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Oxygen bridged nitroanilines for quadratic nonlinear optics

Ramanathan Sudharsanam[a], Srinivasan Chandrasekaran[a,1], PuspenduKumar Das[b,*]

[a]*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India*
[b]*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India*

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Abstract

Several nitro aromatic compounds bridged by an oxygen atom have been synthesized and their linear and nonlinear optical properties have been investigated. In one of the compounds (**1**), a powder SHG efficiency of 6.2 times of urea was observed while its absorption lies in the UV region. The highest molecular hyperpolarizability β, measured was 230×10^{-30} for a compound (**8f**) with increased conjugation. Thermal stability of these compounds has been checked using differential scanning calorimetry and the decomposition temperature (T_d) was found to be high and lying between 266–298 °C. These molecules have potential importance as thermally stable, visible-transparent second order NLO materials.

Keywords: Nitro aromatic compounds; Azo compounds; Ether linkage; Nonlinear Optics; Second harmonic generation

1. Introduction

Over the past decade, due to its applications in optical communication and processing [1], quadratic nonlinear optics has attracted interest of a large number of researchers from all over the world in the search of molecules as well as materials with large microscopic and macroscopic quadratic nonlinear optical (NLO) response. Considerable amount of progress has been made in finding new organic molecules with large second order polarizability, β[2–4]. Dipolar molecules containing a donor and an acceptor across a π-conjugation bridge, have generally been recognized for large second order NLO response. The magnitude of the response can easily be altered by changing the donor, acceptor or the π-backbone. Although large molecular hyperpolarizability, β has been realized in some organic compounds, a large number of them crystallize in a centrosymmetric fashion in the solid state in which case the crystals do not exhibit macroscopic second order nonlinearity, $\chi^{(2)}$. In an alternate strategy, a bulky group such as an alkyl group has been introduced in a donor acceptor aromatic compound, e.g. *para*-nitroaniline [3–7] or nitropyridine [8] to achieve noncentrosymmetric packing in the solid state. In fact, such attempts have met with a fair amount of success in identifying functional groups capable of inducing polar crystal structure. Inclusion complexes containing a guest NLO chromophore inside the cavity of a host such as, molecular sieves [9], cyclodextrin [10], were developed to achieve

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[*] Corresponding author. Fax: +91-80-360-1552.
E-mail address: pkdas@ipc.iisc.ernet.in (P.K. Das).

[1] Honorary Professor, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore.

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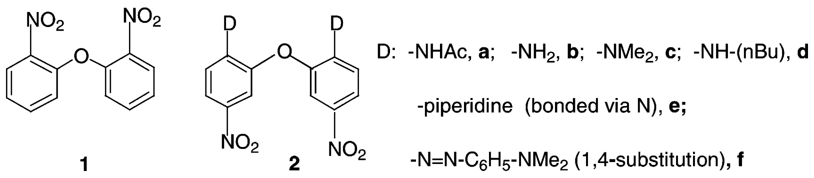


Fig. 1. Oxygen atom bridged nitrobenzenes derivatives.

acentric space groups in the solid state. ‘Lambda-shaped’ and ‘roof-shaped’ [11] molecules in which two independent NLO chromophores have been locked in a specific arrangement, have also been tested. For example, N,N′-bis(4-nitrophenyl) methanediammine (NMDA) in which two nitroanilines have been connected by a methylene bridge tend to adopt a noncentrosymmetric structure.

In this paper, we present a strategy, wherein two NLO moieties have been linked by an ether linkage. We have taken simple chromophores such as nitrobenzenes and paranitroanilines to arrive at structures **1** and **2**, respectively (Fig. 1). Steric interaction between the two nitrobenzene moities would force the molecule to be nonplanar and thus may lead to a noncentrosymmetric packing in the solid state.

