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Non-Linear Optical Properties of Substituted Hexatriene: AM1 and *ab Initio* Quantum Chemical Calculations

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Abstract

We report *ab initio* studies of the dipole polarizabilities (α) and first static hyperpolarizabilities (β) for a set of substituted hexatriene in which electron donating (D) and electron accepting (A) groups were introduced either end parts of the hexatriene chain NO_2-$(CH=CH)_3$-D. Geometries of all molecules were optimized at the Hartree-Fock HF/6-311++G(2d,p) level of theory. Polarizabilities of these molecules were calculated at the same level of theory. To understand this phenomenon in the context of molecular orbital picture, we examined the molecular HOMOs and molecular LUMOs energies. The study revealed that the substituted hexatriene had large β values and hence may have potential applications in the development of non linear optical materials.

1. Introduction

NLO materials have been attractive in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching, and dynamic image processing [1] [2]. Due to their high molecular hyperpolarizabilities, organic materials display a number of significant nonlinear optical properties. NLO materials were categorized as multilayered semi-conductor structures,

molecular based macroscopic assemblies and traditional inorganic solids. A variety of inorganic, organic and organometallic molecular systems have been studied for NLO activity [1]. The design strategy, used by many with success involves connecting donor (D) and acceptor (A) groups at the terminal positions of a Π-bridge to create highly polarized molecules that could exhibit large molecular nonlinearity [3].

The delocalization of Π-electrons in these systems leads to large non resonant optical molecular polarizabilities. Besides, a number of quantum mechanical and experimental studies have shown that geometric changes caused by incorporation of push-pull end groups can enhance the nonlinear polarizabilities of conjugated molecules [4]-[6].

Experimental measurements and theoretical calculations on molecular hyperpolarizability become one of the key factors in the second-order NLO materials design [7] [8]. Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties. It also provides a guideline to experimentalists for the design and synthesis of organic NLO materials [9] [10].

A better understanding of the chemical substitutions effects on the NLO properties of new organic polymers constitutes an important step towards the advance of photonic technologies. Theoretical studies have drawn interesting conclusions on the side-substitution effects on the electric responses of trans PA chains. Marder *et al.* [11] [12] have investigated, on the basis of semi-empirical calculations, relations between structure and polarizabilities in donor-acceptor polyene compounds and have shown that the NLO responses of these systems can be optimized by varying the geometric parameter defined as bond length alternation (BLA).

Hayashi *et al.* [13] have calculated the linear and nonlinear polarizabilities in the side-chain direction (perpendicular to the main chain) of the PA chains with all H atoms substituted by fluorine, hydroxyl and cyano groups. Their HF/STO-3G results have shown that the coupling between electronic states of the side groups with those of the main chain increases the values of the perpendicular polarizabilities. Margulis and Gaiduk [14] have investigated the influence of the phenyl side groups on the third-order nonlinear optical susceptibility of trans PA chains. In the context of the tight-binding approximation, they have shown that an appropriate selection of side groups attached to the main chain can lead to a change of the sign of this property. Besides, effects of the incorporation of terminal donor and acceptor groups as well as the inclusion of singly and doubly charged defects on the polarizabilities of PA chains have also been studied [15]-[21]. These theoretical works have shown that, in general, such modifications increase the electric responses of conjugated polymers. Also general is the fact that the second hyperpolarizability is much more sensitive to substitution effects than the linear polarizability.

Our objective is to design a range of novel molecular systems, which show NLO activity. The approach is based on the concept of charge transfer (CT) between donor and acceptor through hexatriene linear chain. In this research work, isotropic static polarizability (α) and first hyperpolarizabilities (β) are calculated using *ab initio* method using Hartree-Fock level using 6-311G++(2d,p) basis set of disubstituted hexatriene NO_2-$(CH=CH)_3$-D with a number of Π-electron donor substituent at the end part using GAUSSIAN. The designing of systems with high charge transfer (CT) is the key to this part, as intra molecular CT between donor and acceptor will lead to a very large value for β.

