Rapid Communication

Aryl monosulphides and symmetrical disulphides based second order nonlinear optical chromophores with transparency in the visible

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A series of aryl monosulphides and disulphides have been synthesized and characterized. Their molecular hyperpolarizability (β) has been measured in solution with the hyper-Rayleigh Scattering technique and also calculated by semiempirical AM1 method. The trend in the observed and calculated values of first hyperpolarizability of these compounds has been found to be in good agreement. These compounds show moderate β values and excellent transparency in the visible region.

For the last two decades, research in second order nonlinear optics (NLO) received considerable attention from scientists and engineers. The design and synthesis of molecules with high second order nonlinearity is one of the most important activities in this area¹. Traditionally molecules of the type D-π-A, where a donor and an acceptor groups are flanked by a conjugated π-bridge, have been tested for large second order nonlinear optical (NLO) response. Charge asymmetry in these molecules² is the reason for their large first hyperpolarizability(β). Problems associated with this type of molecules are that they absorb light in the visible region and the wavelength of maximum absorption, λmax shifts to the longer wavelength region as the strength of the donor and acceptor groups is increased³. Also, λmax moves to the visible with increase in the number of double bonds connecting the D, A groups. Absorption in the visible region is not conducive for utilizing these molecules in device applications. Hence, the search for new molecules which will have large β and absorption maximum confined to the UV region is still active. To achieve this objective, a variety of strategies were adopted in the past. They include placing dipolar molecules in a parallel fashion as in calixarenes⁴, and hetero atom in conjugation backbone⁵,⁶ thereby reducing the wavelength of absorption maximum. Unfortunately, molecules produced with these strategies although had λmax's confined to the UV region, exhibited only low hyperpolarizability, β.

Here we have taken the traditional D-π-A motif with the sulphur atom as the donor and modified it into a A-π-D-D-π-A motif to attain high nonlinearity and low wavelength absorption. While it is known that the thiomethoxy group can act as an electron donor, it can also be modified to a disulphide linkage easily to obtain a motif of the type A-π-D-D-π-A. In this communication, we report the synthesis of a series of D-π-A and A-π-D-D-π-A type NLO chromophores that exhibit moderate second order nonlinearity and excellent transparency in the visible.

Experimental

The general structure of monosulphides 1 and disulphides 2 with various acceptors is shown in Fig. 1.

Compounds 1a and 1b were obtained by the reaction of 4-thiobenzoic acid with one and two mole equivalents of dimethyl sulphate, respectively. Compound 2a was synthesized following the procedure described in the literature. 2b was also obtained using the same methodology as for 1b. The general methodology for the synthesis of compounds 2c-f is shown in Scheme 1. Arylmethyl sulphide 1 was oxidized to the corresponding sulphotoxide 3 which was then subjected to regiospecific Pummerer rearrangement to produce the sulphone 4. Hydrolysis followed by oxidation of thiol 5 gave the desired disulphide 6. The chromophores 1g and 2g with increased conjugation were obtained by condensation of aldehyde 1e and 2e with malononitrile⁷. (Scheme 1).

The UV-vis absorption spectra of compounds 1a-2g were recorded in chloroform in a Hitachi U-3400 spectrometer. The cutoff wavelength (λcutoff) was taken as the wavelength where the first derivative of absorbance with respect to wavelength becomes zero at the longer wavelength side of the spectrum. All
these compounds exhibit absorption maximum ($\lambda_{\text{max}}$) below 385 nm and have virtually no absorption above 450 nm as seen from their $\lambda_{\text{cond}}$ values (Table 1).

**Results and discussion**

We note that the disulphides (2a-g) have lower $\lambda_{\text{max}}$ than that of the corresponding monosulphides (1a-g). The $\lambda_{\text{max}}$ values in the former are shifted to the blue by about 12 to 29 nm with respect to the latter. This indicates that the conversion of thiomethoxy donor to form the disulphide linkage results in a decrease in the electron donating ability of the sulphur atom thereby reducing the extent of charge transfer in the molecule.

The change in the strength of donor-acceptor groups resulted in a shift in the $\lambda_{\text{max}}$. The acceptor ability of the nitro group is much higher than that of the other acceptors used here. That explains the increase in $\lambda_{\text{max}}$ as we go from compound 1a to 1e. On the other hand, there is a significant reduction in $\lambda_{\text{max}}$ (29 nm) in going from monosulphide 1e to disulphide 2e as shown in Fig. 2. This observation clearly indicates that conversion of the thiomethoxy group into the symmetrical disulphide group decreases the extent of charge transfer.

The $\beta$ values of aryl monosulphides 1 and symmetrical disulphides 2 have been measured using the hyper Rayleigh scattering technique in chloroform at 1064 nm. The $\beta$ values of all the compounds were obtained using $p$-nitroaniline (PNA) in chloroform as an external reference ($\beta = 17 \times 10^{-30}$ esu$^{10}$). The static hyperpolarizability ($\beta_0$) was calculated using the well-known two-state model$^{15}$. The hyperpolarizability values are listed in Table 1. It is apparent from Table 1 that the monosulphides 1 have higher $\beta$ as well as $\beta_0$ values compared to the disulphides 2. Compounds 1b, 1d-g, and 2b, 2d-g have large $\beta$ as well as $\beta_0$ values (1.7 - 3.5 times that of PNA). However, the $\beta$ and $\beta_0$ values of 1a, 2a and 1e, 2e are relatively small. The low hyperpolarizability of these compounds could be due to a small change in dipole moment ($\Delta \mu$) between the ground and the charge transfer excited states. Increased nonlinearity in compounds 1g and 2g is, perhaps, due to increased conjugation length. The
Theoretical ground state dipole moment ($\mu_0$) and static hyperpolarizability, $\beta_0$, of these molecules were calculated using the semi-empirical AM1 parameterization procedure within the MOPAC\textsuperscript{16} package for comparison with experimental results. It is apparent from Table 1 that the calculation follows the same trend with experimental results with the exception of $-\text{CHO}$ and $-\text{COOH}$ substituted compounds.

Bahl et al.\textsuperscript{17} reported 1,8-di(hetero)aryl naphthalenes for excellent transparency in the visible but their $\beta$ values were only in the range $17-44\times10^{-30}$ esu. The $\beta$ values of the monosulphides and symmetrical disulphides reported here are comparable to those of specially designed 1,8-di(hetero)aryl naphthalenes. In optimized structure of disulphide series, the two aromatic rings at the disulphide bridge reside with a C-S-S-C dihedral angle between $92^\circ$-$95^\circ$. Additionally, one aromatic ring means that the plane is twisted relative to that of the other with an angle between $76^\circ$-$102^\circ$ (this was calculated using XPMA)\textsuperscript{18}. In other words, the disulphide linkage lowers the symmetry between the two parts of the molecule. This type of conformation helps to avoid chromophore aggregation in doped polymer films and makes the disulphide chromophores suitable for macroscopic second order nonlinear optical applications. To conclude, we have developed a series of aryl monosulphides and disulphides which show moderate second order optical nonlinearity and excellent transparency in the visible region. Experiments to incorporate these chromophores into a polymer matrix will form the basis of a future work.

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References

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