JOURNAL OF
Materials
CHEMISTRY

Unsymmetrical aryl disulfides with excellent transparency in the visible region for second order nonlinear optics

Ramanathan Sudharsanam,[a] Srinivasan Chandrasekaran[a]† and Puspendu Kumar 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. E-mail: pkdas@ipc.iisc.ernet.in

Received 26th April 2002, Accepted 24th June 2002
First published as an Advance Article on the web 16th August 2002

Several unsymmetrically substituted aromatic donor–acceptor disulfides have been synthesized and analysed for their second order nonlinear optical properties. These molecules exhibit moderately high first hyperpolarizability (β) with excellent transparency in the visible region. Most of the unsymmetrical disulfides have a cut-off wavelength below 420 nm. Calculations show that the molecules have an asymmetric charge distribution around the disulfide bond which is responsible for their high β values. These results provide motivation for the design and synthesis of nonlinear optical chromophores with multiple disulfide bonds for large second order nonlinearity and excellent visible transparency.

Introduction

The design and synthesis of new donor (D)–acceptor (A) substituted organic molecules with asymmetric charge distribution is of current interest in nonlinear optics (NLO). This class of molecules has potential application in optical data processing and communications.[1] It has been generally recognized that molecules of the type D–π–A containing a π-backbone with terminal D, A substitutions and exhibiting charge asymmetry show large second order nonlinearity (β).[2] However, a large number of molecules designed on this basis absorb light in the visible region which is detrimental for their use in optoelectronics. Various molecular arrangements such as orientationally correlated multichromophoric systems,[3] chromophores with heteroatoms connecting the D- and A-substituted π-fragments by σ-bonds (thereby breaking the conjugation),[4] and collinearly oriented dipoles[5] have been prepared and some of them have shown excellent transparency in the visible region but their β values are low.

To achieve high β values with excellent transparency in the visible region the –S–S– linkage has been taken up for consideration in the present study. The influence of an –S–S– linkage has not been investigated in the context of NLO. The –S–S– bridge is very much similar to the $-CH_2-CH_2-$ bridge except that the former is more polarizable than the latter. The –S–S– bond is also desirable because its longest wavelength absorption arises due to a $\pi^*-\sigma^*$ transition around 250 nm, which is far from the visible region. This transition is less likely to be shifted to the visible if we combine an aromatic acceptor and donor through an –S–S– linkage. In fact, by changing the twist around the –C–S–S–C– linkage, it is possible to shift the $\pi^*-\sigma^*$ transition even deeper to the ultraviolet.[6] Also, the electron transfer ability across the bridge joining the aromatic halves is expected to be extremely poor.[7] On the other hand, a π-linkage of the type –C=C– or –N=N– instead of –S–S– will allow facile transfer of charge between the aromatic donor and the acceptor but its longest wavelength charge transfer transition will shift to the red making it unsuitable for use as a NLO material.

The general structure of the donor–acceptor-substituted unsymmetrical aryl disulfides **1** is shown in Fig. 1. Symmetrical aryl disulfides **2** and aryl monosulfides **3** were taken up for comparison.

Results and discussion

Synthesis

Aryl disulfides were synthesized, characterized and their melting points were compared with literature data. Recently in our laboratory, we have shown[8] that benzyltriethylammonium tetrathiomolybdate **5** is able to cleave the disufide bond. It has also been shown that it converts organic thiocyanates to corresponding disulfides. We have extended these routes to prepare unsymmetrical disulfides **1a** and **1b**. Compound **1a** was obtained in the reaction of symmetrical disulfides **2a** and **4** with 2 molar equivalents of benzyltriethylammonium tetrathiomolybdate **5** in acetonitrile as shown in Scheme 1. Synthesis of symmetrical aryl disulfide **2a** was followed according to the literature procedure.[9] Reaction of **2b** and **4** with **5** yielded the corresponding unsymmetrical monosulfide. This could be due to the high electron withdrawing ability of the nitro group. Reaction of 4-thiocyanato-*N*,*N*-dimethylaniline **6** and 4-nitrophenylthiocyanate **7** with 2 equiv. of **5** yielded a mixture of **4**, **2b** and **1b**. Compound **1b** was separated from the mixture by chromatography. Compound **1f**[10] and the donor-substituted symmetrical disulfide **4**[11] were prepared according to literature procedures. Compounds **1c**–**1e**, **1g**, **1h** and **2b** were