2. Computational Procedures

All *ab initio* calculations were made using GAUSSIAN 98 [22]. The geometries were optimized at the Hartree-Fock 6-311G++(2d,p) level. NLO calculations were performed at Hartree-Fock *ab initio* level using the 6-311G++(2d,p) basis set, which has been found to be more than adequate for obtaining reliable trends in (β) values. The semi empirical calculations using AM1 was performed using MOPAC 2000 [23].

3. Results and Discussion

3.1. Selection of Basis Set

To establish an appropriate computational method for studying the static polarizabilities of the substituted trans hexatriene, we compared the HF levels of theory for hexatriene using different basis sets.

Table 1 compares the experimental values of static isotropic polarizabilities for hexatriene with our calculations at the Hartree-Fock level using different basis sets, starting with the minimal basis set and then moved to higher basis sets by inserting polarization and diffusion functions. The basis sets incorporated in this study

Table 1. Representative *ab initio* static isotropic polarizabilities (α) for trans-hexatriene.

Basis set	α_{xx}/au	α_{yy}/au	α_{zz}/au	$\langle\alpha\rangle$/au	Experiment [26] $\langle\alpha\rangle$/au
HF/STO-3G	90.855	34.038	6.763	43.885	87.456
HF/3-21G	136.892	53.327	15.474	68.564	
HF/6-31G	144.270	55.685	9.399	69.784	
HF/6-31+G	156.422	59.211	42.465	86.032	
HF/6-31++G	156.464	59.397	42.857	86.239	
HF/6-311G	147.760	57.251	27.561	77.524	
HF/6-311+G	154.374	59.134	42.365	85.291	
HF/6-311++G	154.406	59.279	42.429	85.371	
HF/6-311++G(d,p)	153.282	60.153	45.711	86.382	
HF/6-311G(2d,p)	145.550	59.172	34.426	79.716	
HF/6-311+G(2d,p)	152.855	60.864	47.641	87.120	
HF/6-311++G(2d,p)	152.890	61.018	47.720	87.209	
HF/6-311++G(2d,2p)	153.400	61.296	48.454	87.716	

include STO-3G, 3-21G, 6-31G, 6-31+G, 6-31++G, 6-311G, 6-311+G, 6-311++G, 6-311++G(d,p), 6-311G(2d,p), 6-311+G(2d,p), 6-311++G(2d,p) and HF/6-311++G(2d,2p). Previous calculations for various small molecules indicate that two sets of polarization functions and a set of diffuse functions are generally needed to obtain satisfactory agreement with experimental polarizabilities [24]. However for the axial polarizability of larger polyenes, there is less need for large basis sets [25].

Examination of the values of polarizabilities shown in **Table 1** illustrates the following well known conclusions: Extended, polarized basis sets are needed for polarizability calculations. A treatment of electron correlation is essential. Diffuse functions (+,++) need to be included in the basis set. The polarizabilities of hexatriene calculated in the present work are 86.382, 87.120, and 87.209 (au) at the HF/6-311++G(d,p), HF/6-311+G(2d,p), and HF/6-311++G(2d,p) levels of theory, respectively. The value of 87.209 (au) fortuitously agrees perfectly with the experimental value of 87.456 (au) [26]. These results confirm once more that to accurately calculate the polarizability of smaller polyene one needs larger basis set [25]. Polarizability calculations performed at *ab initio* using the HF/6-311++G(2d,p) basis set, was found to be more than adequate for obtaining reliable trends in $\langle\alpha\rangle$ values. We decided that the following procedure would be adopted for molecules in the series. Geometry optimisation and polarizability calculation at the HF/6-311++G(2d,p) level of theory.

3.2. Geometry Optimization

The optimized geometries (**Figure 1**) are essentially planar with the $\theta_{C_3C_2C_1N_7}$ and $\theta_{C_4C_5C_6N_8}$ torsion angles torsion angles close to 180°. However, molecules with -NEt$_2$ and -NMe$_2$ show a slight deviation from the planarity due to the steric interactions of protons of methyl and ethyl groups with the protons of hexatriene chain. The torsion and valence angles for -NEt$_2$ and -NMe$_2$ substitued groups are $\theta_{C_4C_5C_6N_8} = -180°$ and $-180°$ and $\theta_{N_8C_6C_5} =$ 129° and 123° respectively. However, a dissimilar scenario occurs with an attractive interactions in molecule with -NHOH substituted groups where the oxygen atom of -NHOH interact with protons of hexatriene chain to form an O···H bond with R$_{O···H}$ = 1.937 Å. The torsion and valence angles for this system are $\theta_{C_4C_5C_6N_8} = 174.4°$ and $\theta_{N_8C_6C_5} = 125°$. The first hyperpolarizability of molecule with -NEt$_2$ groups is much greater than the analogous with NHOH, NH$_2$, NHMe, NEt$_2$, NHNH$_2$ as donor groups. This is due to lack of planarity of substituted hexatriene chain due to the free rotation through the C$_6$-N$_8$ bonds. This will increase the overlap of interacting orbitals, which will eventually increase the CT from donor to acceptor through the linear chain. The functionality of amino groups -NHOH, -NH$_2$, -NHNH$_2$, -NHMe, -NHEt and -NEt$_2$, with the binding by N heteroatom, as a donor and NO$_2$, as an acceptor, are the best D/A pair among all investigated.

3.3. Bond Length Alternation

The works of Marder *et al*. [11] investigated, on the basis of semiempirical calculations, relations between structure and polarizabilities in donor-acceptor polyenes compounds have shown that the NLO responses of theses systems can be optimised by varying the geometric parameter defined as bond length alternation BLA. **Table 2** give the BLA for optimised structure (**Figure 2**).

Table 2. HF/6-311G++(2d,p) optimized bond length (Å) in substituted trans-hexatriene.

Molecule	Bond length (Å)					BLA (average)	Energy (au)
NO_2/Y	$C_1=C_2$	C_2-C_3	$C_3=C_4$	C_4-C_5	$C_5=C_6$		
H	1.341	1.438	1.352	1.446	1.340	0.097	−435.42
CH_3	1.342	1.436	1.354	1.442	1.344	0.092	−474.47
OCH_3	1.345	1.432	1.358	1.432	1.349	0.081	−549.34
OH	1.344	1.432	1.357	1.433	1.346	0.084	−510.30
NHOH	1.345	1.431	1.359	1.431	1.354	0.078	−565.29
NH_2	1.348	1.427	1.362	1.426	1.360	0.070	−490.47
$NHNH_2$	1.348	1.427	1.362	1.426	1.360	0.070	−545.48
NHMe	1.349	1.427	1.363	1.424	1.363	0.067	−529.51
NHEt	1.349	1.426	1.363	1.424	1.363	0.067	−568.56
NMe_2	1.349	1.426	1.363	1.426	1.366	0.067	−568.54
NEt_2	1.350	1.425	1.364	1.424	1.368	0.064	−646.64
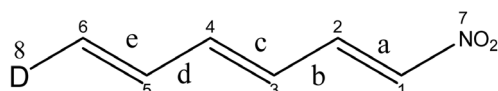
Figure 1. Illustration of the functional groups D and A investigated in this work.
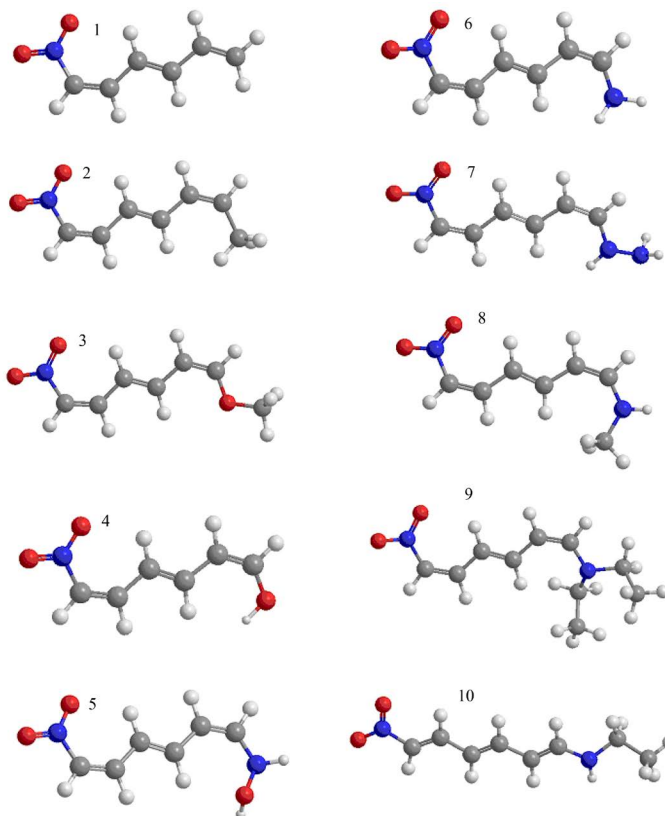
Figure 2. Optimised molecular structure of substituted hexatriene (1-10) by using HF/6-311G++(2d,p).

It can be seen from **Table 2** that, large and strong substituents -NEt_2 and -NMe_2 groups, make greater structural changes as compared to the small donor groups -OCH_3, -CH_3 and -OH. The results first show that the substituents act to reduce the length of the single bonds and to increase the length of the double bonds. As a consequence, the average bond length alternation BLA_{ave} decreases from NO_2/H to NEt_2/NO_2 by $\Delta l = 0.033$ Å. However, the unsubstituted trans hexatriene present, at the same level of theory, a difference of $\Delta l = 0.042$ Å in average BLA. With regards to the bond length alternation BLA values in the middle and at the end, two different tendencies are found: 1) for the substituted groups -H, -CH_3, -OCH_3, -OH, -NHOH, -NH_2, -$NHNH_2$, -NHMe the BLA increases when going from the middle to the end of the molecules. An increase ranging between 0.001 and 0.012 Å in BLA is observed. 2) In the case of very strong substituted donor (-NHEt, -NMe_2, -NEt_2) a small but reverse tendency is observed. A decrease of 0.002 Å to 0.003 Å in bond length alternation takes place from the middle to the end. It is, however important to note that globally it is the compound (11) with -NEt_2 donor group that leads to the smallest BLA. For unsubstituted hexatriene, corresponding to the pure VB case, the BLA at the middle of the chain is 0.100 Å is shorter than its end neighbours were the BLA is 0.109 Å this presented a decrease of 0.009 Å in bond length alternation takes place from the middle to the end.

3.4. Polarizabilities and First Static Hyperpolarizability

The results of the polarizability and the first static hyperpolarizability using *ab initio* at HF/6-311G++(2d,p) for all structures **Figure 2** are given in the **Table 3** and **Table 4**, respectively.

The mean polarizability was calculated from the polarizability components as [27]:

$$\langle \alpha \rangle = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \tag{1}$$

Table 3 compares the calculated values of static isotropic polarizabilities for a number of nitrogen-containing hexatriene with a number of Π-electron donor substituent at the end parts calculated at the HF/6-311G++(2d,p) level of theory. For all series, the smallest enhancement is due to the pair NO_2/OH values of about 112.192 au for $\langle \alpha \rangle$ and the largest enhancement due to the pair NO_2/N(Et)$_2$ values of about 182.653 au for $\langle \alpha \rangle$. The largest increment of static isotropic polarizabilities $\Delta\alpha$ is seen to be due to N(Et)$_2$ donor group $\Delta\alpha = 76.233$ and the two smallest increments are due to OH and CH_3 donor groups respectively ($\Delta\alpha = 5.772$ and 14.436). As regards to these substituted hexatriene, we are able to propose a decreasing classification, relatively to the $\langle \alpha \rangle$ polarizability. The established order is as follows: N(Et)$_2$ > NHEt > NHMe > $NHNH_2$ > OCH_3 > NHOH > NH_2 CH_3 > OH > H.

The graphical representations of dipole polarizabilities (computed at HF/6-311G++(2d,p)) versus the number of electrons are shown in **Figure 3**. It is apparent from this figure that there are significant correlations among components of a tensor and the number of electrons. All components of a tensor have linear relation with N_e. The excellent quality of linear correlation is evident from R coefficients, which are shown in **Figure 3**. Based on this fact, one can extrapolate $\langle \alpha \rangle$ and various components of a tensor for every unlimited disubstituted polyacetylene NO_2-$(CH=CH)_n$-D series.

Table 4 shows all the β components and the final β_{tot} values calculated for the molecules under investigation. The complete equation for calculating the magnitude of β_{tot} from GAUSSIAN98W output is given as follows [28] [29].

$$\beta_{tot} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx} \right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy} \right)^2 \right]^{\frac{1}{2}} \tag{2}$$

Since the values of the first hyperpolarizability tensors of the output file of GAUSSIAN98W are reported in atomic units (au), the calculated values were converted into electrostatic units (1 au = 8.6393×10^{-33} esu).

The magnitude of the first hyperpolarizability tensor of all molecules studied is dependent upon the availability of the lone pair of electrons on the nitrogen atom to conjugate with the hexatriene linear chain. The dramatic increase of first hyperpolarizability has been observed when the lone pair on the nitrogen atom of the donor group is forced to conjugate with the hexatriene linear chain, upon substitution on nitrogen of NH_2 group with other groups, such as methyl, ethyl, hydroxyl etc. It is expected that the molecule with NH_2 as the donor group would give a higher value for first hyperpolarizability with compare to the molecule where the donor group is OCH_3.

Table 3. Principal dipole polarizability tensor components HF/6-311G++(2d,p).

Molecule NO$_2$-(CH=CH)$_3$-D	α_{xx}/au	α_{yy}/au	α_{zz}/au	$\langle\alpha\rangle$/au	Increment $\Delta\alpha$/(au)	N_e
H	195.410	72.224	51.626	106.420	0.00	66
OH	206.252	77.152	53.172	112.192	5.772	74
CH$_3$	219.003	83.138	60.429	120.856	14.436	74
NH$_2$	226.835	81.320	57.140	121.765	15.345	74
NHOH	224.094	88.757	59.373	124.074	17.654	82
OCH$_3$	235.284	87.198	63.691	128.724	22.304	82
NHNH$_2$	248.840	87.461	63.743	133.348	26.928	82
NHMe	246.287	95.615	65.935	135.945	29.525	82
NHEt	284.598	103.775	75.970	154.781	48.361	90
N(Et)$_2$	314.498	133.370	100.091	182.653	76.233	106

$\Delta\alpha$: polarizability difference on substitution of Y into NO$_2$-(CH=CH)$_3$-Y.

Table 4. All β components and β_{tot} calculated at HF level using HF/6-311G++(2d,p) basis set by GAUSSIAN98W for all substituted hexatriene.

