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# Theoretical calculations of Non Linear Optical (NLO) properties of conjugated organic systems using Density Functional Theory (DFT): Investigation of the effect of hyperpolarizability (β) on frontier orbital energies.

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Over the last few decades, non linear optical (NLO) active materials have been extensively investigated. Usually, materials that have considerably large values for first static hyperpolarizability (β) are promising candidates to design novel NLO active materials. Three main charge transfer systems (D-π-A) were modelled and the effect of various donors (D) to the hyperpolarizability was studied under high accurate density functional (DFT) methods, keeping the acceptor (A) fixed. The calculated hyperpolarizability values were then related to frontier orbital energies of the respective molecules, where unexplored relationships between frontier orbital energies and hyperpolarizability can be identified. Initially, all molecule systems were optimized using DFT method using Becke 3 -parameter - Lee Yang Par Correlation functional (B3LYP) and 3-21g basis set. Then the resultant molecule was again o\ptimized with 6-31g basis set. Finally, the β values and orbital eigenvalues were calculated on the optimized structures using same levels of theory using Gaussian 98W. Twenty seven molecules were analyzed in this research. From the results, it is evident that there is an inverse relationship between frontier orbital energies and β values. Furthermore, interesting correlations between frontier orbital energies of some molecules and their hyperpolarizability were discovered. From the calculated β values, it is evident that these substances are very suitable for the development of photonic devices.

**Table 1 – Donor Moieties Used**

| Molecule | -X |
|---|---|
| $a_1$, $a_{10}$, $a_{19}$ | $OCH_3$ |
| $a_2$, $a_{11}$, $a_{20}$ | $NH_2$ |
| $a_3$, $a_{12}$, $a_{21}$ | $N(CH_3)_2$ |
| $a_4$, $a_{13}$, $a_{22}$ | $N(C_2H_5)_2$ |
| $a_5$, $a_{14}$, $a_{23}$ | $N(C_3H_7)_2$ |
| $a_6$, $a_{15}$, $a_{24}$ | $N(C_4H_9)_2$ |
| $a_7$, $a_{16}$, $a_{25}$ | $HN(CH_2)_2NH$ |
| $a_8$, $a_{17}$, $a_{26}$ | $CH_3N(CH_2)_2NH$ |
| $a_9$, $a_{18}$, $a_{27}$ | $CH_3N(CH_2)_2NCH_3$ |

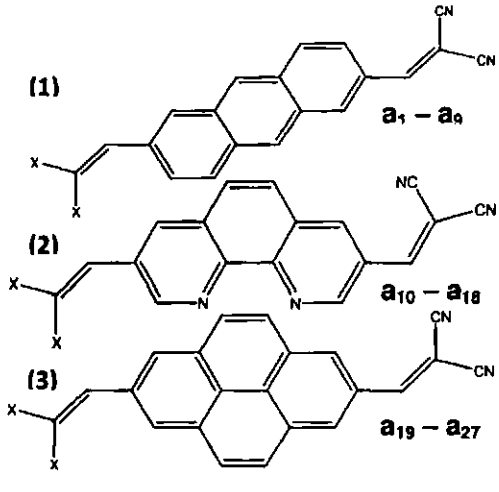


**Figure 1 – Novel NLO Active Molecules**

**Table 2 – Hyperpolarizabilities and HOMO – LUMO Gaps**

| 1) | $(E_{LUMO} - E_{HOMO})$ (Hartrees) | β x10$^{-33}$ ESU | 2) | $(E_{LUMO} - E_{HOMO})$ (Hartrees) | β x10$^{-33}$ ESU | 3) | $(E_{LUMO} - E_{HOMO})$ (Hartrees) | β x10$^{-33}$ ESU |
|---|---|---|---|---|---|---|---|---|
| $a_1$ | 0.09128 | 273.32 | $a_{10}$ | 0.11232 | 161.47 | $a_{19}$ | 0.10744 | 176.41 |
| $a_2$ | 0.08251 | 368.26 | $a_{11}$ | 0.08909 | 336.42 | $a_{20}$ | 0.09198 | 272.80 |
| $a_3$ | 0.08143 | 468.58 | $a_{12}$ | 0.08710 | 431.17 | $a_{21}$ | 0.09125 | 332.88 |
| $a_4$ | 0.08027 | 518.18 | $a_{13}$ | 0.08508 | 484.76 | $a_{22}$ | 0.08954 | 369.04 |
| $a_5$ | 0.07979 | 551.06 | $a_{14}$ | 0.08411 | 521.91 | $a_{23}$ | 0.08781 | 404.61 |
| $a_6$ | 0.07942 | 568.19 | $a_{15}$ | 0.08324 | 564.02 | $a_{24}$ | 0.08736 | 417.74 |
| $a_7$ | 0.07918 | 449.12 | $a_{16}$ | 0.08564 | 409.28 | $a_{25}$ | 0.08789 | 345.11 |
| $a_8$ | 0.07921 | 465.17 | $a_{17}$ | 0.08502 | 445.39 | $a_{26}$ | 0.08752 | 371.54 |
| $a_9$ | 0.07932 | 495.43 | $a_{18}$ | 0.08437 | 453.99 | $a_{27}$ | 0.08754 | 370.92 |

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