2. Experimental

2.1. Synthesis

Para-nitrofluorobenzene **10** and para-nitrophenol **11** were obtained from commercial sources. Commercial grade solvents were distilled prior to use. DMF was shaken with NaOH and distilled over CaO. Toluene was distilled with sodium/benzophenone and stored over sodium wire. DMSO was dried by standing over $CaSO_4$ overnight and filtered. The filtered solvent was fractionally distilled over CaH_2. *n*-butyl amine was dried over KOH. Analytical thin layer chromatography was carried out on Merck precoated silicagel 60F-254, 0.25 mm glass plates. Visualisation of spots was achieved by one or more of the following techniques: (a) UV illumination, (b) exposure to iodine, or, (c) immersion of the plate in a 10% solution of phosphomolybdic acid in ethanol followed by heating to ~200 °C. Column chromatography was carried out using 60–120 and 100–200 mesh Acme silicagel and basic alumina. Flash chromatography was done using TLC grade Acme silicagel. Melting points were measured using a Buchi B-540 instrument; spectroscopic measurements were made in the following instruments; UV–Vis: Hitachi U-3400; FT-IR; Perkin–Elmer-781; ^{1}H: JEOL 300 MHz, BRUKER 200 MHz (NMR chemical shifts are reported in δ values in parts per million down field from the internal reference tetramethyl silane); LRMS: JEOL JMS-DX303 (only principal molecular fragments are reported). Elemental analysis were performed using a Carlo Erba elemental analyser model—1106. Monomers: N,N-Dimethyl-3-nitroaniline [12] **9c**, 3-nitrophenylpiperidine [13] **9e**, 4-(3-nitrophenylazo)-N,N-dimethylaniline [14] **9f**, were synthesized according to literature procedures.

2.1.1. Bis(2-acetamido-4-nitrophenyl) ether (*8a*)

This compound was synthesized according to procedure reported by Randall et al. [15]. Bis(2-acetamidophenyl) ether (**7**) (26 g, 92.0 mmol) was dissolved in hot acetic acid (39 ml) and poured slowly into cold concentrated sulfuric acid (60 ml). A nitrating mixture of concentrated nitric acid (18 ml) and concentrated sulfuric acid (24 ml) was slowly added while the temperature was maintained below 10 °C. The reaction mixture was then allowed to warm up to room temperature and poured over ice. The product was filtered, washed with water and dried. The product was recrystallized from methyl cellosolve to yield **8a** as yellow crystals. Yield: 35.4 g (55%); mp: 261 °C, lit. [15] mp: 258 °C; IR (nujol, cm^{-1}): 3400, 1680, 1530, 1340.

This compound originally thought to have the structure **2a**, turned out to have the structure **8a** (based on single crystal X-ray diffraction).

2.1.2. Bis(2-amino-4-nitrophenyl) ether (*8b*)

The mixture of bis(2-acetamido-4-nitrophenyl) ether (**8a**) (8.1 g, 0.021 mol) and 70% (w/w) sulphuric acid (40 ml) was heated at reflux for 20–30 min. or until the test sample remains clear upon dilution with 2–3 times of its volume of water. The hot solution was then poured into cold water (500 ml) and a precipitate of the bis(2-amino-5-nitrophenyl) ether (**8b**) was obtained by adding an excess of 10% sodium hydroxide solution or concentrated ammonia solution. The mixture was cooled in ice water. The yellow crystalline precipitate was filtered at the pump, washed thoroughly with water and dried. The product was recrystallised three times from methyl cellosolve to give golden crystals of **8b**. Yield: 5.7 g (95%), mp: 245–248 °C (decomp.), lit. [15] mp 248–250 °C; IR (nujol, cm^{-1}): 3490–3440, 3390–3370, 1510, 1340; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.71 (d, $J = 2.6$ Hz, 2 H, Ar H), 7.60 (dd, $J = 9$ Hz, $J = 2.7$ Hz, 2 H, Ar H) 6.64 (d, $J = 4.8$ Hz, 2 H, Ar H), 4.21 (s, 2 H, NH_2).

2.1.3. *Bis(2-N,N dimethylamino-4-nitrophenyl) ether (8c)*

To a stirred solution of 3 M sulfuric acid (5.74 ml, 17.24 mmol) and 40% aqueous formaldehyde (3.8 ml, 4.13 mmol) in an Erlenmeyer flask was added the slurry of bis(2-amino-4-nitrophenyl) ether (**8b**) (1 g, 3.4 mmol) and finely crushed sodium borohydride (1.82 g, 4.82 mmol) in THF (48 ml) slowly by maintaining the temperature of the reaction mixture between − 10 and − 20 °C. After the completion of addition, reaction mixture was made strongly alkaline by adding solid NaOH pellets. The supernatent solution was decanted (and saved) and the solid mass was mixed with water (10 ml), and the resulting solution was extracted with ether (3 × 10 ml). The ether extract was mixed with decanted THF solution. The combined organic solution was washed with saturated NaCl solution and dried over anhydrous $NaSO_4$. The organic solvent was evaporated and the crude product was chromotographed on silicagel column using petroleum ether and EtOAc mixture as eluent to isolate compound **8c** as a solid. It was recrystallized from petroleum ether (60–80 °C) and EtOAc mixture. Yield: 1.08 g (91%) mp: 134.7 °C. IR (nujol, cm^{-1}): 1515, 1344, 1225, 1192; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.78 (d, $J = 2.6$ Hz, 2 H, Ar H), 7.67 (dd, $J = 8.9$ Hz, $J = 2.6$ Hz, 2 H, Ar H), 6.74 (d, $J = 9$ Hz, 2 H, Ar H), 2.84 (s, 12 H, CH_3); LRMS (*m/z*):346 (M^+), 179 (base peak); Analysis (%): Calc. for $C_{16}H_{18}N_4O_5$:C, 55.55; H, 5.20; N, 16.18; Found:C, 55.59; H, 5.19; N, 16.98.

