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## Effect of Twist Angle on Calculated Second Order Non–Linear Responses of Novel Charge Transfer Molecular Systems

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## Effect of Twist Angle on Calculated Second Order Non–Linear Responses of Novel Charge Transfer Molecular Systems<sup>#</sup>

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### Abstract

**Motivation.** Molecules with large optical non–linearities have extensively been studied due to their potential applications in the area of materials science and various photonic technologies, including optical switching and data processing. Semi–empirical quantum chemical calculations are performed on the class of compounds shown in Figure 1 which show very large non–linear optical activity. The effect of twist angle (1234) on the static hyperpolarizability was investigated.

**Method.** Geometries of all molecules were optimized at the semi–empirical level of the theory using AM1 Hamiltonian using MOPAC 6.0 computational package. The static hyperpolarizabilities,  $\beta$ , and frontier molecular orbital energies are studied as a function of the twist angle (1234), between the diaminomethylene unit and the six membered fused rings as shown in Figure 1 using AM1 Hamiltonian within MOPAC 6.0 computational chemistry package.

**Results.** All the  $\beta$  values that we report here are the magnitude of static hyperpolarizability. The enormous enhancement of the hyperpolarizability for a particular dihedral angle of these designed novel molecular systems is also reported.

**Conclusions.** The study reveals that these classes of organic compounds show a very large hyperpolarizability and hence in general may have potential applications in the development of non–linear optical materials.

**Keywords.** Semi–empirical; AM1; nonlinear optics (NLO); polarizability; hyperpolarizability; twist angle.

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## 1 INTRODUCTION

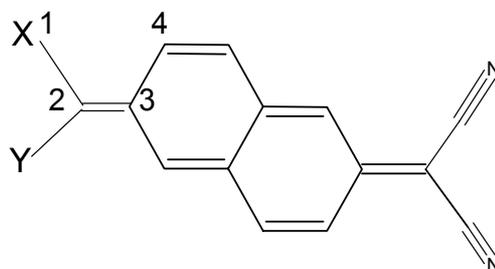
The observation of Kerr effect [1] and Pockel's effect [1] led to the birth of non–linear optics. Since then the non–linear optics developed dramatically, especially during the last decade due to the advancement of both experimental techniques and evolution of molecular modeling and quantum chemical procedures. Molecules with large optical non–linearities have extensively been studied due to their potential applications in the area of materials science and various photonic technologies, including optical switching and data processing. [2–7]. The major candidates for NLO materials are multilayered semi–conductor structures, molecular based macroscopic assemblies and

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traditional inorganic solids. A comprehensive coverage of the development of the field especially for a variety of inorganic, organic and organometallic molecular assemblies has been reported [8]. Polymeric materials in the form of crystals and glasses have also shown non-linear optical activity. Well-known applications being explored are second harmonic generation [9] and electrochemiluminescence [10].



**Figure 1.** The skeleton of the Novel molecular system.

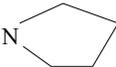
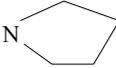
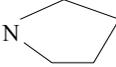
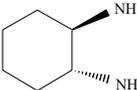
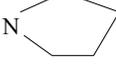
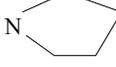
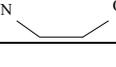
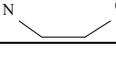
Molecular materials based on  $\pi$  – electron conjugated molecules have been in the forefront in hunting for NLO applications and are considered to be potential alternative to the inorganic materials [2,3,7]. The design of efficient organic materials for the applications in non-linear optical effect is based on asymmetric polarization induced by electron donor and electron acceptor groups on either side of the molecule at appropriate positions in the molecular systems. The positions of the substitutions are crucial as substitution on a wrong place of the molecular system will nullify the conjugation and hence the NLO activity. The so-called push-pull organic molecular systems have been drawn much attention and large number of publications was appeared in the recent literature [11–18].

