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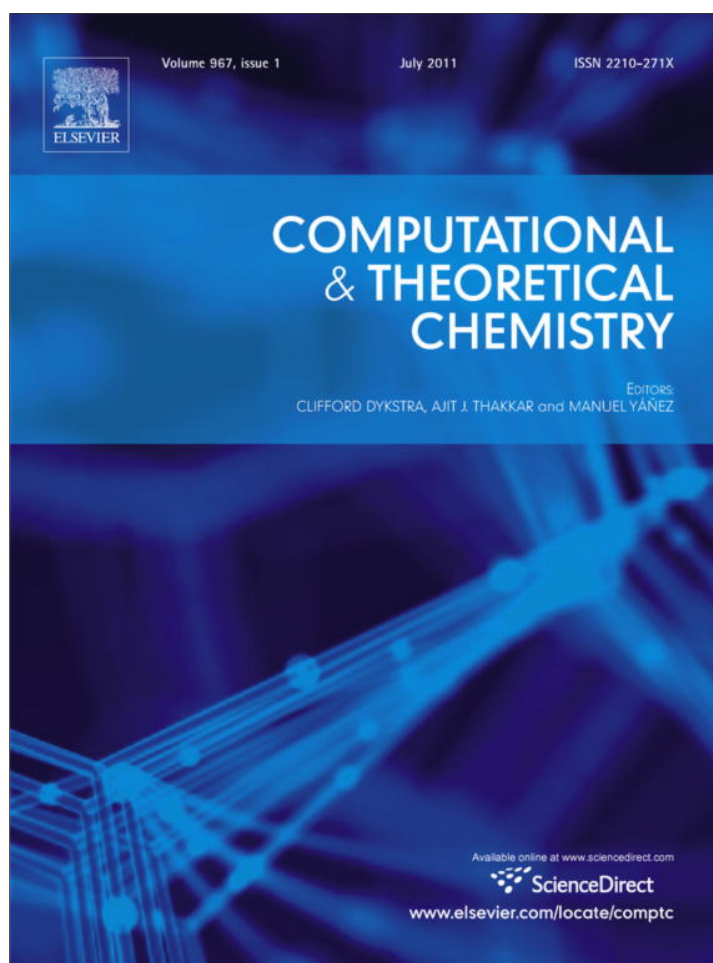


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ABSTRACT

The nonlinear optical (NLO) properties of a series of anilines and *N,N*-dimethylanilines are studied with second-order Møller–Plesset perturbation theory (MP2). The effect of solvents on the calculated NLO properties is investigated by considering a wide range of solvent systems within the polarizable continuum model. In order to identify systems with high first-order hyperpolarizability, the effects of four basic variations to the molecules on the calculated NLO properties are studied. The modifications comprise changes to the donor strength (NH_2 to $\text{N}(\text{CH}_3)_2$), changes to the acceptor strength (NO_2 , CN and CHO), variation of additional substituents (H , CH_3 , Br , OCH_3), and changes in the conjugation length. It is found that the first-order hyperpolarizability increases when the compounds have *N,N*-dimethyl as donor, vinyl nitro group as acceptor at the 4-position, and a methoxy group as substituent at the 2-position.

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1. Introduction

Nonlinear optics (NLO) plays a major role in the advancement of photonics and light-intensity dependent transmission technology [1]. NLO properties enable modification of the amplitude, phase, or frequency of an optical signal, for example, in optical second harmonic generation (SHG), where laser light is converted to light at twice the frequency of the input beam [2]. Other important applications of photonics are the optical processing of information and optical computing [1]. The light-intensity-dependent transmission properties of NLO materials might serve as eye or opto-electronic sensor protection from unwanted sources of laser radiation [1].

In recent years, there has been growing interest in organic materials for nonlinear optics. Numerous experimental [3–16] as well as theoretical [15,17–35] investigations have been performed for the NLO properties of organic molecules. Conjugated organic molecules and molecular materials have been shown to exhibit larger optical nonlinearities than any traditional inorganic materials such as LiNbO_3 [36], KH_2PO_4 [37], LiB_3O_5 [38] etc. and are amenable to optimization of their properties by rational modification of the structures at the molecular or supramolecular levels. Organic materials for NLO applications must have high mechanical strength as well as excellent environmental and thermal stability, low dielectric constants and refractive indices [1]. An important feature