2.1.4. *Bis(N-butylamino-4-nitrophenyl) ether (**8d**)*

A solution of the *n*-butaraldehyde (0.063 ml, 0.69 mmol) in 2-methoxy ethanol/THF (1.6 ml; 3:2) and 3 M sulfuric acid (1.63 ml, 4.8 mmol) was added dropwise to a conical flask containing bis(2-amino-5-nitrophenyl) ether (**8b**) (0.1 g, 0.344 mmol) in 2-methoxy ethanol/THF (5 ml, 2:1). While adding *n*-butaraldehyde solution, powdered $NaBH_4$ (approximately 0.05 g, 1.3 mmol) was added continuously as it was consumed under vigorous magnetic stirring at 0 °C. The mixture was then allowed to warm up to RT over 90 min, diluted with water (2 ml) and made strongly alkaline with sodium hydroxide pellets (cooling). The basic solution was extracted with t-butylmethyl ether (3 × 10 ml). The organic extract was dried over anhydrous sodium sulfate and solvent was removed by distillation. The product (**8d**) from the crude residue was chromotographed on silicagel column using mixtures of petroleum ether and EtOAc. Yield: 0.020 g (15%), mp: 79.1 °C, IR (film, cm^{-1}): 3432, 3020, 2961, 2932, 2874, 1625, 1578, 1531and 1343; ^1H NMR ($CDCl_3$, 200 MHz):δ 7.52 (br, m, 4 H, Ar H) 6.69 (d, $J = 8.4$ Hz, 2 H, Ar H), 4.38 (t, 2 H, NH), 3.22 (br, m, 4 H, CH_2), 1.70 (br, m, 4 H, CH_2), 1.4 (br, m, 4H, CH_2), 0.94 (br, m, 6H, CH_3); LRMS (*m/z*): 402 (M^+), 207 (base peak).

2.1.5. *Bis(2-piperidino-4-nitrophenyl) ether (**8e**)*

A solution of the glutaraldehyde (25% water solution, 0.38 ml, 2.9 mmol) in 2-methoxy ethanol/THF (1.6 ml; 3:2) and 6 M sulfuric acid (1.63 ml, 4.8 mmol) was added dropwise to a conical flask containing bis(2-amino-5-nitrophenyl) ether (**8b**) (0.1 g, 0.344 mmol) in 2-methoxy ethanol/THF (6 ml, 2:1). While adding glutaraldehyde solution, powdered $NaBH_4$ (approximately 0.27 g, 7.2 mmol) was added as soon as the former was consumed, under vigorous magnetic stirring at 0 °C continuously. The reaction mixture was worked up as described earlier to yield **8e** as a solid. Yield: 0.129 g (88%), mp: 116 °C; IR (thin film, cm^{-1}): 3019, 1522, 1343, 1215, 756, 669; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, $J = 2.7$ Hz, 2 H, Ar H), 7.80 (dd, $J = 8.7$ Hz, $J = 2.7$ Hz, 2 H, Ar H), 6.85 (d, $J = 9$ Hz, 2 H, Ar H), 3.8 (br, m, 4 H, CH_2), 1.53 (br, m, 6 H, CH_2); LRMS (*m/z*): 426 (M^+), 204 (base peak); Analysis (%: Calc. for $C_{22}H_{16}N_4O_4,$ C, 61.99; H, 6.10; N, 13.14; Found C, 61.69; H, 6.17; N, 12.57.