Theoretical studies of push-pull organic molecules have shown that the NLO properties are very much dependent on the input geometry of the isolated molecules [8,19] than the theoretical model used in NLO calculations. The dependence of NLO properties with the input structure has been investigated for donor-acceptor conjugated polyenes [20,21]. It is well known that the NLO properties of aryl systems are sensitive to conformational changes [22–29]. The dependence of NLO properties on the twist angle between two aryl units was observed. It is envisaged that the planar conformations would give an enhanced NLO activity where as any deviations from planarity would decrease the mobility of electrons within the  $\pi$ -conjugated molecular system, resulting a reduction in NLO activity.

The large value of second order polarizability,  $\beta$ , which is the measure of the non-linear optical activity of the molecular system, is associated with the Intra molecular Charge Transfer (ICT), resulting from the electron cloud movement through  $\pi$  conjugated frame work from electron donor to electron acceptor groups. The electron cloud is capable of interacting with an external electric field and thereby altering the dipole moment and the second order non-linear optical activity.

In this paper we report the influence of twist angle on NLO properties of  $\pi$  – conjugated novel molecular system shown in Figure 1. The study shows that this class of organic materials has a very large static molecular hyperpolarizability. The influence of molecular structure was investigated using Mopac 6.0. The main structural feature that controls the  $\beta$  was the twist angle (1234) ( $\theta$ ) which is the angle between the two fused rings and the diaminomethylene group (Figure 1). As discussed earlier one would expect the  $\beta$  to be lowered when the twist is changed or when deviated from the planarity. In this investigation we observed that the maximum  $\beta$  is obtained for a non-planar structure. Similar trends have been observed for push–pull polyenes [30,31]. The molecular twist can be attributed to the repulsion between the groups attached to the amino nitrogen atoms and the *ortho* hydrogen atoms on the fused ring system.

**Table 1.** The groups of designed novel molecular systems shown in Figure 1

Molecule	X	Y
1	NH <sub>2</sub>	NH <sub>2</sub>
2	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
3	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
4	HN(CH <sub>2</sub> ) <sub>2</sub> NH	
5	CH <sub>3</sub> N(CH <sub>2</sub> ) <sub>2</sub> NCH <sub>3</sub>	
6	(CH <sub>3</sub> ) <sub>3</sub> CN(CH <sub>2</sub> ) <sub>2</sub> NC(CH <sub>3</sub> ) <sub>3</sub>	
7		NH <sub>2</sub>
8		N(CH <sub>3</sub> ) <sub>2</sub>
9		N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
10		
11		
12		
13		
14		

Our objective is to design a range of novel molecular systems, which show nonlinear optical activity and to study the  $\beta$  –  $\theta$  correlation of these molecular systems. The approach is based on the concept of charge transfer (CT) between donor and acceptor through a fused conjugated six-membered ring system shown in Figure 1. In this paper, first hyperpolarizabilities ( $\beta$ ) are calculated using semi-empirical method using AM1 Hamiltonian for fourteen derivatives shown in Table 1, using Mopac 6.0. The designing of systems with high charge transfer is key to this part, as intra molecular charge transfer between donor and acceptor will lead to a very large value for  $\beta$ . The investigation of  $\beta$  –  $\theta$  correlation is explained by the calculation of frontier molecular orbital

energies which will help to use the intramolecular charge transfer model to explain the hyperpolarizability.

## 2 MATERIALS AND METHODS

All hyperpolarizability calculations of these derivatives (Table 1) were performed using Mopac 6.0 [32], on an Intel Pentium III 550MHz processor with 128 MB RAM and Microsoft windows 98 as the operating system. The geometry optimization was performed in a series of steps for each molecule listed in the Table 1. The variation of static hyperpolarizabilities against the twist angle ( $\theta$ ) was scanned by fully optimization of the rest of the geometry at every point. The points were selected at intervals of  $5^\circ$  for  $\theta$  ranging from  $0^\circ - 90^\circ$ .

