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\(^1\). 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\(^2\). 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\(^4\). 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\(^3\) 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>
<thead>
<tr>
<th>State</th>
<th>SAC-CI</th>
<th>Exptl.</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)A'</td>
<td>3.44</td>
<td>1.6709</td>
<td>0.95 (H→L)</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>4.32</td>
<td>0.0571</td>
<td>-0.58(H-4→L)+0.57(H→L+2)-0.36 (H→L+4)</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>5.05</td>
<td>0.0000</td>
<td>-0.73(H-1→L) – 0.63(H→L+1)</td>
</tr>
</tbody>
</table>

Stilbene (1) has planar ground state which is corroborated by other experimental\(^6\) and theoretical\(^7\) investigations. At the B3LYP/6-31G* level, with average discrepancies of 0.03 Å on bond lengths from the available experimental\(^10\) 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\(^5\) (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
In conclusion, we can say that the SAC-CI theory is useful to reproduce the experimental spectra quite well for these molecules.

Reference: