

Articles

A New Class of Heterocyclic Compounds for Nonlinear Optics

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We discuss both theoretically and experimentally a new class of second-order nonlinear optical materials which utilizes the coupling of electron-rich and electron-deficient aromatic heterocyclic units to provide the charge asymmetry necessary for the nonlinear optical effect. This new class of nonlinear optical materials as compared with the previously known materials has the following merits: (i) wide optical transparency, high molecular nonlinear coefficient and small dipole moment; (ii) independent manipulation of the nonlinear coefficient and ground-state dipole moment by using multiple heterocyclic (oligomeric) units or appropriately modified heterocycles as well as by varying the linkage position; (iii) potentially greater thermal stability of the heterocyclic units; (iv) the potential for greatly reduced chemical toxicity.

Introduction

Nonlinear optics is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technology of photonics. Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials.^{1,2}

The more immediate application of nonlinear optics will utilize second-order processes. One example is second harmonic generation characterized by a nonlinear bulk susceptibility tensor $\chi^{(2)}(-2\omega; \omega, \omega)$ in which the medium generates an output wave at 2ω from an input wave of frequency ω . The corresponding molecular hyperpolarizability is $\beta(-2\omega; \omega, \omega)$. A major application of this process is the doubling of the diode laser to generate shorter wavelengths for a more compact storage of optical information. The second example is the electrooptic effect, characterized by the bulk nonlinear

susceptibility tensor $\chi^{(2)}(-\omega; \omega, 0)$ and the corresponding molecular hyperpolarizability $\beta(-\omega; \omega, 0)$, which leads to rotation of the polarization (change of phase) of an input wave of frequency ω by the application of an electric field (of relatively low frequency (≈ 0) compared to that of the optical field). This effect can provide modulation of the optical signal using a high frequency (> 80 GHz) electric field. The driving force for this application has been the potential of using electrooptics for communication and optical processing at highly increased speed.

The common material requirements for the two applications are (i) noncentrosymmetric structure at both the molecular and bulk levels, respectively as β and $\chi^{(2)}$ are both third-rank tensors, (ii) large values of both $\chi^{(2)}$ and β (organic materials have exhibited large β values derived from polarization of the π -electrons which has generated the large interest in them^{1,2}) (iii) greater chemical and thermal stability, and (iv) wider optical transparency.

For frequency doubling the preferred bulk form has been crystals with which one can take advantage of the natural anisotropy of the medium and obtain a phase-matching condition to efficiently convert the fundamental (ω) wave to the second harmonic (2ω). It, therefore, is necessary that the crystalline form be noncentrosymmetric. For electrooptic modulation poled polymeric structures (either covalently bonded or guest–host systems) have emerged as a promising class of materials primarily because of the potential for ease of processing.

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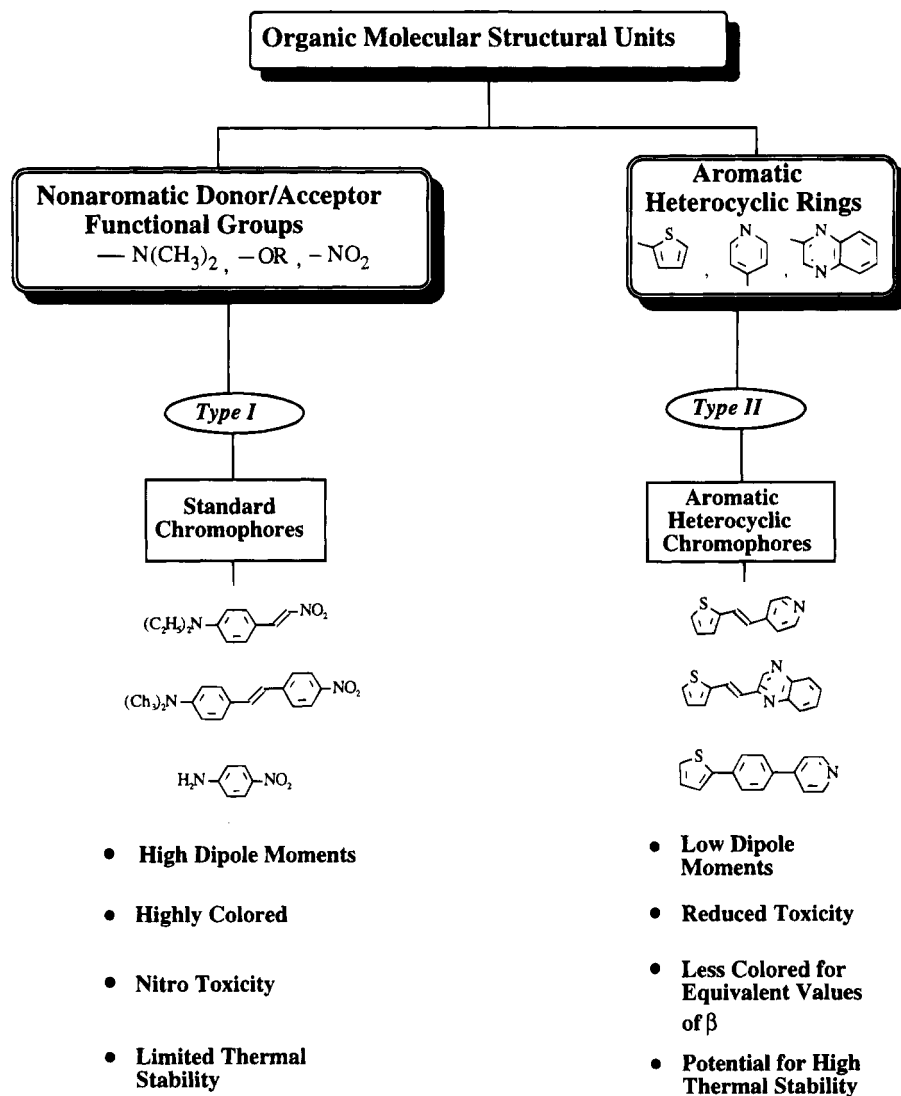


Figure 1. Organic chromophore types and characteristics.

Here the noncentrosymmetry is induced by the application of an external electric field. The three important relevant parameters are the hyperpolarizability β , the dipole moment μ and the optical transparency, often indicated by λ_{\max} , the wavelength of peak absorption.

For both types of materials, one desires a large β , and a small λ_{\max} . In contrast the dipole moment (μ) requirement is variable. A strong dipole-dipole interaction in the presence of a large dipole moment favors a centrosymmetric crystalline arrangement leading to a vanishing $\chi^{(2)}$ value even from molecules with a large β value. From this point of view one would like to design molecules with a small μ , although a small μ does not automatically ensure a noncentrosymmetric crystal. For efficient electric field poling, one needs a relatively large dipole moment as the induced orientation is determined by $\mu \cdot \mathbf{E}$, \mathbf{E} being the applied field strength. Therefore, it is highly advantageous to have molecular designs where one can independently manipulate μ and β and achieve a wider optical transparency (small λ_{\max}).

The organic structures used currently for second-order materials design are designated as type I in Figure 1. A type I chromophore utilizes a nonaromatic electron-donor group separated from a nonaromatic electron acceptor group by a π -electron bridging unit. A common example of a type I chromophore is *p*-nitroaniline

(PNA).^{3,4} In this group of compounds, there is a long-range charge transfer from the donor group to the acceptor group facilitated by the π -electron conjugation. The lowest excited state which makes the largest contribution to β is a charge-transfer state. In type I materials a large β is accompanied by a large μ , although μ can be reduced by appropriate chemical modification of the donor and acceptor groups.⁵ A large β is often accompanied by a decrease in the band gap. In addition, the thermal stability of the members of this group is limited by the nature of the nonaromatic donors and acceptors which are known to exhibit at least a moderate amount of chemical reactivity especially in the presence of air.

The overall lack of chemical and thermal stability of type I chromophores coupled with their tendency to be highly colored motivated us to develop a new class of materials (type II) which is the focus of this paper. This new molecular design includes linkage of an electron-deficient heterocyclic unit with an electron-rich heterocyclic unit to produce a charge distribution asymmetry

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for the nonlinear optical effect. To the best of our knowledge, the use of electron-deficient and electron-rich heterocyclic rings in the same molecule and the study of NLO property/molecular structure correlations of such materials have not been presented. Figure 1 shows schematically how types I and II compare and lists some of their more well-defined characteristics.

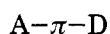
In this paper we report our initial work in the design and characterization of the new type II chromophores. In our initial studies a simple carbon-carbon double bond has been used as a π -electron bridging group. This was done primarily because of the ease of synthesis of a large number of structurally varied compounds with recognition that more thermally stable bridges will be investigated in future studies.

The NLO behavior of these materials differs from a mechanistic point of view since there is no long-range charge transfer in the ground state. Both the theoretical modeling and the experimental studies of such compounds synthesized show the following features: (i) a large β value but a small dipole moment; (ii) consequently, a noncentrosymmetric crystal structure and crystal second harmonic generation exhibited by many; (iii) almost independent manipulation of β and μ ; (iv) amplification of nonlinearity by the use of multiple heterocyclic ring or fused ring heterocycles; and (v) improved optical transparency.

The use of a totally aromatic heterocyclic structure can also lead to improved thermal stability. Highly aromatic structures, because of the electron resonance stabilization they exhibit, have long been known to be some of the most thermally stable organic materials. The type II chromophores also offer greatly reduced toxicity due to the absence of nitro, amino, and azo groups.

Theoretical Considerations

The widely used molecular design (type I) can be represented by^{1,2}



in which A represents a traditional acceptor (NO_2 , CN, etc.), D is a traditional donor ($-\text{NH}_2$, $-\text{NR}_2$, etc.), and π is a π electron or conjugated unit (an ethylenic or polyenic unit, an aromatic unit, a heterocyclic unit, etc.). For this class of compounds the dipole moment vector can be written as

$$\mu = \sum \mu_{\text{component}}^i + \mu_{\text{CT}} \quad (1)$$

where $\mu_{\text{component}}^i$ represents the dipole moment associated with the structural units A, D, π , etc., and μ_{CT} is the dipole moment due to charge transfer from the donor to the acceptor. For this class of materials even in the ground state, μ_{CT} makes the dominant contribution. Therefore, the direction of the dipole vector is the D-A charge-transfer axis.

A similar expression can be written for β :

$$\beta = \sum \beta_{\text{component}}^i + \beta_{\text{CT}} \quad (2)$$

Similarly as with μ , the β_{CT} contribution is the dominant term. Consequently, the largest component of the β tensor and hence the vector part of β , β , is along the charge transfer axis, i.e., along the direction of the

dipoles. The projection $\mu \cdot \beta$, measured by the commonly used technique of electric-field-induced second harmonic generation (EFISH) for characterization of β , is maximized.

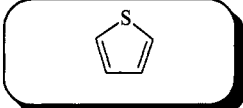
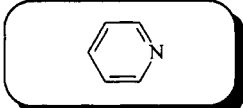
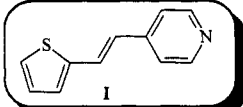
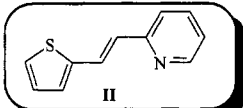
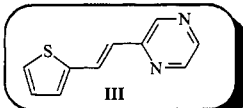
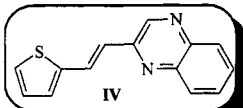
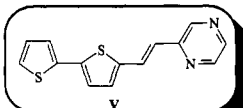
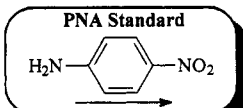
The new class of compounds reported here utilizes the linking of a sulfur-containing heterocycle (electron rich) with a nitrogen-containing heterocycle (electron deficient) through a π unit. In these compounds our theoretical and experimental analyses show that μ_{CT} is small, the dominant contribution coming from the vector addition of $\mu_{\text{component}}^i$. Therefore, by appropriate modification of the sulfur-containing and the nitrogen-containing heterocyclic units as well as by changing their linkage position, one can manipulate the net ground-state dipole moment. Furthermore, the direction of the net dipole moment is not necessarily the long axis as in the previous case. The picture of β for these materials is more complex. Here the net β is not due to $\sum \beta_{\text{component}}^i$. A large contribution comes from the interaction between the units. The largest component of the β tensor is along the long axis. Therefore, by appropriate design, one can change the angle between net μ and the largest β component and consequently manipulate the projection $\mu \cdot \beta$. This is very different from the widely investigated type I compounds for which the largest components of both β and μ are collinear.

We have conducted quantum chemical calculations of β for both classes (type I and type II) of compounds. The two approaches used in our laboratory are (i) ab initio time-dependent-coupled-perturbed Hartree-Fock⁶ and (ii) semiempirical INDO sum-over-states.⁷ Even though the first approach is more sophisticated with a sound ab initio foundation, our extensive work on many model compounds show that the much simpler latter approach provides a reasonable agreement of β with the experimentally measured values. Thus, we have used the INDO sum-over-states method for the new class of materials containing heterocyclic rings.⁸ We used the basic INDO program developed by Professor Zerner and his group (ZINDO).⁸ Geometry optimization and calculation of polarizabilities were performed using ZINDO, a semiempirical SCF/CI package running on a dedicated IBM RISC system/6000-550 machine. The input for geometry optimization was the molecular structure constructed from standard bond lengths and bond angles. The optimized molecular geometry obtained as output of the program was then used to calculate the spectroscopic properties using intermediate neglect of differential orbitals (INDO) molecular orbital (MO) method within the sum-over-states (SOS) approximation. In the sum-over-states expression, all electronic states generated by singly exciting all electrons in the highest 10 occupied molecular orbitals to 10 virtual orbitals with respect to the ground state were included. The calculated values of the dipole moment μ , the tensor component β_{xxx} , the vector component β_{μ} in the dipole direction, and λ_{max} for some selected representative structures are shown in Figure 2 along with those of the widely adopted standard PNA. The coordinate system used is shown in Figure 3.