## 3 RESULTS AND DISCUSSION

The novel molecular systems studied in this investigation using semi-empirical approach, are shown in the Table 1. The study involves the calculation of first static hyperpolarizability tensor for all fourteen derivatives by changing the dihedral angle (1234) to determine the optimum dihedral angle which gives the largest static hyperpolarizability. It is also intended to compare the electronic effect on the first hyperpolarizability of these derivatives upon substitution of different donor groups and keeping the acceptor group as cyanide.

**Table 2.** Maximum total static hyperpolarizability for all the molecules

Molecule	Dihedral Angle (Degrees) (1234)	Hyperpolarizability ( $\beta \times 10^{-30}$ esu)
1	75	259.31
2	70	344.77
3	70	373.84
4	75	322.40
5	75	326.91
6	50	374.86
7	65	294.14
8	60	332.57
9	65	373.49
10	70	369.38
11	45	347.69
12	55	348.31
13	55	347.24
14	65	369.50

Many types of hyperpolarizabilities have been discussed in the literature denoted as  $\beta_{\text{vec}}$  ( $\beta$  vector),  $\beta_{\parallel}$  ( $\beta$  parallel),  $\beta_{\text{tot}}$  ( $\beta$  total).  $\beta_{\text{vec}}$  which is the component along the dipole moment direction, can be measured experimentally using Stark Spectroscopy [33]. But the theoretical chemists are concerned with  $\beta_{\parallel}$  which is the component parallel to the ground state charge transfer direction and the other is the total hyperpolarizability  $\beta_{\text{tot}}$ . In this investigation we report  $\beta_{\text{tot}}$  for all the molecules

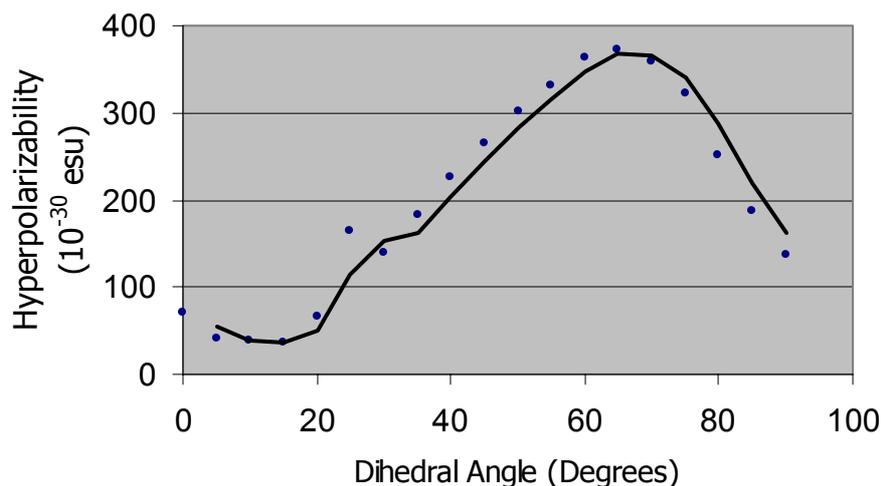
listed in Table 1. Since the values of the first hyperpolarizability tensors of the output file of Mopac 6.0 are reported in atomic units (au), the calculated values were converted into electrostatic units. ( $1 \text{ au} = 8.6393 \times 10^{-33} \text{ esu}$ ). The magnitude of the first hyperpolarizability is dependent on the twist angle and can be increased by the availability of the lone pair of electrons on the nitrogen atoms of the substituted groups to conjugate through the fused six membered ring systems and towards the cyanide group. The maximum  $\beta_{\text{tot}}$  for a particular dihedral angle was calculated and reported in Table 2.