Molecule	β_{XXX}	β_{XXY}	β_{XYY}	β_{YYY}	β_{XXZ}	β_{XYZ}	β_{YYZ}	β_{XZZ}	β_{YZZ}	β_{ZZZ}	β_{tot}/au	$\beta_{tot} \times 10^{-30}$ (esu)
1	486.9406	28.9009	108.2542	39.5937	−0.2455	−0.0892	0.0388	−65.6319	11.0294	−0.0182	535.500	4.626
2	−828.3495	80.6883	−123.1313	40.1633	0.0562	0.1294	−0.0603	45.0978	4.2979	0.0780	914.982	7.904
3	−1055.3987	−92.2003	−147.7486	−49.0719	0.9528	−0.6031	−0.5544	76.7740	34.6523	1.8092	1131.41	9.774
4	−1043.0015	94.8534	−161.4728	32.7181	−0.0319	0.0075	−0.0027	26.4609	−10.1908	0.0174	1183.847	10.227
5	−1258.0218	72.1084	−165.6371	32.7033	−11.9212	0.3332	3.2941	18.8223	−9.9188	−2.2753	1408.080	12.164
6	1486.3942	132.4900	184.8757	22.2281	17.1001	5.3185	1.7527	−46.1323	−3.8384	5.8278	1632.313	14.102
6	1616.6333	−134.6059	158.9510	−39.4687	79.0381	−6.6086	4.7495	−74.8318	19.3561	31.5056	1711.662	14.787
7	1856.1625	187.1026	212.6315	64.6901	−0.0252	−9.0031	3.6189	−17.9819	−2.3930	19.7970	2066.053	17.849
8	2224.9184	234.3071	190.3488	94.0446	−57.2048	−4.9263	−28.7311	−114.7208	1.9063	−72.2354	2329.506	20.125
9	3406.1656	646.6501	−140.6919	−30.0006	42.9215	−18.6552	13.5288	−68.8335	7.8635	37.4629	3258.426	28.150

The result indicates also that the magnitude of first hyperpolarizability β of molecules is dependent upon the availability of the lone pair of electrons on the nitrogen atom to conjugate with the hexatriene linear chain. The dramatic increase of first hyperpolarizability has been observed when the lone pair on the nitrogen atom of the donor groups is forced to conjugate with the hexatriene linear chain, upon substitution on nitrogen of -NH$_2$ group with other groups, such as methyl, ethyl, hydroxyl, etc. Molecule with -NEt$_2$ group shows 54% and 70% increase of first hyperpolarizability with compare to molecule with -OCH$_3$ and -CH$_3$ donor groups, respectively. As regards to the Π-electron donating capacity of the typical substituted groups, we are able to propose a decreasing classification, relatively to b hyperpolarizability. The established order is as follows: NEt$_2$ > NMe$_2$ > NHEt > NHMe > NHNH$_2$ > NH$_2$ > NHOH > OCH$_3$ > OH > CH$_3$ > H.

The molecular hyperpolarizability value of molecule with -NEt$_2$ group (28.15 × 10^{-30} esu) is about 200 times grater than that of urea (0.14 × 10^{-30} esu) [30], 10 times grater than that of 2,4,6-trinitrophenol (2.99 × 10^{-30} esu) [31] and the same with the fluorenyl derivative (7-nitro-9H-fluoren-2-ylamine 30.20 × 10^{-30} esu) [32].

The *ab initio* optimization of all molecules in this investigation shows that the molecules are almost planer. However, molecules 8, 9 and 10 show a slight deviation from the planarity due to the steric interactions of protons of methyl and ethyl groups with the protons of hexatriene chain. The same scenario occurs in molecule 5
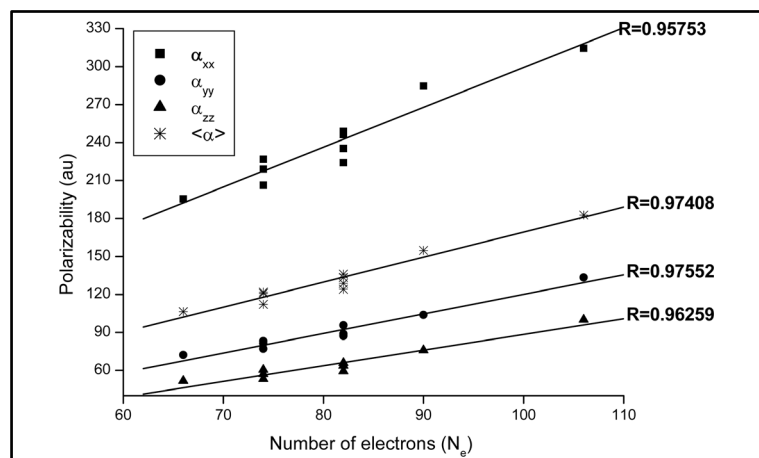
Figure 3. Graphical representation of calculated dipole polarizabilities for substituted hexatriene by the HF/6-311G++(2d,p).