of organic molecules with significant NLO activity is that they generally consist of a π -electron conjugated moiety substituted with an electron donor group (D) on one end of the structure and an electron acceptor group (A) on the other end, forming a “push–pull” conjugated structure [39]. The conjugated π -electron moiety provides a pathway for the redistribution of electronic charge across the entire length of conjugation under the perturbation of external electric field. In addition, the asymmetric substitution of a conjugated chain with A and D groups on either end provides the non-centrosymmetry required for a second-order nonlinearity. In general, the NLO susceptibilities of a material provide a quantitative measure of the ability of a bulk material to alter the optical properties. The microscopic nonlinear coefficients, or molecular hyperpolarizabilities, can be defined as the molecular equivalents of bulk nonlinear optical susceptibilities. Hyperpolarizabilities may be deduced experimentally from direct observations of harmonic generations [40,41] and from the measurements of the Kerr effect [42]. Since the NLO response is mainly governed by the chromophores, the optical nonlinearity is primarily derived from molecular structure. An understanding of the structure–property relations for the NLO responses provides guidelines for the design of novel molecular NLO materials. In this respect, quantum chemical investigation can help to rationalize the experimental results and rank the existing molecular structures according to their linear and nonlinear susceptibilities prior to experiment and thus help to direct the synthesis of new promising compounds to organic chemists [24].

In this paper, we present a theoretical investigation of the electronic and NLO properties (such as dipole moment (μ),

* Corresponding author. Tel.: +61 2 9850 8291; fax: +61 2 9850 8313.

E-mail address: andrew.try@mq.edu.au (A.C. Try).

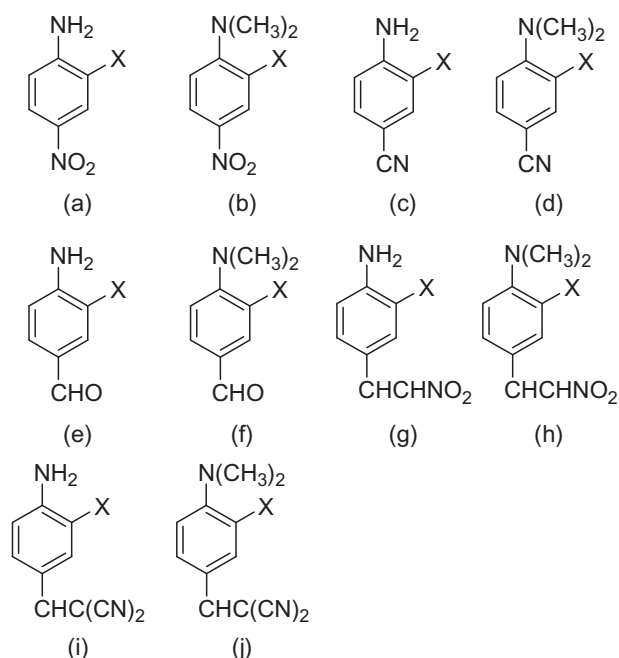


Fig. 1. Structures of the compounds studied in this work. (a) 4-Nitroanilines, (b) 4-nitro-*N,N*-dimethylanilines, (c) 4-cyanoanilines, (d) 4-cyano-*N,N*-dimethylanilines, (e) 4-aminobenzaldehydes, (f) 4-(*N,N*-dimethylamino)benzaldehydes, (g) 4*E*-vinyl-nitroanilines, (h) 4*E*-vinylnitro-*N,N*-dimethylanilines, (i) 4-vinyldicyanoanilines, and (j) 4-vinyldicyano-*N,N*-dimethylanilines. X represents the substituents H, Br, CH₃ or OCH₃.

polarizability (α), hyperpolarizability (β) and optical band gap (ΔE) of a series of anilines and *N,N*-dimethylanilines with the MP2 method. This investigation helps to understand the structure–property relationships in terms of acceptor strength, substitution pattern and conjugation length. A series of *ortho*-substituted 4-nitroanilines, 4-nitro-*N,N*-dimethylanilines, 4-cyanoanilines, 4-cyano-*N,N*-dimethylanilines, 4-aminobenzaldehydes, 4-(*N,N*-dimethylamino)benzaldehydes, 4*E*-vinylnitroanilines, 4*E*-vinylnitro-*N,N*-dimethylanilines, 4-vinyldicyanoanilines, and 4-vinyldicyano-*N,N*-dimethylanilines (as depicted in Fig. 1) are examined. The trends of the calculated values are compared with theoretical and experimental data available from literature.