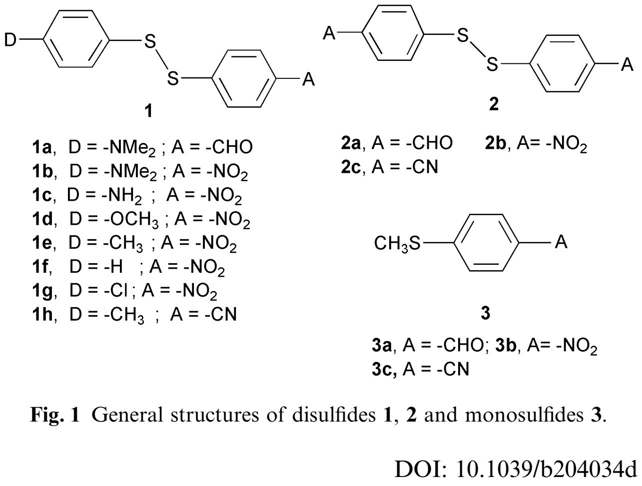
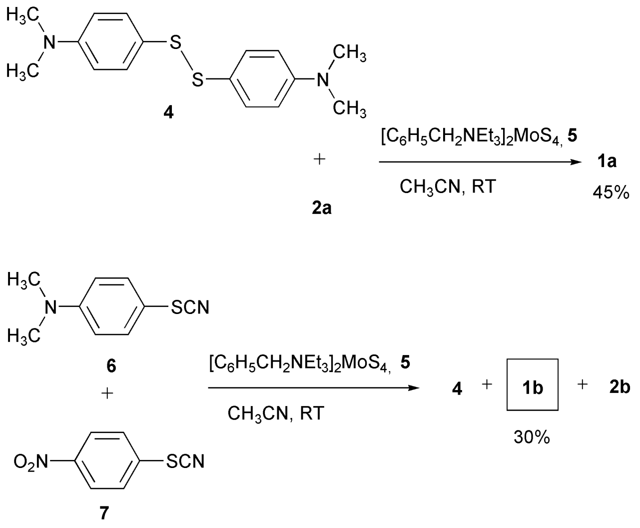


Fig. 1 General structures of disulfides **1**, **2** and monosulfides **3**.

---

†Honorary Professor, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India.

DOI: 10.1039/b204034d



Scheme 1

prepared by oxidizing the respective donor- and acceptor-substituted aryl thiols, and the products were separated by column chromatography on neutral alumina.[9]

Linear optical properties

The UV-Vis absorption spectra were recorded in chloroform for compounds **1**–**3a,b** and for **1c**–**h** in methanol using a Hitachi U-3400 spectrometer. A representative absorption spectrum is displayed in Fig. 2. All these compounds exhibit an absorption maximum (λ_{max}) in the ultraviolet region much below 400 nm and have virtually no absorption at 532 nm as seen from their cut-off wavelengths ($\lambda_{cut\text{-}off}$) in Table 1. The $\lambda_{cut\text{-}off}$ is defined as the wavelength where the first derivative of absorbance with respect to the wavelength at the lower energy side of the spectrum becomes zero.

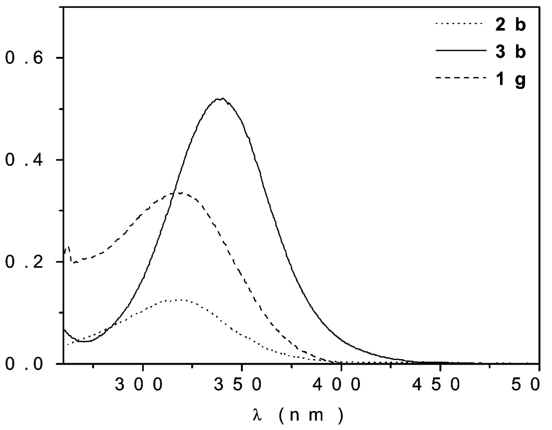


Fig. 2 UV-Vis absorption spectra of **1g**, **2b** and **3b** in methanol.