2.1.6. 4,4′-[Oxybis(3-nitro-o-phenyleneazo)]bis(N,N-dimethyl-aniline) (8f)

This compound was synthesised from bis(2-acetamido-4-nitrophenyl) ether (**8a**), according to procedure reported by Randall et al. [15] Bis(2-amino-4-nitrophenyl) ether (**8b)** (1.1 g, 3.8 mmol) was dissolved in 5 N hydrochloric acid (10 ml) and cooled to 0–5 °C by adding ice. A solution of sodium nitrite (1 N, 8 ml, 8.0 mmol) was added slowly at 0–5 °C and stirring was continued for 1 h. N,N-dimethylaniline (1 g, 8.3 mmol) was dissolved in dilute hydrochloric acid (10 ml) and was added in one portion. The pH of the solution was adjusted to about five with sodium acetate. The solid separated was filtered, air-dried and recrystallized from toluene. Yield:2.1 g (100%), mp: 217 °C, lit. [15] mp: 217–219 °C; IR (film, cm^{-1}): 1590, 1520, 1340; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.60 (d, $J = 2.8$ Hz, 2 H, Ar H), 8.20 (dd, $J = 8.6$ Hz, $J = 3.2$ Hz, 2 H, Ar H), 7.54 (d, $J = 9.2$ Hz, 2 H, Ar H), 7.35 (d, $J = 3.4$ Hz, 2 H, Ar H), 6.59 (d, $J = 9.4$ Hz, 2 H, Ar H), 3.01 (s, 6 H, CH_3). This compound originally thought to have the structure **2f**, turned out to have the structure **8f**.

2.1.7. Synthesis of Bis(4-Nitrophenyl) ether (12)

A stirred solution of para-fluoronitrobenzene **10** (0.5 g, 0.59 mmol), *para*-nitrophenol **11** (1 g, 7.18 mmol) and potassium carbonate (1.4 g) in dry DMSO (5 ml) was heated at 140 °C for 4 h. The solution was cooled to room temperature and was poured into ice water (10 ml). The resulting solid was filtered and washed well with water. The compound was recrystallized from ethanol. Yield: 0.93 g (100%). mp: 146 °C, lit. [16]143–144 °C; IR (KBr, cm^{-1}): 1580, 1510, 1490, 1340 and 1240

2.2. Crystal structure determination

X-ray data were collected in a computer controlled Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. Data were corrected for Lorentz and polarization effects and the position of the heavy atoms were determined by Patterson methods using SHELXS86. The remaining atoms were found by Fourier analysis using SHELXL-93. Hydrogen atoms are not shown in Fig. 2. The crystal data and experimental details are shown in the Table 1. Atomic coordinates, bond lengths, bond angle and torsion angles will be deposited in the Cambridge Structural Data Base.

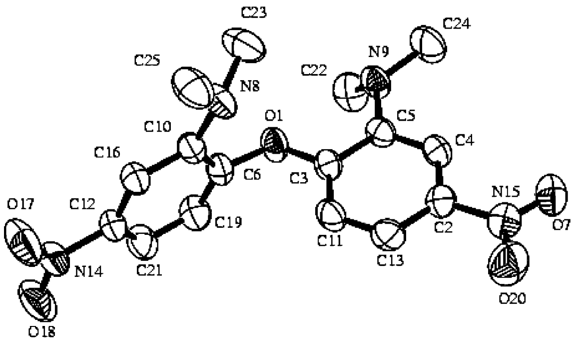


Fig. 2. ORTEP diagram of Bis(2-N,N-dimethylamino-4-nitro)ether **8c.**

2.3. Hyperpolarizability measurements

The first hyperpolarizability, β values of all the molecules have been measured using the hyper-Rayleigh scattering (HRS) technique [17,18] in solution at 1064 nm. Chloroform was used as the solvent, and the β values were obtained using PNA in chloroform as an external reference ($\beta = 17 \times 10^{-30}$ esu) [19].