2. Computational method

The investigation of the NLO properties of a series of substituted anilines and *N,N*-dimethylanilines was performed with the MP2 method [43] based on the Møller–Plesset perturbation theory [44]. This method is applied as implemented in the quantum chemistry package GAUSSIAN09 [45]. The polarizabilities and hyperpolarizabilities were computed with an analytical differentiation procedure using static frequency ($\omega = 0$). The choice of the MP2 method was made on the basis of a series of test calculations using various methods applying a standard 6-311G(*d,p*) basis set. The calculated properties of a representative molecule, 4-nitroaniline, are compared with the available experimental data [5,46–49] in Table 1. Based on the comparison of the calculated results with available experimental data, it can be concluded that the MP2 method is the best method among all those examined.

The choice of basis set (BS) is an important criterion in order to describe the electronic distribution reorganization that results from the external perturbation. The quality of the atomic basis sets determines the reliability of the results. Therefore, we have tested basis sets (BS) of increasing quality starting from a split valence

Table 1

Comparison of calculated and experimental values of dipole moment μ (Debye), polarizability ($\alpha \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$), hyperpolarizability ($\beta \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) and ionization potential (IP) eV for 4-nitroaniline with different methods using a 6-311G(*d,p*) BS.

Methods	Solvents	Properties			
		μ	α	β	I.P
HF	Gas	6.61	1.27	2.92	8.96
	Acetone	8.61	1.58	10.18	8.50
PW91PW91 [55]	Gas	7.32	1.40	7.08	5.66
	Acetone	12.00	2.11	19.34	5.32
mPW1PW91 [56]	Gas	7.15	1.31	6.18	6.68
	Acetone	10.10	1.95	25.32	6.40
BLYP [57,58]	Gas	7.30	1.42	7.48	5.46
	Acetone	10.60	2.14	18.92	5.22
B3LYP [58,59]	Gas	7.20	1.34	6.64	6.44
	Acetone	9.73	1.89	21.67	6.05
MP2 [43,44]	Gas	5.50	1.29	5.99	9.11
	Acetone	7.62	1.85	26.02	8.75
Exp	Gas	6.30 ^a			8.85 ^d , 8.60 ^e
	Acetone	7.30 ^b	1.70 ^c	25.90 ^b	

^a [46].

^b [47].

^c [5].

^d [48].

^e [49].

Table 2

Convergence of basis sets (BS) on the calculated properties, dipole moment μ (Debye), polarizability ($\alpha \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$), hyperpolarizability ($\beta \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) and ionization potential (IP) eV for 4-nitroaniline with MP2 method.

BS	Solvents	μ	α	β	I.P
Def2-SVP	Gas	6.26	1.25	6.57	9.05
	Acetone	8.03	1.71	22.05	8.83
Def2-TZVP	Gas	6.21	1.42	6.87	9.04
	Acetone	8.27	2.01	26.47	8.81
Def2-TZVPP	Gas	6.1	1.43	6.68	9.06
	Acetone	7.63	2.02	25.86	8.88
Exp	Gas	6.30 ^a			8.85 ^d , 8.60 ^e
	Acetone	7.30 ^b	1.70 ^c	25.90 ^b	

^a [46].

^b [47].

^c [5].

^d [48].

^e [49].

basis set with polarized functions (Def2-SVP) to triple zeta valence basis sets with polarization functions (Def2-TZVP and Def2-TZVPP) [50]. We observed that the calculated properties are converged with a Def2-TZVPP BS (see Table 2). Therefore, this BS was used for the entire study. Solvent effects on the calculated properties are examined by applying the polarizable continuum model (PCM) [51].

3. Results and discussion

We present the results for the calculated dipole moment, polarizability, hyperpolarizability and optical band gap for a series of related anilines and *N,N*-dimethylanilines. Since polarizability and hyperpolarizability properties are very sensitive to geometry, first a full optimization was performed. The origin of NLO properties is the polarization induced by high order terms of optical electric fields. The molecular polarization resembles the molecular dipole moment, μ , under an electric field from a laser light, which is computed as in the following equation:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (3.1)$$

where μ_x , μ_y and μ_z are induced dipole moment vectors along the x , y , and z directions. The polarizability α was calculated using the following equation:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3.2)$$

The hyperpolarizability β is the measure of the nonlinear optical activity which can be of different types and has been discussed in the literature in many ways such as β_{vec} (β vector), β_{II} (β parallel), β_{tot} (β total). Here we present our findings in terms of β_{vec} , according to the available literature data. β relates to the induced dipole moment vectors (μ_x , μ_y and μ_z) which are affected by an external electric field along the a -axis ($a = x, y$ or z) and b -axis ($b = x, y$ or z). Therefore, β is considered to be a value based on two-photon processes. This β tensor can be described by a $3 \times 3 \times 3$ matrix. The 27 components can be reduced to 10 components due to the Kleinman symmetry [52].