We note that the disulfides **1a**,**1b** and **2a**, **2b** have lower λ_{max} values than those of the corresponding monosulfides **3a**,**3b**. Their λ_{max} value is blue-shifted by *ca.* 10–30 nm relative to the monosulfides. This indicates that the disulfide linkage hinders to a large extent the charge transfer possible from the donor to the acceptor. The peak position of this charge transfer band varies as a function of the donor–acceptor strength.

Nonlinear optical properties

The β values of disulfides **1** and **2** and monosulfides **3** have been measured using the hyper-Rayleigh scattering technique[12,13] in solution at 1064 nm. Chloroform and methanol were used as solvents, and the β values were obtained using *p*-nitroaniline (PNA) as an external reference ($\beta = 17 \times 10^{-30}$ esu in CHCl$_3$, $\beta = 22.4 \times 10^{-30}$ esu in MeOH).[14] These molecules did not exhibit any single photon fluorescence band near 532 nm when they were excited at their respective λ_{max}s and, therefore, two/multi-photon fluorescence contribution to β was not expected. To ascertain that the SHG signal was free from any two/multi-photon fluorescence, the signal from the HRS experiments was dispersed through a monochromator. No broad band fluorescence was detected around the second harmonic wavelength.

The static hyperpolarizability (β_o) was calculated using the well known two-state model which is, generally, applicable far from a resonant absorption band. The β values are listed in Table 1. It is apparent from the table that all the mono- and di-sulfides **1**–**3** have significantly higher β as well as β_o values compared with the reference compound PNA. In fact, β_o of **1b** is seven times of that of PNA. These β and β_o values are higher than those of specially designed 1,8-di(hetero)aryl naphthalenes reported by Bahl *et al.* for blue-transparency frequency doublers.[15] The β values of the symmetrically substituted disulfides **2** were found to be lower than those of the corresponding monosulfides **3**. This is due to the well-known nonlinearity-transparency trade-off and is quite expected. What is interesting as well as surprising is that the unsymmetrical disulfides **1**, in spite of similar absorption characteristics to those of symmetrical disulfides **2** and monosulfides **3**, exhibit much higher molecular hyperpolarizability. Of course, the size increases by a factor of two in going from the monosulfide to the unsymmetrical disulfide and one expects an increase in hyperpolarizability. But if we compare symmetrical disulfides with unsymmetrical disulfides of similar lengths, the β_o values of the unsymmetrical disulfides **1** are *ca.* 2.5 times higher than those of the symmetrical disulfides **2**. It is also

Table 1 UV-Vis absorption maximum (λ_{max}), cut-off wavelength ($\lambda_{cut\text{-}off}$), molar extinction coefficient (ε_{max}), molecular hyperpolarizabilities ($\beta_{cal}{}^{AM1}$, β and β_o) and calculated ground state dipole moment (μ_g) of compounds **1**–**3**

S. no.	λ_{max}/nm	ε_{max}/M^{-1} cm^{-1}	$\lambda_{cut\text{-}off}$/nm	$\mu_{cal}{}^{AM1}$/D	$\beta_{cal}{}^{AM1}$/10^{-30} esu	β^a/10^{-30} esu	β_o/10^{-30} esu
1a	304	32 000	434	5.9	34.4	36.0	22.2
1b	319	17 000	448	9.1	40.2	102	59.4
1c	321	30 000	421	8.7	30.2	98	56.6
1	319	11 000	420	7.8	23.3	86	37.8
1e	322	11 000	419.6	6.7	18.3	80	46.0
1f	319	11 000	416.6	6.3	14.8	36	20.9
1g	317	7920	398	5.4	17.3	44	25.7
1h	269	26 000	361.0	4.6	14.7	89	62.0
2a	304	40 500	395	3.6	8.4	18.0	11.1
2b	317	26 800	410	4.6	8.4	38.6	22.6
3a	316	80 500	371	2.7	10.0	20.0	11.8
3b	346	18 200	450	6.0	10.3	59.8	30.8
PNA	348	14 200	428	7.2	4.6	17.0	8.60

[a] Measured at 1064 nm.

