.46	125.8	179.9

16	C	15	1	2	1.41	119	-178.5	1.41	118.8	-174.1
17	C	15	1	2	1.41	123.9	1.4	1.41	123.8	5.8
18	C	16	15	1	1.39	122	179.4	1.39	121.8	179.5
19	H	16	15	1	1.09	119.2	0.4	1.09	119.1	0.6
20	C	17	15	1	1.38	121.5	-179.7	1.38	121.4	-179.3
21	H	17	15	1	1.09	120.3	1.2	1.08	120.3	1.8
22	C	18	16	15	1.41	120.4	0.4	1.4	119.8	0.1
23	H	18	16	15	1.09	119.8	-179	1.09	120.3	-178.2
24	H	20	17	15	1.09	119.6	-179.1	1.09	120.1	-178.6
25	N	22	18	16	1.4	121.2	-179.8	1.41	120.3	-179.6
26	C	25	22	18	1.42	120.8	-32.1	1.41	119.7	-43.2
27	C	26	25	22	1.4	120.2	134.8	1.41	120.1	142
28	C	26	25	22	1.4	120.5	-45.9	1.41	119.9	-37.2
29	C	27	26	25	1.39	120.2	179	1.39	119.7	-179.5
30	H	27	26	25	1.09	119.6	-0.8	1.08	119.8	-1.4
31	C	28	26	25	1.39	120.1	-179.6	1.39	119.7	179.7
32	H	28	26	25	1.09	119.6	0.1	1.08	119.7	-1.9
33	C	29	27	26	1.4	120.5	0.7	1.4	120.4	-0.2
34	H	29	27	26	1.09	119.4	-179.9	1.09	119.4	179
35	H	31	28	26	1.09	119.4	179.9	1.09	119.4	179
36	C	25	22	18	1.42	120.4	146.2	1.41	119.7	136.4
37	C	36	25	22	1.4	120.2	135.1	1.41	120.2	142.4
38	C	36	25	22	1.4	120.5	-45.5	1.41	119.9	-36.8
39	C	37	36	25	1.39	120.1	179.2	1.39	119.7	-179.5
40	H	37	36	25	1.09	119.5	-0.7	1.08	119.8	-1.4
41	C	38	36	25	1.39	120.1	-179.9	1.39	119.7	179.7
42	H	38	36	25	1.09	119.6	0	1.08	119.8	-1.9
43	C	39	37	36	1.4	120.5	0.9	1.4	120.4	-0.2
44	H	39	37	36	1.09	119.4	180	1.09	119.4	179
45	H	41	38	36	1.09	119.4	179.9	1.09	119.4	179
46	N	12	8	6	1.45	119.4	-179.8	1.41	120.2	-179.7
47	O	46	12	8	1.23	118.4	179.9	1.27	119	-179.6
48	O	46	12	8	1.23	118.4	0	1.27	119	0.3
49	H	43	39	37	1.09	120.3	179.5	1.09	120.1	-179.7
50	H	33	29	27	1.09	120.3	179.7	1.09	120.1	-179.7

Table 14. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from MPW1PW91

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.35	--	--	1.36	--	--
3	H	1	2		1.09	118.8	--	1.09	119.3	--
4	H	2	1	3	1.09	119.2	-179.1	1.09	118.4	-178.7
5	C	2	1	3	1.45	126.2	0.3	1.45	127.3	0.6
6	C	5	2	1	1.41	118.4	-178.5	1.41	119	-177.8
7	C	5	2	1	1.41	123.8	1.3	1.42	123.6	2
8	C	6	5	2	1.38	121.7	179.7	1.38	122	179.5
9	H	6	5	2	1.08	119.2	-0.1	1.09	119	-0.2
10	C	7	5	2	1.38	121.2	-179.6	1.38	121.5	-179.5
11	H	7	5	2	1.08	120.4	0.4	1.08	120.1	0.5