GAUSSIAN provides 10 components of this matrix as β_{xxx} , β_{yxx} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{zyy} , β_{zxx} , β_{yzz} , β_{zzz} , respectively, from which all x , y and z components of β can be calculated. The complete equation for calculating the magnitude of the vector first static hyperpolarizability is given by:

$$\beta = \frac{3}{5}[(\beta_x^2 + \beta_y^2 + \beta_z^2)]^{\frac{1}{2}} \quad (3.3)$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yxx} + \beta_{yyy} + \beta_{yzz}$$

$$\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$$

The solvent effect on the calculated NLO properties was investigated by the application of a series of solvents where data are available in the literature in order to compare with the experimental data. A systematic variation was performed to investigate the effect of donor–acceptor groups, the effect of substituents and the effect of conjugation length on the NLO properties.

3.1. Effect of solvents

3.1.1. 4-Nitroaniline

In order to study the effect of solvents, first we have considered the model system 4-nitroaniline as it has been extensively studied in a number of solvents [Ref. [47] and references therein]. The electronic and NLO properties such as dipole moment (μ), polarizability (α), hyperpolarizability (β) are calculated in presence of various solvents such as 1,4-dioxane, chloroform, tetrahydrofuran (THF), acetone, methanol, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) within the PCM. The calculated values are compared with the available experimental data [47] in Table 3. In making these comparisons, it should be noted that the trend observed in the calculated values (using the B convention) is essentially the same as that observed in the experimentally derived values (derived from EFISH experiments, using the B⁺ convention), and this is more informative than a comparison of the actual numerical values. In fact, it has been noted previously that caution must be applied even when comparing experimental data reported from different laboratories, as measurements can be made at different wavelengths of excitation.[53] It is noted that there is a gradual increase in the calculated properties with the increase in dielectric constant (ϵ). The NLO properties are plotted against the ϵ values in Fig. 2. It is observed that the experimental data show oscillation with respect to the increasing ϵ values. The discrepancies in the measured NLO values arise from a number of sources which are denoted as ‘solvent effect’ in [53]. One source of this effect is the

Table 3

Effect of solvents on the calculated properties, dipole moment μ (Debye), polarizability ($\alpha \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$) and hyperpolarizability ($\beta \times 10^{-30} \text{ cm}^3 \text{ esu}^{-1}$) for 4-nitroaniline with MP2 using Def2-TZVPP BS.

Solvents	E		μ	α	β
1,4-dioxane	2.2	Calc	6.6	1.66	12.7
		Exp ^a	7.0		16.3
CHCl ₃	4.8	Calc	7.1	1.84	18.7
		Exp ^a	6.4		16.8
THF	7.6	Calc	7.4	1.92	21.6
		Exp ^a	7.1		21.4
Acetone	20.7	Calc	7.6	2.02	25.9
		Exp ^a	7.3	1.70	25.9
Methanol	32.6	Calc	7.7	2.04	26.9
		Exp ^a	6.1		32.0
DMF	36.7	Calc	7.7	2.05	27.2
		Exp ^a	7.3		30.0

^a [47] with irradiation at 1064 nm. Calculated β values are expressed in the B convention, whilst the experimentally derived values (derived from EFISH experiments) are expressed in the B⁺ convention.

chromophore dipole induced reaction field that could modify the local field experienced by NLO chromophores [53]. Another reason is the effect of intermolecular interactions on the transition dipole associated with the charge transfer transition band [53].

Clays and Persoons [54] suggested that the ‘solvent effect’ of NLO properties can be described by an empirical linear relationship between β and $(\epsilon - 1)/(2\epsilon + 1)$. Fig. 2c shows the β vs $(\epsilon - 1)/(2\epsilon + 1)$ plots obtained for the experimental [47] and calculated values. It is observed that most of the experimental β values do not fit in the linear relationship, whereas the calculated values obey the β vs $(\epsilon - 1)/(2\epsilon + 1)$ linear relationship. This might be due to the application of a meanfield model (PCM) for the solvent, which more closely resembles the simple electrostatic approach by Clays and Persoons [54]. In real solvents, direct individual intermolecular interactions via hydrogen bonding and charge transfer processes are likely to occur.