where O atoms of NHOH interact with protons of hexatriene chain. The first hyperpolarizability of molecule 10 is much greater than the analogous with NHOH, NH_2, NHMe, $N(Et)_2$, $NHNH_2$ as donor groups. This is possibly due to lack of planarity of hexatriene chain due to the free rotation through the carbone-carbone σ-bond. This will increase the overlap of interacting orbitals, which will eventually increase the CT from donor to acceptor through the linear chain.

To understand this phenomenon in the context of molecular orbital picture, we examined the molecular HOMOs and molecular LUMOs generated via GAUSSIAN98W. The results for all disubstituted hexatriene are summarized graphically in **Figure 4**. **Figure 5** shows the variation of HOMO-LUMO difference for all disubstituted hexatriene.

As shown in **Figure 4** substitution of different electron donor groups on nitrogen of NH_2 group in molecules 1 - 10 increases the energy of the molecular HOMO, while leaving the LUMO energy essentially unchanged due to the same acceptor group. Thus, the energy gap decreases with the substitution on nitrogen of NH_2 and produces a larger hyperpolarizability.

Figure 5 shows the variation of first hyperpolarizability and energy gap E_{gap} for molecules under investigation. The enhancement of first hyperpolarizability of these molecules is directly related to the HOMO-LUMO energy gap, an inverse relationship was found between E_{gap} (E_{LUMO} - E_{LUMO}) and hyperpolarizability. Compounds with the smallest energy gap produce the larger β_{tot} value, while the larger energy gap produces a decrease in hyperpolarizability value. It could be interesting to synthesize compounds 5 - 10 having the greatest and the lowest, respectively β_{tot} and E_{gap} values.

Table 5 shows the comparison of linear and non-linear optical properties of disubstituted hexatriene calculated using different methods.

The HF/6-311G++(2d,p) polarizabilities are generally a few percent higher than the corresponding values calculated at AM1 level (15% for $NHNH_2$, 10% for OH, 9.79% for $N(Et)_2$, 8.40% for NHEt, 6.87% for NHMe and 5% for NH_2). There is good absolute agreement between the HF/6-311G++(2d,p) values and the AM1 results, they give a correlation coefficient of 0.98 which means that AM1 results can be accurately scaled for such molecules. The AM1 produces better results for polarizability which are comparable with the experimental results and the *ab initio* value calculated at HF/6-311++G(2d,p) level.

AM1 semi empirical method yielded extremely higher value for the hyperpolarizability. The AM1 method showed a much higher value, which is divergent with that of *ab initio* level. It was found that the AM1 semi-empirical value of β_{tot} is 16% - 60% more than the *ab initio* value calculated at HF/6-311++G(2d,p) level. Therefore, AM1 method would not be a better option for calculating hyperpolarizability of these types of molecules.