**Table 3.** Change of static hyperpolarizability and HOMO–LUMO gap with the dihedral angle (1234) for molecule **9**

Dihedral Angle (Degrees)	Hyperpolarizability ( $\beta \times 10^{-30} \text{ esu}$ )	HOMO–LUMO (Hartrees)
0	70.08	0.5185
5	40.87	0.4923
10	39.10	0.4936
15	35.49	0.5020
20	65.57	0.5076
25	164.66	0.3910
30	139.98	0.5086
35	182.91	0.4461
40	225.32	0.3121
45	264.46	0.2797
50	300.89	0.2254
55	330.54	0.1649
60	363.39	0.1374
65	373.49	0.5449
70	358.43	0.5983
75	322.19	0.6320
80	252.12	0.6661
85	187.68	0.6906
90	136.09	0.7218

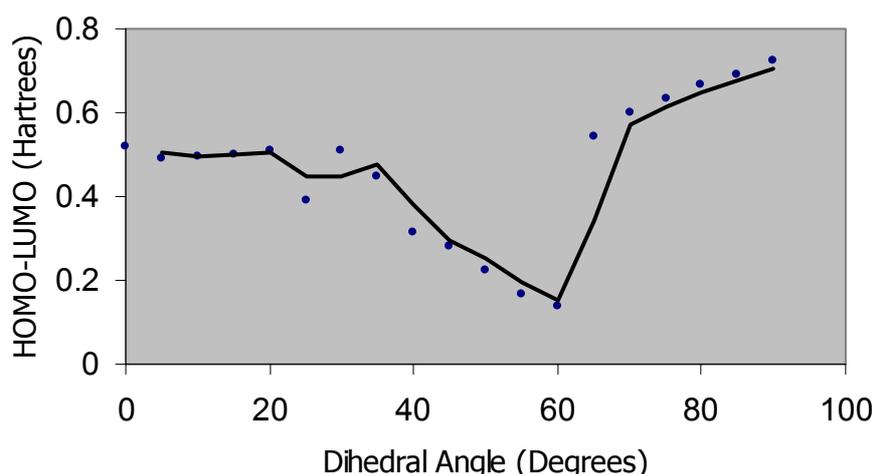
The massive increase of first hyperpolarizability has been observed for a particular twist angle for each molecule listed in the Table 1. All the molecules were investigated as a function of the twist angle and calculated the hyperpolarizability for all the twist angles ranging from  $0^\circ$ – $90^\circ$ . As this will yield an extensive amount of data we have selected the molecule **9** to show the effect of twist angle on the hyperpolarizability. The data for molecule **9** is shown in Table 3.

The maximum NLO response is obtained by promoting the lone pair on the nitrogen atom of the donor group to conjugate through the ring system towards the cyanide moiety. The substitution on nitrogen of  $\text{NH}_2$  group with other groups listed in Table 1, in general enhance the NLO activity. The general belief is that the planarity is one of the criteria to satisfy for a molecule to be NLO active. However the molecules investigated under this project have shown much higher value for a non-planar structure. The variation of first static hyperpolarizability with the twist angle for molecule **9** is graphically shown in Figure 2.



**Figure 2.** The variation of first static hyperpolarizability with the twist angle for molecule 9.

The study shows that by changing the dihedral angle (1234) should reduce the HOMO–LUMO energy gap for a particular dihedral angle allowing the molecular orbitals to overlap to have a proper conjugation. This is obvious when the frontier molecular orbital energies are studied using the Mopac 6.0. The variation of HOMO–LUMO energy gap with the dihedral angle for molecule 9 is given in Figure 3. The general trend for all the molecules is that the optimum dihedral angle for maximum hyperpolarizability would be  $60^{\circ}\pm 15^{\circ}$ . This will clearly show that the maximum hyperpolarizability is obtained for a non-planar structure for all the molecules. It is also seen that from Figure 2 and Figure 3 there is an inverse relationship between hyperpolarizability and the HOMO–LUMO gap. The same type of dependency was obtained for all other molecular systems.