3.1.2. Substituted anilines and *N,N*-dimethylanilines

Davydov et al. [3] showed that dipolar aromatic molecules possessing an electron donor group (D) and an acceptor group (A) contribute to large optical nonlinearity arising from the intramolecular charge transfer between two groups of opposite nature. In the present study, the effect of donor and acceptor groups on the NLO properties is investigated by using NH₂ and (CH₃)₂N as donors and NO₂, CN, and CHO (all in the *para*-position with respect to the donors) as acceptors on an aromatic ring. As it is evident (see the previous section) that the NLO properties have gradually increased with the increase of dielectric constant (with the variation of solvent systems) and a good linear relationship exists for the calculated β vs $(\epsilon - 1)/(2\epsilon + 1)$ plot (Fig. 2c), we have considered only acetone as representative solvent to compare with the calculated properties in the gas phase.

It is observed (Fig. 3) that the presence of *N,N*-dimethylamine as donor (D) will enhance the NLO properties (in comparison to the unsubstituted amino group), namely, dipole moment, polarizability and hyperpolarizability, on average. The *N,N*-dimethylamine group has a higher electron density than the NH₂ group. The electron pair forming the σ bond between the methyl group and the N atom in *N,N*-dimethylaniline can never be shared equally due to the difference in electronegativity. The flow of electron density in the C–N bond will be always towards the C → N direction and this flow is extended up to the aromatic ring, thereby enhancing the NLO properties.

Another important factor is the intramolecular charge transfer between the donor and acceptor groups. If electron density increases at the donor end, electrons can be easily transferred

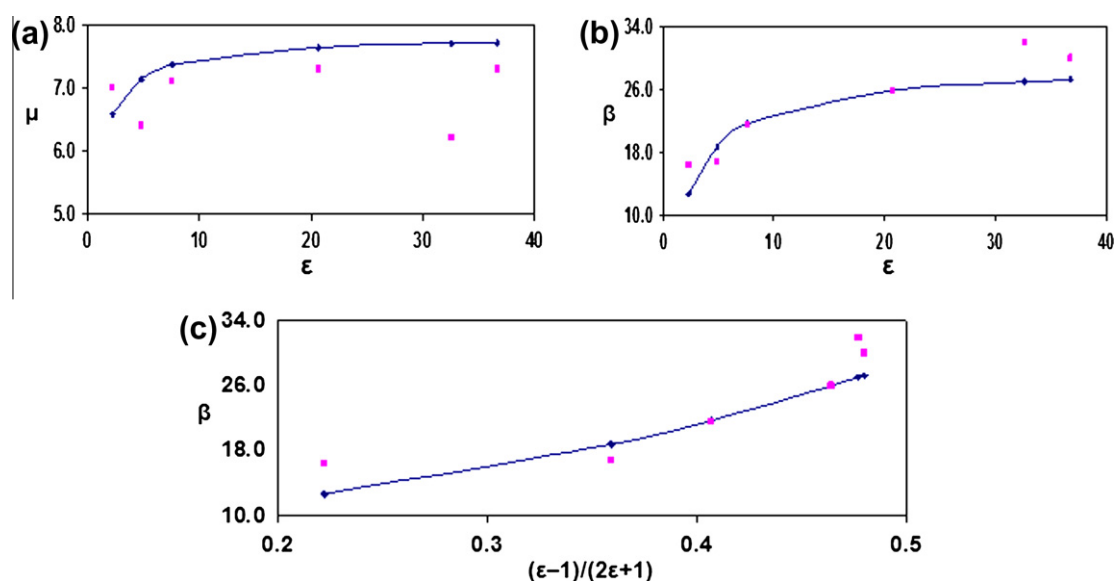


Fig. 2. Solvent effect on the calculated NLO properties for 4-nitroaniline. (a) μ vs ϵ , (b) β vs ϵ and (c) β vs $(\epsilon - 1)/(2\epsilon + 1)$. The blue points represent the calculated data and the red points represent the experimental data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