3. Results and discussion

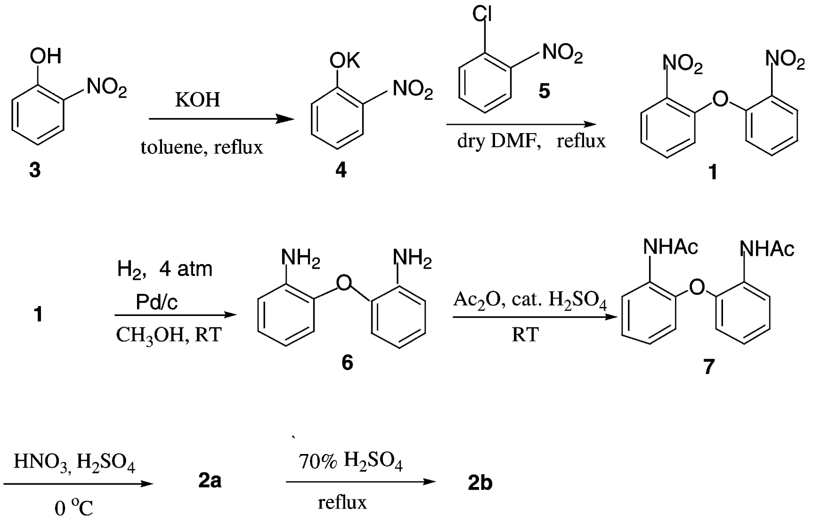
Synthesis of compounds **1**, **2a–b** has been reported in the literature by Randall et al. [15] following the route presented in Scheme 1. Compound **2a** was identified as the product of nitration of compound **7** and product of hydrolysis of **2a** was characterized as **2b**. Following the same procedure for the synthesis of **2a** and **2b** we isolated the two compounds whose melting points matched with those reported in the literature [15]. A reductive alkylation [12] of alleged **2b** was carried out with formaldehyde and sodium borohydride to get the *N*-dimethylated derivative **2c**. Since this compound was not reported in the literature spectral and analytical data for this compound were collected. The compound showed IR (nujol, cm^{-}):1515, 1344, 1225, 1192 and ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.78 (d, $J = 2.6$ Hz, 2 H, Ar H), 7.67 (dd, $J = 8.9$ Hz, $J = 2.6$ Hz, 2 H, Ar H), 6.74 (d, $J = 9$ Hz, 2 H, Ar H), 2.84. While it was not unambiguous,

Table 1
Crystal data and structure refinement for **8c**

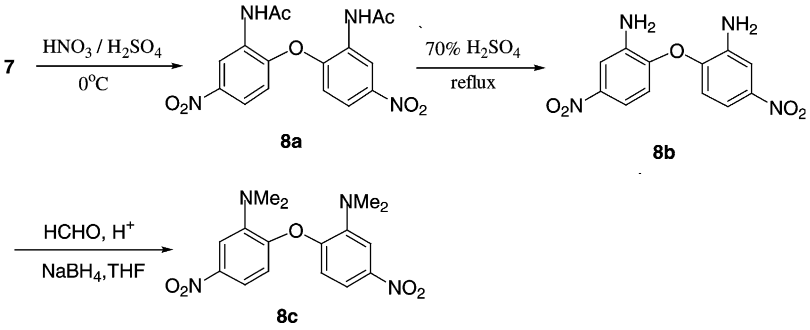
Empirical formula	$C_{16}H_{18}N_4O_5$
Formula weight	346.34
Temperature	293(2) K
Wavelength (Mo Kα)	0.71073 Å
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions	$a = 8.947(2)$ Å, $\alpha = 65.19(3)°$; $b = 9.936(4)$ Å, $\beta = 81.86(2)°$; $c = 10.808(3)$ Å, $\gamma = 77.12(2)°$.
Volume	849.0(5) $Å^3$
Z	2
Density (calculated)	1.355 mg/m^3
Absorption coefficient	0.103 mm^{-1}
$F(000)$	364
Crystal size	$0.18 \times 0.2 \times 0.22$ mm^3
Theta range for data collection	2.08–26.97°.
Index ranges	$0 < = h < = 11, -12 < = k < = 12, -13 < = l < = 13$
Reflections collected	3943
Independent reflections	3700 [R(int) = 0.0187]
Completeness to theta = 26.97°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3700/0/299
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\mathrm{sigma}(I)$]	$R1 = 0.0465$, $wR2 = 0.1166$
R indices (all data)	$R1 = 0.0816$, $wR2 = 0.1364$
Extinction coefficient	0.007(3)
Largest diff. peak and hole	0.192 and -0.218 e $Å^{-3}$