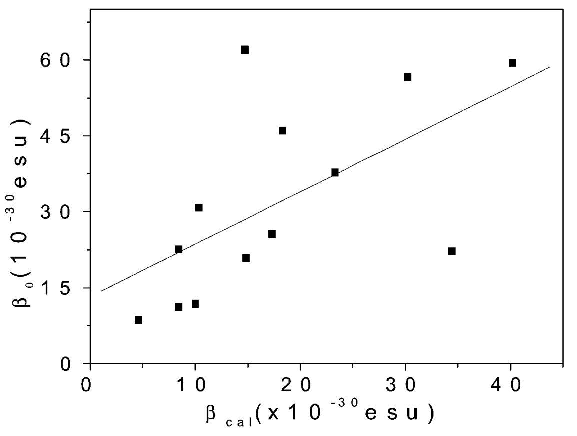
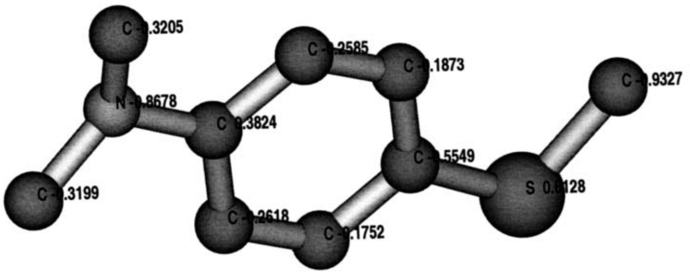


Fig. 3 Plot of experimental β_o values *vs.* calculated β values for **1**, **2**, **3** and PNA (*R* factor 0.6).

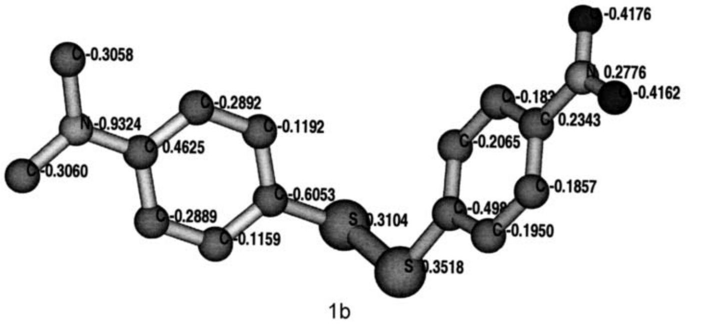
noteworthy that 4-dimethylamino-4′-nitrostilbene, which is analogous to **1b**, has $\beta_o = 55.4 \times 10^{-30}$ esu[16] which is lower than that of **1b**, while the λ_{max} of this stilbene derivative (427 nm) is higher than that of **1b** by 110 nm. In spite of the weak donor and acceptor in **1g**, it shows the highest β_o value.

The measured hyperpolarizability, β_o, of the compounds has been plotted against the calculated finite field hyperpolarizability in Fig. 3. The correlation between the semi-empirical values and measured values of hyperpolarizability is not great. This is partly because the solvent effects are not included in the finite field calculations, and both the solvents, chloroform and methanol, that have been used for the measurements can interact with the disulfides strongly. Also, dispersion effects can influence the measured β values since the monosulfides, symmetrical and unsymmetrical disulfides are expected to exhibit different dispersion behaviour.

