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High accuracy theoretical calculations of NLO properties of conjugated organic systems using Hartree–Fock (HF), Møller-Plesset perturbation theory (MP2) and Density Functional Theory (DFT): A comparative investigation

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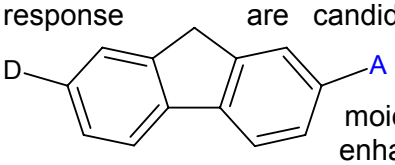
The advancement of experimental techniques and evolution of quantum chemical theoretical procedures lead to the dramatic development of materials with nonlinear optical properties (NLO) during the last decade. Therefore, the hyperpolarizability which is the measure of NLO activity of various systems is theoretically investigated because compounds with large NLO response are candidates in photonic technologies. We report a comparative investigation of the first static hyperpolarizabilities (β) of fluorenyl derivatives with a number of donor- acceptor (D-A) moieties (9 molecules) on either side of the fluorenyl ring system enhancing the π-electronic charge distribution through the π-conjugation. The first static hyperpolarizabilities (β) of fluorenyl derivatives were obtained by Møller-Plesset perturbation theory (MP2) and the density functional theory (DFT) and compared the values with the published data using Hartree–Fock (HF) method. Fully optimized molecular geometries were obtained using HF, MP2 and B3LYP (DFT) methods employing 6-31G basis set. Then the β values were calculated for each molecule with the same level of theory using GAUSSIAN 98W. It can be seen that there is a two fold increase in MP2 hyperpolarizability values compared to the HF method and three fold increase in hyperpolarizability values of DFT method compared to the HF method. When comparing the DFT and HF methods, DFT includes some component of electron correlation for much the same computational cost as HF methods. This means that it is a highly efficient and accurate way of performing a advanced calculation for the fluorenyl system. This shows that this system can be a potential NLO material which can be synthesized in a standard laboratory.



	HYPERPOLARIZABILITY (β)			Increase		
	HF (10^{-30} esu)	MP2 (10^{-30} esu)	DFT (10^{-30} esu)	Increase in MP2 compared to HF	Increase in DFT compared to HF	Increase in DFT compare to MP2
1	30.19	61.21	91.56	31.02	61.37	30.34
2	37.51	82.14	128.1	44.62	90.57	45.95
3	39.77	88.80	140.9	49.03	101.1	52.06
4	42.94	91.70	143.7	48.76	100.8	52.03
5	20.42	38.77	65.91	18.35	45.49	27.14
6	16.30	29.62	36.49	13.32	20.19	6.870
7	52.98	105.4	144.8	52.46	91.81	39.35
8	81.45	153.2	242.5	71.71	161.0	89.30
9	130.4	253.7	765.9	123.3	635.5	512.2

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