the spectral data of **2c** could also fit in with an isomeric structure **8c**. Since this compound turned out to be crystalline, a single crystal was grown from a solution of ethylacetate/petroleum ether (60–80 °C) and the crystal structure was solved by X-ray diffraction. The ORTEP diagram of this compound is given in Fig. 2. Surprisingly in this compound, the nitro groups were found to be para to the bridged oxygen atom and not to the amino groups. This is contrary to the structure proposed by Randall et al. [15]. Thus, the compound originally thought to be **2c** turned out to have the structure, **8c**. Obviously, in the nitration of compound **7**, the actual compound isolated by Randall et al was **8a** rather than **2a**. Therefore, all the compounds thought to have structure **2** turned out to be derivatives of **8**. These structures are shown in Scheme 2. The presence of only the *meta* isomer is also supported by differential scanning calorimetry (DSC). Only one sharp endothermic peak was obtained corresponding to the melting of the *meta* isomer in the nitrated product (mp = 261 °C, the DSC thermogram is shown later). Due to poor solubility of **8a** and **8b** in organic solvents, several attempts to grow single crystals of these compounds failed.

Now that we have synthesized substituted diaryl ether derivatives **8** rather than the originally planned **2**, it was decided to prepare a few more derivatives in



Scheme 1.

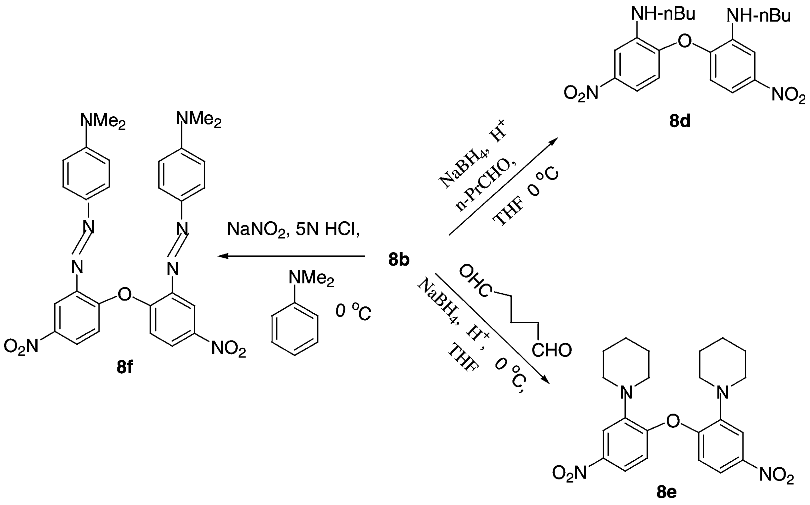


Scheme 2.

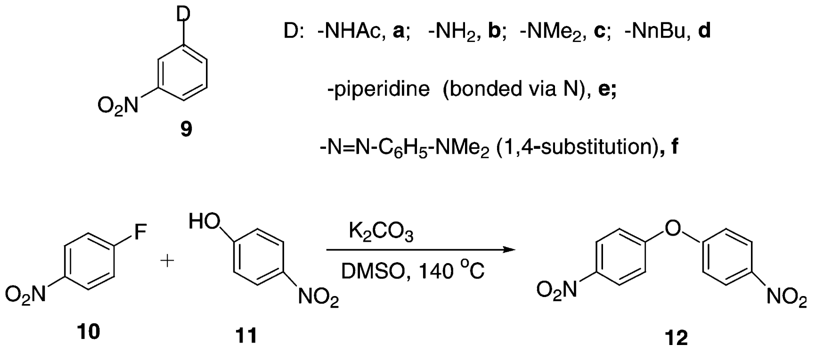
this series and investigate their linear and nonlinear optical properties. Each free amine in compound **8b** was monobutylated [13] by *n*-butyraldehyde and sodium borohydride in the presence of 3 M sulfuric acid to prepare compound **8d**. Further, the nitrogen atom in the free amine of compound **8b** was converted to be part of a piperidine ring by reductive alkylation [13] using 25% glutaraldehyde and sodium borohydride to give compound **8e**. The piperidine ring in **8e** is one of the strongest donors employed in this study. The conjugation length between the donor and the acceptor was increased from amine functionality by diazotizing the free amine in compound **8b** with sodium nitrite, 5 N HCl at 0 °C and coupled with N,N-dimethylaniline to give compound **8f**. These reactions are given in Scheme 3. Similarly, bis(4-nitrophenyl)ether **12** without the amino groups was synthesized in quantitative yield by the reaction of p-fluoro nitrobenzene **10** with p-nitrophenol **11** in DMSO at 140 °C. (Scheme 4). The linear and nonlinear optical properties of these new sets of compounds were then examined and compared with those of the corresponding monomers.