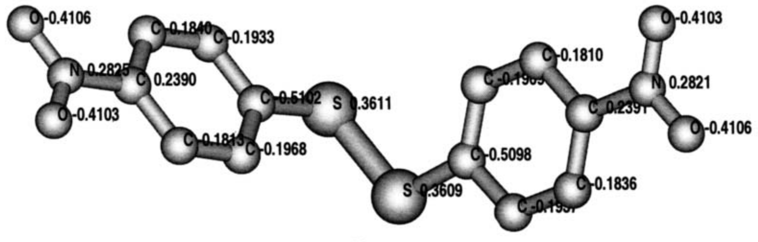
The theoretical ground state dipole moment (μ_g) and finite field hyperpolarizability (β_o) for **1**–**3** were calculated using the semi-empirical AM1 procedure within the MOPAC package and are listed in Table 1. The large ground state dipole moments of the unsymmetrical disulfides **1** are well expected due to the presence of the terminal donor and acceptor groups. Charge density on each atom for **1** and **2** has also been calculated using the GAUSSIAN 94 and MOLDEN programs using the AM1 optimized geometry as the input. One representative example for the charge densities on **1** and **2** is given in Fig. 4. These results show that an appreciable difference in electron densities exists between the two sulfur atoms in the unsymmetrical disulfides **1**, whereas charges are symmetrically distributed in **2**, as expected. The charge separation in the dimethylaminophenylsulfide portion of the unsymmetrical disulfide **1b** is large. To check whether the corresponding monosulfide (donor half of the unsymmetrical disulfide) would also exhibit such a large charge separation, we calculated the ground state dipole moment and first hyperpolarizability of *p*-methylthio-*N*,*N*-dimethylaniline. We find that the ground state dipole moment of *p*-methylthio-*N*,*N*-dimethylaniline is low (1.9 D) and the charge distribution is shown in Fig. 4. The calculated hyperpolarizability $\beta_{cal}{}^{AM1}$ for this molecule is only 3.1×10^{-30} esu. Thus, we infer that the charge asymmetry that is present in unsymmetrical disulfides is responsible for their large hyperpolarizability. Perhaps, a large change in dipole moment upon excitation or an appreciable change in the transition dipole moment explains the origin of the large β values in them.



4-(methylthio)-N,N-dimethylaniline



1b



2b

Fig. 4 Charge distribution in *p*-methylthio-*N*,*N*-dimethylaniline, **1b** and **2b** (for clarity, H atoms are not shown).

Conclusions

In conclusion, we have demonstrated that unsymmetrical aryl disulfides **1** show high second order optical nonlinearity and excellent transparency in the visible region. Many natural molecules such as peptides and proteins contain more than one disulfide linkage. Modifying and designing NLO chromophores with multiple disulfide bonds may provide an alternate strategy for developing new optical materials.

Experimental

4-Methylthiobenzaldehyde (**3a**), 4-nitrothioanisole (**3b**), 4-methylbenzenethiol (**8c**), 4-aminobenzenethiol (**8a**), 4-methoxybenzenethiol (**8b**) and 4-nitrobenzenethiol (**9a**) were obtained from commercial sources. 4-Cyanobenzenethiol (**9b**) was obtained from 4-(methylthio)benzonitrile (**3c**), and bis(4-formylphenyl) disulfide (**2a**) was from **3a** following the procedure by Young *et al.*[9] Commercial grade solvents were distilled prior to use. Analytical thin layer chromatography was carried out on Merck precoated silica gel 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 *ca.* 200 °C. Column chromatography was carried out using 60–120 and 100–200 mesh Acme silica gel and neutral alumina. Thin layer chromatography was performed using TLC grade neutral alumina. Melting points were measured using a Buchi B-540 instrument. Spectroscopic measurements were made using the following instruments: UV-Vis, Hitachi U-3400; FT IR, Perkin Elmer 781; ^{1}H NMR, JEOL 300 MHz, BRUKER 200 MHz (NMR chemical shifts are reported in δ values in parts per million downfield from the internal reference tetramethylsilane); LRMS, JEOL JMS-DX303 (only principal molecular fragments are reported). Elemental analysis was performed using a Carlo Erba elemental analyser model – 1106.