12	C	8	6	5	1.39	118.7	0	1.41	119.4	0.1
13	H	8	6	5	1.08	121.3	-179.8	1.08	121.4	-179.8
14	H	10	7	5	1.08	121	180	1.08	121.1	-179.9
15	C	1	2	5	1.45	126.9	179.8	1.45	125.7	179.8
16	C	15	1	2	1.41	119	-177.3	1.41	118.9	-176.2
17	C	15	1	2	1.41	123.9	2.5	1.42	123.9	3.6
18	C	16	15	1	1.39	121.9	179.2	1.38	121.9	179.4
19	H	16	15	1	1.09	119.2	0.3	1.09	119	0.7
20	C	17	15	1	1.38	121.5	-179.6	1.38	121.5	-179.1
21	H	17	15	1	1.08	120.3	1.4	1.08	120.2	2
22	C	18	16	15	1.4	120.4	0.5	1.41	119.9	0
23	H	18	16	15	1.08	119.8	-178.9	1.08	120.2	-178.1
24	H	20	17	15	1.08	119.6	-179.1	1.08	120	-178.5
25	N	22	18	16	1.4	121.2	-179.7	1.4	120.5	-179.3
26	C	25	22	18	1.42	120.8	-32	1.41	120.1	-38.2
27	C	26	25	22	1.4	120.1	135	1.4	120	140.7
28	C	26	25	22	1.4	120.5	-45.7	1.4	120	-39
29	C	27	26	25	1.39	120.2	179	1.39	119.7	-179.7
30	H	27	26	25	1.08	119.6	-0.8	1.08	119.8	-1.2
31	C	28	26	25	1.39	120.1	-179.7	1.39	119.6	179.8
32	H	28	26	25	1.08	119.6	0.1	1.08	119.7	-1.7
33	C	29	27	26	1.39	120.5	0.7	1.4	120.4	0
34	H	29	27	26	1.09	119.4	-179.9	1.08	119.5	179.2
35	H	31	28	26	1.09	119.4	179.9	1.08	119.4	179.1
36	C	25	22	18	1.42	120.3	146	1.41	119.9	141.2
37	C	36	25	22	1.4	120.2	135.6	1.4	120.1	140.4
38	C	36	25	22	1.4	120.5	-45	1.4	119.9	-39.4
39	C	37	36	25	1.39	120.1	179.1	1.39	119.6	-179.8
40	H	37	36	25	1.08	119.5	-0.6	1.08	119.8	-1.3
41	C	38	36	25	1.39	120.1	-179.9	1.39	119.7	179.9
42	H	38	36	25	1.08	119.6	0	1.08	119.8	-1.6
43	C	39	37	36	1.39	120.5	0.9	1.4	120.4	0
44	H	39	37	36	1.08	119.4	-179.9	1.08	119.5	179.2
45	H	41	38	36	1.09	119.4	180	1.08	119.5	179.1
46	N	12	8	6	1.45	119.3	-179.8	1.4	120.2	-179.7
47	O	46	12	8	1.23	118.3	179.8	1.26	119.1	-179.7
48	O	46	12	8	1.23	118.3	-0.1	1.26	118.9	0.2
49	H	43	39	37	1.08	120.3	179.5	1.08	120.1	-179.9
50	H	33	29	27	1.08	120.3	179.7	1.08	120.1	-179.9

Table 15. Bond lengths (in Å) and angles (in degree) of diphenylamino-nitro-trans-stilbene in dichloromethane at the ground state and excited S_1 state from ωB97XD

Tag	atom	Na	Nb	Nc	Ground state			Excited state		
					bond	**angle**	**torsion**	**bond**	**angle**	**torsion**
1	C				--	--	--	--	--	--
2	C	1			1.34	--	--	1.41	--	--
3	H	1	2		1.09	119.1	--	1.09	118.5	--
4	H	2	1	3	1.09	119.5	-178.8	1.09	118.1	177.8
5	C	2	1	3	1.47	125.9	0.2	1.4	126.2	-2.2
6	C	5	2	1	1.41	118.4	-177.6	1.44	119.5	179.4
7	C	5	2	1	1.41	123.4	2.1	1.44	123.7	-1