3.1. Linear optical properties

The electronic spectra of all the compounds have been recorded in chloroform and results are listed in Table 2. A representative UV spectrum of the oxygen atom bridged molecules is shown in Fig. 3. Only one peak has been observed for nitrobenzene at 259 nm. When two nitrobenzene units were bridged by an oxygen atom at *ortho* positions as in **1a**, a new absorption band appeared at 309.8 nm.



Scheme 3.



Scheme 4.

However, when the nitro groups were placed para to the bridged oxygen atom only one band at 304 nm was observed as seen in **12**. Due to the mesomeric (−M) effect of the nitro group the primary benzene $^1L_a \leftarrow {}^1A_{1g}$ transition (203 nm) shifts to the red in **1** and **12**. Compound **1** has a λ_{cutoff} wavelength (the wavelength at which the absorption becomes zero on the longer wavelength side is taken as λ_{cutoff}) in the UV region, which is conducive for application. Normally three bands are observed in the donor-acceptor *meta* disubstituted benzene compounds [20,21]. All the three bands arise due to the three primary transitions in benzene but they are red-shifted because of substitution. However, only two bands were resolved when the donor strength is high as seen for **9c–f**. In the case of the dimers, **8**, the lone pairs on the bridge oxygen atom interact with the ring π-electrons and displace the primary transitions in the benzene ring. The peak positions are also affected by the nature of the amine group. No correlation was observed between the λ_{max}'s of the dimers. This result is in sharp contrast to what happens in 1, 4- donor–acceptor disubstituted benzenoid compounds, where CT exists from the donor to the acceptor via the benzene ring. This absence of the CT band could be due to the presence of the bridged oxygen atom, which contributes to the CT and weak interactions between the amine and the nitro groups positioned in the *meta*-position with respect to each other. In compounds **8f** and**9f**, there is a pronounced red shift in λ_{max}, which may very well be due to an increased conjugation between the donor and the acceptor.

3.2. Powder SHG studies

Compound **1** shows SHG efficiency of 6.2 times of that of urea. This is the highest value obtained among the oxygen atom bridged compounds studied here. Unfortunately, several attempts to grow single crystal of this compound were not successful. Dimers **8** show low or no SHG when the size of the amine group is small. Higher SHG efficiency compared to the monomers was observed when the size of the amine group was increased as in **8d–8f**. The implication is that steric constraints provided by large groups that are ortho to the ether linkage, lead to noncentrosymmetric packing arrangement. It also points to the fact that the presence of large substituents ortho to the bridged oxygen atom is essential for higher SHG efficiency.

3.3. First hyperpolarizability

First hyperpolarizability, β of all the compounds were measured in chloroform by the HRS technique and also calculated by the semiempirical AM1 method. The scattering signal was dispersed through a monochromator and checked for two/multiphoton fluorescence contribution. No significant fluorescence contribution was observed for any compound. The results are listed in Table 2. The intrinsic hyperpolarizability, β_0 values were derived from the well known two-state model [22]. The results show a good agreement in the trend in β values obtained from measurements and calculations. Among the dimers **8a–e** (compounds with similar conjugation length), 8e shows the highest

Table 2
Absorption maximum λ_{max}/nm, molar extinction coefficient ε_{max} /M^{-1}cm^{-1} at λ_{max}, cut-off wavelength $\lambda_{cut\text{-}off}$/nm, molecular hyperpolarizabilities β_{cal}, β_{HRS}, β_0 /10^{-30} esu, calculated ground state dipole moment μ_{cal}/D, powder SHG (X U) and decomposition temperature T$_d$/°C for compounds, **1, 8, 9** and **12**