Hyper-Rayleigh scattering (HRS) measurements

The hyper-Rayleigh technique was used to measure the first hyperpolarizability of all the compounds at 1064 nm using a Q-switched Nd:YAG laser (Spectra Physics, 10 Hz, 8 ns). The experimental set-up used for the HRS is described in detail elsewhere.[13] All data were collected at laser powers $\leqslant$24 mJ pulse^{-1} and the exciting beam was focussed by a biconvex lens (f.l. 10 cm) to a spot 5 cm away after passing through the glass cell containing the sample solution. The second harmonic signal was collected at a perpendicular direction thorough a set of collection optics which contained a concave mirror, an aspherical lens, a collimating lens and a couple of filters including a 4 nm bandwidth interference filter at 532 nm. A high through-put monochromator (Czerny Turner, 0.25 m) replaced the collection optics for wavelength dispersion experiments. The resolution of the monochromator was 0.4 nm and both the entrance and exit slit-widths were kept at 1.25 mm. The monochromator was scanned at 2 nm intervals and at each wavelength the signal output from the PMT was averaged over 400 laser shots. The input power was monitored using a power meter. The set-up was standardized by measuring the β value of PNA in chloroform as well as in methanol as external reference. All concentrations of the solutions were kept at $\leqslant 10^{-5}$ M.

Synthesis of (4-formylphenyl)-4′-*N*,*N*-dimethylaminophenyl disulfide (1a)

To a stirred solution of bis(4-formylphenyl) disulfide (**2a**) (0.152 g, 1 mmol) and bis[4-(*N*,*N*-dimethylamino)phenyl] disulfide (**4**) (0.304 g, 1 mmol) in dry acetonitrile (3 mL) was added tetrathiomolybdate **5**[17] (1.016 g, 2 mmol) in acetonitrile (3 mL). The reaction was continued overnight and the solvent was evaporated under vacuum. The residue was dissolved in dichloromethane (2 mL) and diethyl ether (40 mL) was added. The resulting solution was filtered through a Celite pad. The organic solvent was evaporated and the crude product was chromatographed on neutral alumina TLC using a petroleum ether (60–80 °C)–CH_2Cl_2 mixture (7 : 3) as eluent which yielded compound **1a** (0.173g, 30%) as a pale yellow solid. LRMS (DI, *m*/*z*): 289 (M^+), 152. This sample decomposes slowly at room temperature (25 °C) after a few hours (3 h).

Synthesis of 4-(*N*,*N*-dimethylamino)phenyl 4′-nitrophenyl disulfide (1b)

Following the procedure described above, instead of symmetrical disulfides, the reaction between 4-thiocyanato-*N*,*N*-dimethylaniline (**6**) (0.151 g, 0.846 mmol) and 4-thiocyanatonitrobenzene (**7**) (0.153 g, 0.846 mmol) was carried out using tetrathiomolybdate **5** (1.028 g, 1.692 mmol). The product was purified by chromatography on a neutral alumina column. Yield: 0.116 g (45%), m.p.: 100 °C, (lit.[18] m.p.: 100–101 °C); ν_{max}/cm^{-1}: 1509, 1337; δ_H ($CDCl_3$, 300 MHz): 8.17 (d, J = 9.3 Hz, J = 2.7 Hz, 2 H, Ar H), 7.71 (d, J = 9 Hz, 2 H, Ar H), 7.39 (d, J = 7 Hz, 2 H, Ar H), 6.6 (d, J = 9.4 Hz, 2 H, Ar H), 2.98 (s, 6 H, 2 CH_3); LRMS (DI, *m*/*z*): 306 (M^+), 152.

General procedure for the synthesis of 1c–e, 1g and 1h

To a stirred solution of the donor-substituted aryl thiol **8** (1 equiv.) and acceptor substituted aryl thiol **9** (1 equiv.) in dichloromethane (10 mL) was added an aqueous solution (10 mL) of I_2 (10 equiv.) and KI (10 equiv.). Stirring was continued overnight (10 h) and the solution was washed with a saturated solution of Na_2SO_3 until the dichloromethane solution was free from iodine. The organic layer was finally washed with water (10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum at 25 °C and the unsymmetrical disulfide **1** was separated from symmetrical disulfides by chromatographic purification on a neutral alumina column or by preparative TLC.