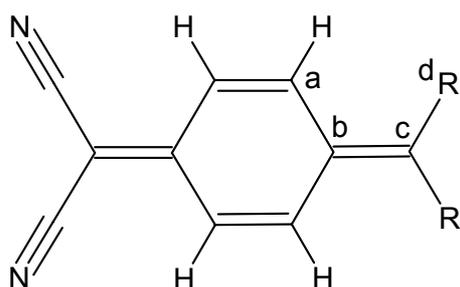


**Figure 3.** The variation of HOMO–LUMO energy gap with the twist angle for molecule 9.

It is expected that the molecules with increasing donor ability would yield a higher value for first hyperpolarizability and this can be seen when we move from molecule 1 to 14. The donor ability of amino groups from molecule 1 to 3 is increased resulting increase in first hyperpolarizability.

However molecule 4 shows a lower hyperpolarizability due to strained weak donor group which is not capable of communicating with cyanide groups as effective as the previous groups.

Molecule 4 to 6 show an increase of hyperpolarizability due to alkyl groups present in the ring. Similar trends for other molecules have been observed as shown in the Table 2. The enhancement of first hyperpolarizability is attributed to the enhanced availability of the two lone pairs on two nitrogen atoms, for conjugation with the fused ring system. These values of hyperpolarizability are much higher than value of a normal organic conjugated system such as *para*-nitro aniline or molecular systems that we reported earlier [16–18].



**Figure 4.** Molecular system reported in the literature [34].

**Table 4.** Hyperpolarizabilities, AM1 dihedral angles and experimental dihedral angles of some of the molecules (Figure 4) reported in the literature [34]

R	R'	AM1 abcd angle	Experimental abcd angle	( $\beta \times 10^{-30}$ esu)
		58.4	56.7 [39]	79.8
		59.3	73.8 [38]	81.1
		33.5	48.6 [36]	22.9

The hyperpolarizabilities of these molecular systems can be compared with a similar systems found in the literature [34]. They have investigated such systems (Figure 4) both experimentally and theoretically and calculated the molecular hyperpolarizability as a function of the dihedral angle and reported the optimum twist angle. It is interesting to see that these twist angles investigated here have been found experimentally [35–40]. Single crystal X-ray investigations of several members of the molecule shown in Figure 4 have shown a wide range of dihedral angles. As we discussed earlier this molecular twist is a result of the steric repulsion between the groups attached to the amino nitrogen atom and the *ortho* hydrogen atoms of the ring. So the concept of designing of molecules with different donor groups to effect the desired intermolecular interactions to obtain a specific twist angle and a large hyperpolarizability is justified.

Table 4 shows the dihedral angles obtained by AM1 calculation for the molecular system shown in Figure 4 with different donor groups [34]. The Table 4 also gives the twist angles determined

from single X-ray crystal analysis for these molecular systems. It is clear that crystal structures of these compounds agree with the AM1 calculations [34]. This finding is in agreement with our results as we have found that the optimal hyperpolarizability is obtained for a non-planar structure and the optimal twist angle is dependent on the donor groups attached to the molecular system. In comparison to the molecular system shown in Figure 4, the molecular systems investigated in this study show comparable twist angles and more importantly at least five fold increases in the hyperpolarizability which is essential for these materials to be used as optical devices.

## 4 CONCLUSIONS

It is obvious that the first hyperpolarizability is strongly dependent on the extent of the electronic communication between the donor group and the acceptor group through the bridge. We have also observed that the hyperpolarizability is dependent on the twist or the dihedral angle ( $\theta$ ) as shown in Figure 1. This result shows that the larger hyperpolarizability is obtained for a non-planar structure of all molecular systems. The hyperpolarizability values reported in this investigation are much higher than the reported organic molecular systems with comparable atomic skeletons. A particular dihedral angle may be responsible for the complete overlap of orbitals to facilitate the charge transfer (CT) from donor to acceptor through the bridge. The HOMO LUMO calculations show that the first hyperpolarizability of these derivatives is directly related to the HOMO-LUMO energy gap with an inverse relationship between two properties. This study reveals that these novel molecular systems have large first static hyperpolarizabilities and may have potential applications in the development of NLO materials. The study also suggests that the dihedral angle could be used through different donor groups to tune the value of hyperpolarizability of these molecular systems.

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