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Structure	Calculated	Experimental
	$\mu = 1.39^a$ $\beta_{xxx}^* = 0.0, \beta_{\mu} = 0.69$ $\lambda_{max} = 245.6^b$	Γ_{EFISH} too small to be measured
	$\mu = 2.50$ $\beta_{xxx} = -0.51, \beta_{\mu} = 0.85$ $\lambda_{max} = 263.2$	Γ_{EFISH} too small to be measured
	$\mu = 3.74, \mu_x = -3.55$ $\beta_{xxx} = -19.7, \beta_{\mu} = 15.6$ $\lambda_{max} = 329.2$	$\mu = 2.80, \mu_{CT} = 0.41^c$ $\beta_{\mu} = 33, \mu \cdot \beta = 9.24^d$ $\theta = 191^e, \lambda_{max} = 329^f$
	$\mu = 0.99, \mu_x = 0.71$ $\beta_{xxx} = -11.3, \beta_{\mu} = -3.5$ $\lambda_{max} = 343.3$	$\mu = 1.50, \mu_{CT} = 0.33$ $\beta_{\mu} = g, \mu \cdot \beta = g$ $\theta = 66, \lambda_{max} = 333$
	$\mu = 1.56, \mu_x = -1.09$ $\beta_{xxx} = -17.0, \beta_{\mu} = 15.1$ $\lambda_{max} = 355.1$	$\mu = 1.10, \mu_{CT} = 0.81$ $\beta_{\mu} = 23, \mu \cdot \beta = 2.51$ $\theta = 209, \lambda_{max} = 351$
	$\mu = 2.20, \mu_x = -1.57$ $\beta_{xxx} = -29.4, \beta_{\mu} = 23.9$ $\lambda_{max} = 399.5$	$\mu = 0.92, \mu_{CT} = 0.60$ $\beta_{\mu} = 50, \mu \cdot \beta = 4.62$ $\theta = 215, \lambda_{max} = 382$
	$\mu = 0.97, \mu_x = -0.97$ $\beta_{xxx} = -95.7, \beta_{\mu} = 101.5$ $\lambda_{max} = 432.1$	$\mu = 1.19, \mu_{CT} = 1.19$ $\beta_{\mu} = 92, \mu \cdot \beta = 11.0$ $\theta = 180, \lambda_{max} = 395$
	$\mu = 8.6, \mu_x = -8.6$ $\beta_{xxx} = -29.4, \beta_{\mu} = 26.4$ $\lambda_{max} = 336.2$	$\mu = 6.09, \mu_{CT} = 4.54$ $\beta_{\mu} = 28, \mu \cdot \beta = 17.3$ $\theta = 180, \lambda_{max} = 349$

* All β values in units of 10^{-30} esu

a. In units of Debye; b. In units of nm; c. Assuming $\mu(-NH_2) = 1.23$ D (Ref. 3), $\mu(-NO_2) = 0.316$ D, $\mu(\text{thiophene}) = 0.55$ D, and $\mu(\text{pyridine}) = 2.19$ D (Ref. 22); d. In units of 10^{-47} esu; e. In units of Degrees; f. All λ_{max} measured in chloroform; g. too small to be measured.

The dipole moment and EFISH measurements are precise to $\pm 2\%$ and $\pm 10\%$, respectively.

Figure 2. Comparison of calculated and experimental parameters for heterocyclic chromophores.

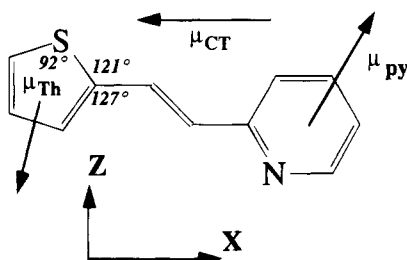
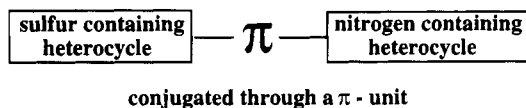
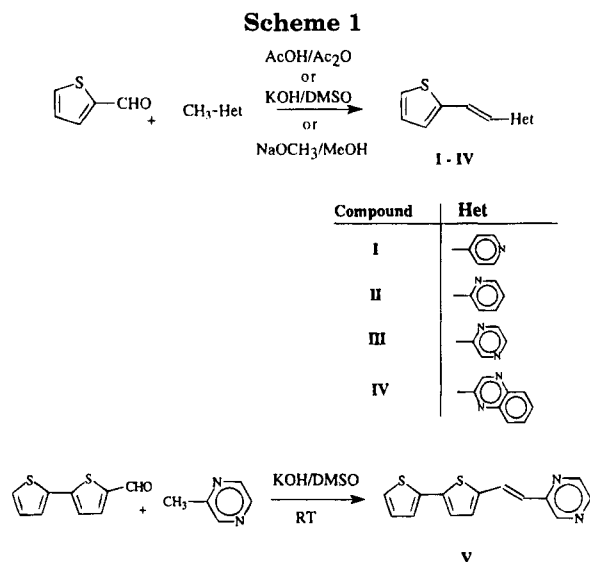