Synthesis of 4-aminophenyl 4′-nitrophenyl disulfide (1c)

Following the general procedure described above, 4-aminobenzenethiol (0.2 g, 1.597 mmol) (**8a**) and 4-nitrobenzenethiol (0.247 g, 1.595 mmol) (**9a**) were reacted in dichloromethane (10 mL) using I_2 (4.05 g, 15.97 mmol) and KI (2.65 g, 15.97mmol) in aqueous solution (10 mL) for 10 h. The disulfide **1c** was isolated in the pure form as a solid after chmatographic purification. Yield: 0.066 g, (15%), m.p.: 118 °C (lit.[19] m.p.: 118–120 °C); ν_{max}/cm^{-1}: 3475, 3384, 1509, 1337; δ_H ($CDCl_3$, 300 MHz): 8.17 (d, J = 10.2 Hz, 2 H, Ar H), 7.68 (d, J = 6 Hz, 2H, Ar H), 7.31 (d, J = 9.6 Hz, 2 H, Ar H), 6.59 (d, J = 5.7 Hz, 2 H, Ar H), 3.83 (br, 2 H, NH_2); LRMS (DI, *m*/*z*): 278 (M^+), 124.

Synthesis of 4-methoxyphenyl 4′-nitrophenyl disulfide (1d)

Following the general procedure described above, 4-methoxybenzenethiol (0.180 g, 1.288 mmol) (**8b**) and 4-nitrobenzenethiol (0.2 g, 1.288 mmol) (**9a**) were reacted in dichloromethane (10 mL) using I_2 (3.27 g, 12.88 mmol) and KI (2.13 g, 12.88mmol) in aqueous solution (10 mL) for 10 h. Yield: 0.0078 g (2%), m.p.: 71–71.5 °C (lit.[20] m.p.: 72.5–73 °C); ν_{max}/cm^{-1}: 1508, 1336.

Synthesis of 4-methylphenyl 4′-nitrophenyl disulfide (1e)

Following the general procedure described above, 4-methylbenzenethiol (0.160 g, 1.288 mmol) (**8c**) and 4-nitrobenzenethiol

(0.2 g, 1.288 mmol) (**9a**) were reacted in dichloromethane (10 mL) using I_2 (3.27 g, 12.88 mmol) and KI (2.13 g, 12.88 mmol) in aqueous solution (10 mL) for 10 h. Yield: 0.046 g (13%), m.p.: 62.5 °C (lit.[18] m.p.: 62–63 °C).

Synthesis of 4-chlorophenyl 4′-nitrophenyl disulfide (1g)

To a stirred solution of bis(4-chlorophenyl) disulfide (0.7 g, 2.4 mmol) in a mixture of dioxane (8 mL) and water (2 mL) was added triphenylphosphine (0.575 g, 2.19 mmol). The solution was heated at 100 °C overnight and then the solution was cooled and the solvent was evaporated. Following the general procedure described above, the crude residue was reacted with 4-nitrobenzenethiol (0.377 g, 2.42 mmol) (**9a**) in dichloromethane (10 mL) using I_2 (6.171 g, 24.2 mmol), KI (4.03g, 24.29 mmol) in aqueous solution (15 mL) for 10 h. The unsymmetrical disulfide **1g** was obtained as a pale yellow solid. Yield: 0.0062 g, 1%, m.p.: 95–96 °C (lit.[18] m.p.: 92–93 °C).

Synthesis of 4-cyanophenyl 4′-methylphenyl disulfide (1h)

Following the general procedure described above, 4-sulfanylbenzonitrile (0.2 g, 1.479 mmol) (**9b**) and 4-methylbenzenethiol (0.183 g, 1.47 mmol) (**8c**) were reacted in dichloromethane (10 mL) using I_2 (3.756 g, 14.79 mmol), KI (2.45 g, 14.79 mmol) in aqueous solution (15 mL) for 10 h. Yield: 0.043 g (17%), m.p.: 88–89 °C; ν_{max}/cm^{-1}: 2228; LRMS (DI, *m*/*z*): 257 (M^+), 123. Anal. calc. for $C_{14}H_{11}NS_2$: C, 65.35; H, 4.27; N, 5.44. Found: C, 63.71; H, 4.32; N, 4.8%.

