

## 2P073

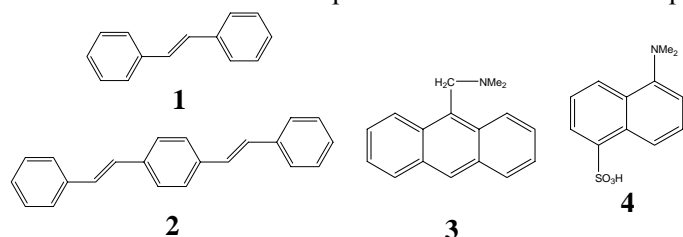
### Excitation properties of molecules in organic light emitting device and biosensor

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Two types of interesting molecules are studied in this research. First, poly-para-phenylene vinylene (PPV)-based chromophores can serve as a model for photo luminescent conducting polymers, widely used in organic light emitting device<sup>1</sup>. Unsubstituted PPV (**1** and **2**) has attracted considerable interest, both in terms of its basic properties and its applications. Second, fluorophores N, N-dimethyl-9-Anthracenemethanamine (**3**) and DANS acid (**4**) which are promising fluorescent labels for biosensor applications and frequently used by the scientific community<sup>2</sup>. SAC-CI method has been employed successfully to investigate the electronic excitation properties of these molecules. Ground state was optimized using DFT(B3LYP)/6-31G\* while the excited states were optimized using CIS/D95(d). Absorption and emission spectra have been calculated using SAC-CI/D95(d). Gaussian 03 suite of program was utilized for the computation. In the calculation of excitation properties, the 1s core of C and O atoms 2s2p core of S atom and corresponding virtual MOs were excluded from the



active space. Absorption and emission spectra agree well with the available experimental data. A comparison of the excitation properties and optimized geometry with the other computations also has been made.

Singlet excited states of **2** are displayed in Table 1. The lowest singlet transition corresponds to HOMO-LUMO transition with excitation energy 3.44 eV which shows excellent agreement with the experimental one<sup>4</sup>. Corresponding HOMO-LUMO transition energy of **1** is 4.26 eV. This shows that the lowest energy absorption peak gets red shifted with increasing chain length, in agreement with various theoretical and experimental studies<sup>3</sup> and the line becomes stronger. The central vinylene C=C bond relates to bonding and antibonding overlaps of  $\pi$ -orbitals in the HOMO and LUMO, respectively, whereas the opposite phase relationships are seen along the vinylene C-C bond (Fig. 1).

Table 1. Absorption spectra of PPV3 (**2**).

State	SAC-CI			Exptl. $\Delta E$ (eV)	Other $\Delta E$ (eV)
	$\Delta E$ (eV)	f	Main CI description ( $ C  > 0.3$ )		
<sup>1</sup> A'	3.44	1.6709	0.95 (H $\rightarrow$ L)	3.44 <sup>4</sup>	3.45 <sup>5</sup>
<sup>1</sup> A'	4.32	0.0571	-0.58(H-4 $\rightarrow$ L)+0.57(H $\rightarrow$ L+2)-0.36 (H $\rightarrow$ L+4)		
<sup>1</sup> A'	5.05	0.0000	-0.73(H-1 $\rightarrow$ L) - 0.63(H $\rightarrow$ L+1)		

Stilbene (**1**) has planar ground state which is corroborated by other experimental<sup>6</sup> and theoretical<sup>7</sup> investigations. At the B3LYP/6-31G\* level, with average discrepancies of 0.03 Å on bond lengths from the available experimental<sup>10</sup> data were observed. The CIS/D95(d) optimization shows that the lowest two singlet excited states of **1** are planar. In the lowest excited state of **1**, the central vinylene C=C bond increases by 0.015Å while the vinylene C-C bond decreases by 0.057Å. The ground and excited state geometries agree well with the other available computational values<sup>8</sup> (Fig. 2). The ground state and two lowest singlet excited states of **2** are also planar. But in this case the vinylene C=C bond increases by 0.026Å while the C-C

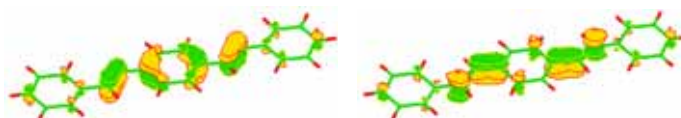


Fig. 1 HOMO (left) and LUMO (right) MOs of PPV3 (**2**).



Fig 2. Optimized geometries for the ground (left) and lowest singlet excited state (right) of PPV2 (**1**). Upper values represent present calculation, lower ones from other computation (Reference 8).

decreases by 0.022Å. In the excited state the C=C bond increases due to reduction in bond order while the C-C bond shrinks. We obtained the vinylenic C=C bond length as 1.398Å, although quite low value 1.318Å for this bond was reported experimentally<sup>10</sup>.

The absorption spectra of **3** have displayed in Table 2. The lowest singlet transition energy 3.16 eV is deviated by 0.21 eV from the experimental value of 3.37 eV<sup>9</sup>. This is a  $\pi$ - $\pi^*$  transition. We obtained a very strong absorption at 5.28 eV which is a  $\pi$ - $\pi^*$ . The emission spectra of **3** have displayed

Table 2. Absorption spectra of N, N-dimethyl-9-Anthracenemethanamine (**3**).

State	SAC-CI			Exptl.
	$\Delta E$ (eV)	f	Main CI description ( $ C  > 0.3$ )	$\Delta E$ (eV)
<sup>1</sup> A	3.16	0.1323	0.95(H→L)	3.37 <sup>9</sup>
<sup>1</sup> A	3.41	0.0006	-0.67(H-1→L)-0.65(H→L+1)	
<sup>1</sup> A	5.09	0.0600	-0.90(H-2→L)	
<sup>1</sup> A	5.28	1.8636	0.62(H→L+1)-0.60(H-1→L)+0.30(H→L+1)	
<sup>1</sup> A	5.69	0.0053	-0.85(H→L+3)+0.36(H-4→L)	

in Table 3. We obtained the lowest singlet transition energy as 2.80 eV which deviates by 0.17 eV only from the experimental value of 2.97 eV<sup>8</sup>.

The lowest singlet transition corresponds to HOMO-LUMO transition. A very strong emission is observed at 5.23 eV which is also a  $\pi$ - $\pi^*$  transition. Only the MOs from the anthracene moiety are involved in these transitions. A weak transition at 4.69 eV obtained which corresponds to n- $\pi^*$  transition. In this case a transition of the lone pair electron of nitrogen

Table 3. Emission spectra of N, N-dimethyl-9-Anthracenemethanamine (**3**).

State	SAC-CI			Exptl.
	$\Delta E$ (eV)	f	Main CI description ( $ C  > 0.3$ )	$\Delta E$ (eV)
<sup>1</sup> A	2.80	0.1307	-0.94 (H←L)	2.97 <sup>9</sup>
<sup>1</sup> A	3.37	0.0007	0.67 (H-1←L) + 0.66 (H←L+1)	
<sup>1</sup> A	4.69	0.0023	0.91(H-2←L)	
<sup>1</sup> A	5.23	1.0473	0.66(H←L+2)-0.48(H←L+1)+0.47(H-1←L)	

atom to the LUMO of the anthracene moiety is occurred.

In conclusion, we can say that the SAC-CI theory is useful to reproduce the experimental spectra quite well for these molecules.

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