S.No	λ_{max} (nm)	ε_{max} (10^2)	λ_{cutoff} (nm)	μ_g (D)	β_{cal} (AM1)	β_{HRS}/10^{-30} (esu)	β_o/10^{-30} (esu)	SHG × U	T$_d$ (°C)
1	309.8	53	397	6.9	2.5	6.0	3.6	6.2	
	253.4	122							
	259.6	96	382	3.1	3.5	7.0	5.0	L	
8a	288.8	830	400	6.4	4.3	14.4	9.4	0	288
	243.0	1400							
9a	325.6	15	387	8.4	1.8	17.0	9.6	0	
	275.2	59							
	243.0	169							
8b	368.6	84	448	6.1	2.8	22	10.6	0	292
	251.4	239							
9b	358.6	17	443	5.9	2.8	11	5.3	0	
	278.2	42							
	243.4	1092							
8c	388.2	64	494	6.1	4.3	16.6	6.7	0.1	280
	263.2	319							
9c	407	12	511	6.2	3.3	19.2	6.7	0	
	256.6	1962							
8d	396.2	26	484	6.5	8.2	26.2	10.0	0.7	266
	259.2	101							
9d				6.3	2.6				
8e	377.4	68	488	6.1	8.9	36	15.6	0.4	298
	267.2	297							
9e	392.6	11	512	5.5	2.9	29.2	11.4	L[a]	
	257.8	1872							
8f	449.8	529	577	7.6	7.6	230	53.8	0.95	288[b]
	276.2	314							
9f	434.4	296	554	8.8	24.7	182	50.5	0.4	
	261.4	182							
12	304.2	186	395	3.1	1.8	14.2	8.7	0	

values are obtained by AM1 method using the MOPAC package.

[a] L = liquid sample.

[b] By TGA.

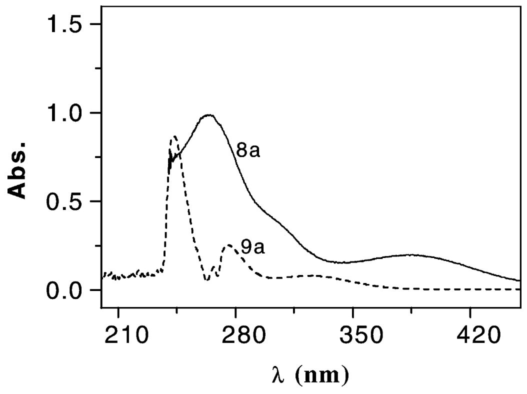


Fig. 3. UV-visible absorption spectra of **8a** and **9a** in chloroform.

$\beta = 36 \times 10^{-30}$ esu. This could be due to the strong donating ability of piperidine compared to other amine donors. The highest $\beta = 230 \times 10^{-30}$ esu was observed for compound 8f which is ascribed to the increased conjugation length between the donor and the acceptor. The hyperpolarizability of **8f** is ca. 20% higher than that of the monomer **9f**.

3.4. Thermal stability

Thermal stability of the dimers **8a–e** was checked by measuring the decomposition temperature (T_d) under nitrogen atmosphere using scanning calorimetry and the results are listed in Table 2. The DSC

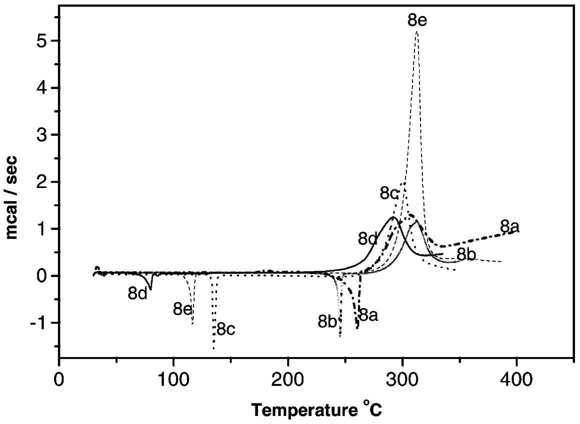


Fig. 4. DSC thermograms of compounds **8a–e**.

thermograms of dimers **8a–e** are displayed in Fig. 4. There are two types of peaks in the thermogram. One is an endothermic peak due to the melting of the sample and the other is an exothermic peak corresponding to the decomposition of the sample. The decomposition temperatures for all the compounds lie in the range 266–298 °C. This temperature range is rather high and renders these compounds suitable for processing at elevated temperatures. Due to evaporation of the monomers **9** while heating, we could not record T_d of **9a–f**.

4. Conclusion

In summary, we have synthesized a series of oxygen atom bridged *meta* nitroaniline dimers **8** which were originally thought to have structure **2**. The linear and nonlinear optical properties of these compounds have been measured and compared with those of the *meta* monomers **9**. The highest β value, 230×10^{-30} esu was obtained for compound **8f** and this value is ca. 20% higher than that of the monomer **9f**. The SHG efficiency of compound **1** is about 6.2 times that of urea, while the compound remains transparent in the visible region. Some of the oxygen-bridged dimers show relatively higher SHG activity than the monomers **9**. The results presented here are encouraging and oxygen atom bridged dimers and trimers of NLO chromophores show promise for large microscopic as well as macroscopic NLO response.

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