Synthesis of bis(4-nitrophenyl) disulfide (2b)

A solution of of 4-nitrobenzenethiol (0.200 g, 1.28 mmol) (**9a**) in DMSO (2 mL) was heated at 80 °C overnight and the solution was cooled to room temperature (25 °C). The solution was poured into cold water (50 mL). The precipitated pale yellow solid was filtered and washed thoroughly with water. The solid was recrystallised from acetic acid and compound **2b** was isolated in quantititave yield, m.p.: 182 °C (lit[21] m.p.: 181 °C); ν_{max}/cm^{-1}: 1515, 1343; δ_H($CDCl_3$, 200 MHz): 8.2 (d, $J = 12$ Hz, 4 H, Ar H), 7.62 (d, $J = 8$ Hz, 4 H, Ar H); LRMS (DI, *m*/*z*): 308 (M^+).

Acknowledgement

This work was partially supported by the Council of Scientific and Industrial Research, Govt. of India.

References

1 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991.

2 S. R. Marder, L. T. Cheng and B. G. Tiemann, *J. Chem. Soc., Chem. Commun.*, 1992, 672; A. K.-Y. Jen, V. Pushkara Rao, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 90.

3 M. Kauranen, T. Verbiest, C. Boutton, M. N. Teerenstra, K. Clays, A. J. Schouten, R. J. M. Nolte and A. Persoons, *Science*, 1995, **270**, 966.

4 J. Qin, X. Wu, X. Zhang, C. Zhan and D. Liu, *Synth. Met.*, 1995, **71**, 1711.

5 X.-M. Duan, T. Kimura, S. Okada, H. Oikawa, H. Matsuda, M. Kato and H. Nakanishi, *Jpn. J. Appl. Phys.*, 1995, **34**, L1161.

6 P. C. Kahn, *Methods Enzymol.*, 1979, **61**, 339.

7 J. D. Korp and I. Bernal, *J. Mol. Struct.*, 1984, **118**, 157.

8 K. R. Prabhu, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1998; K. R. Prabhu, P. S. Sivanand and S. Chandrasekaran, *Angew. Chem., Int. Ed.*, 2000, **39**, 4316.

9 R. N. Young, J. Y. Gauthier and W. Coombs, *Tetrahedron Lett.*, 1984, **25**, 1753.

10 T. Mukaiyama and K. Takahashi, *Tetrahedron Lett.*, 1968, 5907.

11 K. R. Prabhu, A. R. Ramesha and S. Chandrasekaran, *J. Org. Chem.*, 1995, **57**, 7142.

12 K. Clays and A. Persoons, *Phys. Rev. Lett.*, 1991, **66**, 2980.

13 P. C. Ray and P. K. Das, *J. Phys. Chem.*, 1995, **99**, 14414.

14 T. Kodaira, A. Watanabe, O. Ito, M. Matsuda, K. Clays and A. Persoons, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3039.

15 A. Bahl, W. Grahn, S. Stadler, F. Feiner, G. Bourhill, C. Brauchle, A. Reisner and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1485.

16 L. T. Cheng, W. Tam, H. S. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.*, 1991, **95**, 10631.

17 A. R. Ramesha and S. Chandrasekaran, *Synth. Commun.*, 1992, **22**, 3277.

18 B. I. Stepanov, V. Ya. Rodionov, T. A. Chibisova, L. A. Yagodina and A. D. Stankevich, *J. Org. Chem., USSR*, 1977, **13**, 334.

19 D. A. R. Happer, J. W. Mitchell and G. J. Wright, *Aust. J. Chem.*, 1973, **26**, 121.

20 E. Campaigne, J. Tsurugi and W. W. Meyer, *J. Org. Chem.*, 1961, **26**, 2486.

21 I. Danielsson, J. E. Christian and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, 1947, **36**, 261.