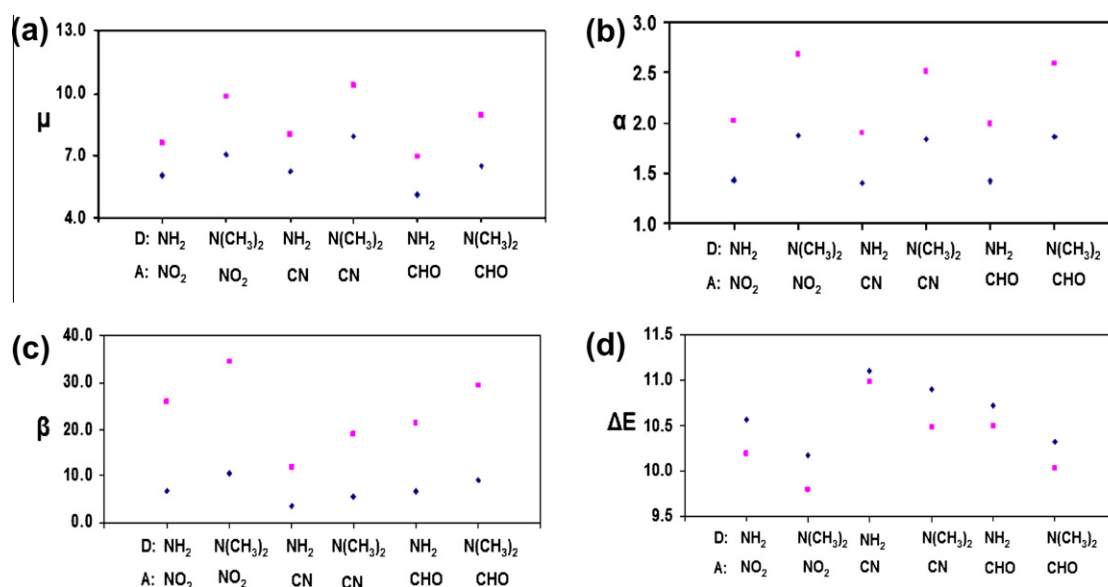


Fig. 3. Calculated NLO properties for substituted anilines and *N,N*-dimethylanilines in gas phase (blue points) and acetone solvent (red points). (a) Dipole moment μ , (b) polarizability α , (c) hyperpolarizability β , and (d) HOMO–LUMO energy gap (ΔE). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

through the conjugated system towards acceptor [8,22]. Therefore, the substituted anilines with *N,N*-dimethylamine as a donor exhibit higher values for μ , α , β . With a given donor, *N,N*-dimethylamine for instance, the μ value decreases gradually with changing the acceptor from nitro to nitrile or aldehyde. The polarizability remains nearly unchanged, whereas hyperpolarizability decreases due to the change of nitro to nitrile but increases for the presence of the aldehyde group. The decrease of NLO properties due to the presence of nitrile as an acceptor is attributed to the π -bonding nature of the nitrile group. The carbon in the nitrile is sp -hybridised, while the carbon to which it is attached on the benzene ring is sp^2 -hybridised. This mismatch of the hybridisation leads to a decrease in electron delocalisation and consequently the dipole moment, polarizability and hyperpolarizability decrease. This is in good agreement with the experimental observations of Cheng

et al. [9]. In the case of the aldehyde group, there is no mismatch in hybridisation. However, it shows less tendency to attract electrons compared to nitro group, as the carbon of the carbonyl group is less electronegative than the nitrogen of the nitro group.

The optical gap (ΔE), i.e., the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the molecular orbital picture plays a vital role in the charge transfer, which in turn affects the NLO activity [11]. A smaller band gap facilitates charge transfer. Therefore, the HOMO largely dictates the source of charge transfer, and the details of the molecular LUMO govern the acceptor portion of the excitation. It is evident from our investigation (Fig. 3d) that 4-nitro-*N,N*-dimethylaniline (which shows the largest β value) has the smallest ΔE (10.17 eV in gas phase and 9.60 eV in acetone solvent), whereas 4-cyanoaniline (smallest β) has the largest ΔE

(11.11 eV in gas phase and 10.99 eV in acetone solvent). The order of acceptor strength was found to be $\text{CN} < \text{CHO} < \text{NO}_2$ and donor strength was found to be $\text{NH}_2 < \text{N}(\text{CH}_3)_2$.

In general, the presence of a solvent enhances the calculated NLO properties compared to the gas-phase results, without affecting the trends. Therefore, in the following sections, we have employed only gas phase calculations, in order to reduce the computational effort.