5. Conclusions

It is evident that the first hyperpolarizability tensor of substituted hexatriene strongly depends on the electronic
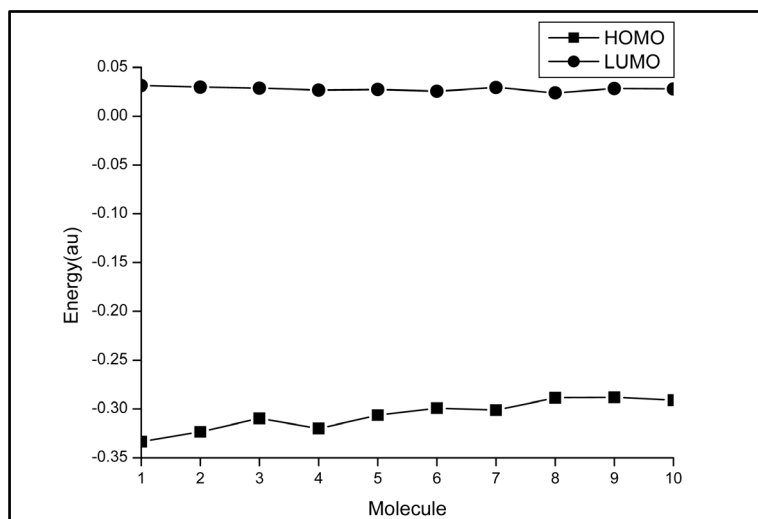
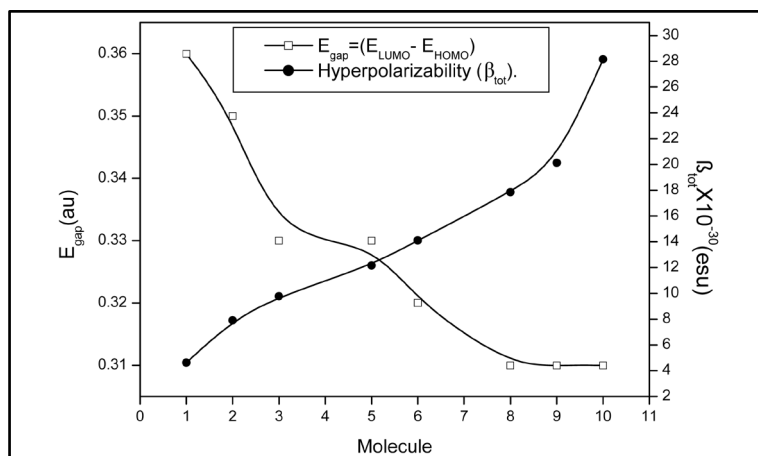**Figure 4.** Changes in the energy levels of HOMO-LUMO orbital of molecule 1-10.

Figure 5. Variation of β_{tot} and E_{gap} values for compounds under study.

Table 5. Comparison of linear and non-linear optical properties of molecules 1-10 calculated using both *ab initio* and semi empirical levels of theory.

Molecule	HF/6-311G++(2d,p)		AM1	
	$\langle \alpha \rangle \times 10^{-30}$ (esu)	$\beta_{tot} \times 10^{-30}$ (esu)	$\langle \alpha \rangle \times 10^{-30}$ (esu)	$\beta_{tot} \times 10^{-30}$ (esu)
1	0.919	4.626	0.781	7.671
2	1.044	7.904	0.909	11.459
3	1.112	9.774	0.980	16.430
4	0.969	10.227	0.871	14.210
5	1.071	12.164	0.959	15.839
6	1.051	14.102	0.992	25.565
7	1.152	14.787	0.977	17.650
8	1.174	17.849	1.093	27.800
9	1.577	20.125	1.423	49.722
10	1.337	28.150	1.224	37.181

structure of the molecule. The molecules linked together through the linear chain tend to rotate, about carbon-carbon σ-bond; this will increase overlap of interacting orbitals, which eventually increase the CT from donor to acceptor through the linear moiety.

The HOMO-LUMO calculations show that the first hyperpolarizability of the compounds is directly related to the HOMO-LUMO energy gap. This is the highest in molecules 10 while the smallest is in 2, which has the highest energy gap. The study reveals that the substituted hexatriene has important first static hyperpolarizabilities. They may have potential application in the development of NLO materials.

It is important to stress that, in the calculated β values, we do not take into account the effect of the field strength on the nuclear positions. We evaluate only the electronic component of β. The vibrational contributions which, for conjugated systems, can be important depending on the NLO process are the subject of further investigations.

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