8	C	6	5	2	1.39	121.5	179.5	1.37	122	179.6
9	H	6	5	2	1.09	119.4	-0.3	1.09	118.6	-0.4
10	C	7	5	2	1.38	121.2	-179.3	1.37	121.4	-179.4
11	H	7	5	2	1.08	120.6	0.7	1.08	120.1	0.3
12	C	8	6	5	1.39	118.6	0	1.42	120	0
13	H	8	6	5	1.08	121.2	-179.8	1.08	121.2	180
14	H	10	7	5	1.08	120.9	179.9	1.08	120.8	179.8
15	C	1	2	5	1.47	126.7	179.2	1.4	125.6	177.4
16	C	15	1	2	1.4	118.9	-174.6	1.43	119.5	-179.6
17	C	15	1	2	1.41	123.7	4.9	1.44	124.1	-0.4
18	C	16	15	1	1.39	121.8	178.4	1.37	122.2	178.7
19	H	16	15	1	1.09	119.4	-0.4	1.09	118.5	0.2
20	C	17	15	1	1.38	121.3	-179	1.37	121.6	-178
21	H	17	15	1	1.09	120.4	2	1.08	120.1	2.6
22	C	18	16	15	1.4	120.3	0.8	1.42	120.9	-0.4
23	H	18	16	15	1.08	119.8	-178.8	1.08	120	-178.4
24	H	20	17	15	1.08	119.7	-179.3	1.08	119.8	-179.1
25	N	22	18	16	1.41	121.1	-179.6	1.37	120.8	178.8
26	C	25	22	18	1.42	120.2	-30.9	1.43	121.1	155.9
27	C	26	25	22	1.4	120.3	129.4	1.4	119.7	129.3
28	C	26	25	22	1.4	120.1	-50.8	1.4	119.9	-51.6
29	C	27	26	25	1.39	120.1	179.4	1.39	119.6	179.3
30	H	27	26	25	1.09	119.6	-0.4	1.09	119.8	-0.8
31	C	28	26	25	1.39	120.1	179.7	1.39	119.6	-179.5
32	H	28	26	25	1.09	119.5	-0.1	1.09	119.8	-0.1
33	C	29	27	26	1.39	120.4	0.8	1.39	120.3	0.5
34	H	29	27	26	1.09	119.4	180	1.08	119.5	179.7
35	H	31	28	26	1.09	119.4	-179.9	1.09	119.5	179.8
36	C	25	22	18	1.42	120.5	142.2	1.43	121.2	-25.6
37	C	36	25	22	1.4	119.9	139.8	1.4	119.7	132.7
38	C	36	25	22	1.4	120.7	-40.9	1.4	119.9	-48.6
39	C	37	36	25	1.39	120.1	178.8	1.39	119.6	178.9
40	H	37	36	25	1.09	119.5	-0.8	1.09	119.7	-1
41	C	38	36	25	1.39	120.1	-179.6	1.39	119.6	-179.2
42	H	38	36	25	1.09	119.7	0.2	1.09	119.8	0
43	C	39	37	36	1.39	120.5	1	1.39	120.3	0.6
44	H	39	37	36	1.09	119.4	-179.7	1.09	119.5	179.7
45	H	41	38	36	1.09	119.4	-179.9	1.08	119.5	179.8
46	N	12	8	6	1.46	119.2	-179.7	1.4	119.8	179.8
47	O	46	12	8	1.23	118.3	179.9	1.25	119.3	0
48	O	46	12	8	1.23	118.3	0	1.25	119.1	-179.9
49	H	43	39	37	1.09	120.3	179.4	1.08	120.1	179.6
50	H	33	29	27	1.09	120.3	179.6	1.08	120.1	179.7

4. Conclusions

In this work, we performed DFT and TD-DFT calculations DFT calculations on diphenylamino-nitro-trans-stilbene using eleven functionals, B3LYP, HSEH1PBE, CAM-B3LYP,

PBE, HCTH, LSDA, BVP86, B3PW91, MPW1PW91, ωB97XD, and TPSS. Geometry optimizations of both ground and excited states of diphenylamino-nitro-trans-stilbene were performed. However, only the first ten functionals were successful to obtain both ground and excited state structures. TPSS was failed to obtain the excited state of the molecule. Comparisons were therefore made among ten functionals in the energies of the frontier orbitals, UV-vis and fluorescence spectra of diphenylamino-nitro-trans-stilbene and with the experimental results. For the HUMO and LUMO energies, B3LYP and B3PW91 provide the best result with respect to the experiment, while for UV-vis and fluorescence, CAM-B3LYP and MPW1PW91 results are closer to the experiments. Structural comparisons between the ground and excited states of the molecule show that the bond between C and N of nitrite decreases and the two N-O bonds of nitrites increase upon absorption of photons predicted by all ten functionals. The work illustrated that further research in functional is needed to accurately describe excitation of organic small molecules.

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