3.2. Effect of substituent

The effect of an additional substituent on simple phenyl based NLO materials is a less studied area in NLO research. Recently, Davis et al. [24] investigated the effect of a methyl substituent at different positions on 4-nitroaniline and 4-nitro-*N,N*-dimethylaniline. It was concluded that the presence of a methyl group *ortho* to the donor had a fairly neutral effect on the dipole moment and hyperpolarizability, whilst a deleterious effect resulted from its presence *ortho* to the acceptor group. Here we present the effect of substituents on NLO properties employing some model compounds with π -electron acceptor groups (NO_2 , CHO or CN) oriented *para* to either amino or *N,N*-dimethylamino donor group, with either a bromo, methyl or methoxy group *ortho* to the amino (or *N,N*-dimethylamino) group. These substituents were chosen because of their different electronic properties. Hence, it is of interest to determine if their presence is predicted to have a deleterious, positive, or neutral effect on the NLO properties. The results of the present study are shown in Table 4. When the benzene ring of 4-nitroaniline or 4-nitro-*N,N*-dimethylaniline is substituted with an additional group, the resulting maximum acentricity to the molecule gives rise to a non-centrosymmetric crystal structure. This is expected to enhance the NLO activity of the system. The presence of a methoxy group at the *ortho* position of the donor group enhances the charge transfer which is also consistent with the small ΔE value. The methoxy substituent on the aromatic ring provides

more electron density for the acceptor, resulting in a larger β value. Compared to unsubstituted systems, the dipole moment of methoxy substituted compounds decreases due to a perturbation of the donor–acceptor charge transfer. Due to the electron withdrawing nature of bromine, it can increase the HOMO energy to produce a small ΔE value. This, as in the case of methoxy group, will enhance the β value compared to unsubstituted systems. Therefore, the presence of a methoxy group *ortho* to the donor group is predicted to enhance the polarizability and hyperpolarizability in all cases. The effect of having a methyl or bromo group *ortho* to the donor is generally unfavorable, although there are exceptions.

3.3. Effect of conjugation length

The effect of conjugation length on the NLO properties was investigated by using vinylnitro and vinylidicyano as the π -electron acceptor groups for the substituted anilines and *N,N*-dimethylanilines. The results are illustrated in Table 5.

The trend reported in the literature with a host of other compounds is certainly that increasing the length of the conjugation pathway between the donor and acceptor groups leads to an increase in the μ and β values [4,8,9,14,18,25]. Within both amino- and *N,N*-dimethylamino-substituted compounds, indeed the hyperpolarizability is almost linearly dependent on the conjugation length. For a given donor, *N,N*-dimethylamine for instance, the dipole moment increases by 1–2 D ($\approx 25\%$), whereas β value increases by a factor of 3, comparing the acceptors NO_2 (Table 4) and (*E*)-CHCHNO₂ (Table 5). Similarly, $\text{CHC}(\text{CN})_2$ as acceptor also enhances the μ , α and β values compared to CN as an acceptor. This is the well recognized enhancement resulting from the charge transfer interactions between the donor and acceptor groups, which is also evident from the smaller optical gap due to the presence of the (*E*)-CHCHNO₂ group compared to NO_2 . This is an indication that the donor electron is transferred to the acceptor in the ground state and the polarization of the conjugation is extended up to the substituents. Since the molecular dipole is the vectorial sum of these two “local” dipoles, which are often dominated by the group dipole moments of the substituents, increasing their separation does not result in significant increase in the total dipole moment [8]. It is apparent that the largest β value is obtained with the *N,N*-dimethylamine group as the donor and nitro-substituted vinyl group as the acceptor. Here too the methoxy group *ortho* to the donor group produces the largest β value.

Table 4

Substituent effect on the calculated dipole moment (μ) Debye, polarizability ($\alpha \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$), hyperpolarizability ($\beta \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) and the HOMO–LUMO energy gap ΔE (eV) (MP2, Def2-TZVPP). Donor and acceptor are in a *para*-relationship with respect to one another; donor and substituent X are in an *ortho*-relationship with respect to one another.

Donor	Acceptor	X	μ	α	β	ΔE
NH_2	NO_2	H	6.10	1.43	6.68	10.56
		Br	5.77	1.72	7.00	10.42
		CH_3	6.29	1.62	6.53	10.44
		OCH_3	5.63	1.70	8.26	10.08
$\text{N}(\text{CH}_3)_2$	NO_2	H	7.06	1.87	10.39	10.17
		Br	5.51	2.08	6.36	10.36
		CH_3	5.81	1.98	6.20	10.41
		OCH_3	5.29	2.10	12.20	9.93
NH_2	CN	H	6.25	1.40	3.57	11.11
		Br	5.92	1.70	3.64	10.99
		CH_3	6.41	1.58	3.29	11.01
		OCH_3	5.72	1.66	4.42	10.73
$\text{N}(\text{CH}_3)_2$	CN	H	7.96	1.84	5.60	10.90
		Br	5.66	2.07	5.80	10.71
		CH_3	5.96	1.96	2.96	10.98
		OCH_3	5.41	2.06	6.20	10.59
NH_2	CHO	H	5.16	1.42	6.68	10.72
		Br	4.70	1.71	6.35	10.57
		CH_3	5.20	1.60	5.58	10.67
		OCH_3	4.93	1.68	6.81	10.34
$\text{N}(\text{CH}_3)_2$	CHO	H	6.54	1.86	9.07	10.32
		Br	3.56	2.07	5.50	10.58
		CH_3	4.56	1.96	5.24	10.63
		OCH_3	4.55	2.07	10.50	10.22

Table 5

Effect of conjugation length on the calculated dipole moment (μ) Debye, polarizability ($\alpha \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$), hyperpolarizability ($\beta \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) and the HOMO–LUMO energy gap ΔE (eV). Donor and acceptor are in a *para*-relationship with respect to one another; donor and substituent X are in an *ortho*-relationship with respect to one another.

Donor	Acceptor	X	μ	α	β	ΔE
NH_2	(E)-CHCHNO ₂	H	7.21	2.00	22.33	9.45
		Br	6.62	2.30	22.60	9.42
		CH_3	7.46	2.20	23.01	9.36
		OCH_3	6.86	2.29	26.25	9.11
$\text{N}(\text{CH}_3)_2$	(E)-CHCHNO ₂	H	8.06	2.53	34.82	8.80
		Br	6.20	2.67	20.56	9.45
		CH_3	6.80	2.57	21.83	9.41
		OCH_3	6.37	2.70	36.25	8.72
NH_2	$\text{CHC}(\text{CN})_2$	H	8.35	2.27	21.01	9.23
		Br	8.39	2.55	21.18	9.18
		CH_3	8.43	2.46	21.35	9.14
		OCH_3	7.51	2.56	24.58	8.89
$\text{N}(\text{CH}_3)_2$	$\text{CHC}(\text{CN})_2$	H	9.93	2.82	27.07	9.22
		Br	6.66	2.96	22.63	9.50
		CH_3	7.92	2.85	22.60	9.45
		OCH_3	8.21	2.99	29.80	9.10

4. Conclusions

The dipole moment, polarizability, hyperpolarizability and optical band gap for a series of anilines and *N,N*-dimethylanilines were investigated theoretically to understand the structure–property relationship in terms of acceptor strength, substitution pattern and conjugation length. The effect of donor and acceptor groups on the NLO properties was initially investigated by using NH_2 and $(\text{CH}_3)_2\text{N}$ as donors and NO_2 , CN, and CHO as acceptors on a benzene ring. It was found that $(\text{CH}_3)_2\text{N}$ as donor and NO_2 as acceptor will enhance the dipole moment by ≈ 1 D, polarizability by $\approx 0.5 \times 10^{-23} \text{ cm}^3 \text{ esu}^{-1}$ and hyperpolarizability by $1-3 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$, compared to NH_2 as donor and CN or CHO as acceptor. This is due to the enhanced charge transfer interactions between the donor and acceptor groups. The trend of the calculated properties is in good agreement with the available experimental data. The effect of an additional substituent was investigated with either a bromo, methyl or methoxy group *ortho* to the amino (or *N,N*-dimethylamino) donor group. The presence of a substituent, such as a methoxy group, provides the maximum acentricity (of the three groups examined in the present study) to the molecule. This enhances the charge transfer resulting in a large β value. Finally, the effect of conjugation length on NLO properties was investigated by using vinylnitro and vinylidicyano as the π -electron acceptor groups. Both vinylnitro and vinylidicyano were found to enhance the NLO properties compared to NO_2 and CN as acceptors.

In all cases, the enhanced NLO properties are associated with a decreased HOMO–LUMO gap, which is a consequence of the enhanced charge transfer interaction between the donor and acceptor group. From a chemical perspective, the most important feature of the NLO active organic molecules is the strong donor–acceptor intramolecular charge transfer interaction. This can be further tailored by varying substitution pattern at the *ortho* position of the donor groups or by extending the conjugation length of the π acceptors. Synthetic organic chemistry offers a wealth of possibilities to design new materials with anticipated optical or electronic properties. Theoretical and experimental studies are currently underway, with the aim of investigating the NLO properties of more complex molecules.

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