Figure 3. Directions of dipoles of various groups for a representative compound of type II.

In Figure 2, comparing I with the standard PNA, one finds a much smaller μ value, yet a comparable β value (especially when taking into consideration the experi-

mental values discussed below). The directions of largest β component and μ are almost collinear for I, as β_{xxx} and μ_x are the dominant components. The λ_{max} shows a wider transparency for I compared to PNA. This feature is clearly supported by the experimental result, also shown in Figure 2. Comparing II with I, one finds β of the same order of magnitude but $\mu \cdot \beta$ ($=\mu\beta_{\mu}$) is much smaller since the direction as well as the magnitude of the net dipole have changed due to the change in the linkage position. The λ_{max} values are close in magnitude for these two examples. Comparing IV with III, the values of β and λ_{max} have increased considerably. This is due to enhanced π -electron interactions derived from the presence of the fused ring in IV. Comparing V with III, one notices a comparable μ but a much larger β as a result of enhanced conjugation due to the presence of multiple sulfur-containing heterocyclic rings. Therefore, multiple ring units or a fused ring heterocycle can be used to successively amplify (or tune) the nonlinear coefficient.



Experimental Studies

Synthesis. The compounds I–V (Scheme 1) were prepared in reasonable yields from either the acetic anhydride or base-catalyzed condensation of the appropriate methyl-substituted nitrogen heterocyclic with either thiophene-2-carboxaldehyde or 2,2'-bithiophene-5-carboxaldehyde. Elemental analysis was not carried out on compound I since its melting point corresponded to that reported in the literature and its molecular weight was confirmed by electron impact mass spectral analysis. The melting point reported for compound II differed substantially from that reported in the literature for a compound assumed to have the same structure. This discrepancy is thought to be due to different *E* and *Z* isomer ratios since the compounds were synthesized by different methods. It is documented in the literature⁹ that acetic anhydride–acetic acid catalyzed condensations to form styrylpyridines produce specifically the *E* isomer.

All reagents were commercially available and were used without further purification. All melting points are uncorrected. Electron impact mass spectra (EIMS) were recorded on a Finnegan Model 4021 GC/MS/DS system.

2-(2-Thienyl)-1-(4-pyridyl)ethene (I): Thiophene-2-carboxaldehyde, (2.80 g, 0.025 mol), 4-picoline, (2.33 g, 0.025 mol), acetic anhydride (6 mL), and acetic acid (3 mL) were heated at reflux for 48 h. The reaction mixture was cooled, diluted with water, and extracted with toluene. The toluene layer was washed with an equal volume of water and dried over anhydrous magnesium sulfate. The toluene was removed under reduced pressure and the resulting residue chromatographed on silica gel using 95:5 hexane–ethyl acetate. Removal of the solvent followed by recrystallization from hexane gave compound I in 66% yield, mp 151–151.5 °C; lit.¹⁰ mp 146–147 °C. EIMS (70 eV) 187 (M^+ , 100).

2-(2-Thienyl)-1-(2-pyridyl)ethene (II): This compound was prepared from thiophene-2-carboxaldehyde and 2-picoline using a procedure identical to that described above except purification was accomplished by column chromatography on silica gel using 90:10 hexane–ethyl acetate followed by recrystallization from hexane to give a 29% yield of compound II, mp 104–104.5 °C; lit.¹⁰ mp 78–78 °C. Anal. Calcd for $C_{11}H_{10}NS$: C, 70.57; H, 4.84; N, 7.49; S, 17.00. Found: C, 70.71; H, 4.86; N, 7.35; S, 17.09; EIMS (70 eV) 187 (M^+ , 100).

2-(2-Thienyl)-1-(2-pyrazinyl)ethene (III): Thiophene-2-carboxaldehyde (2.80 g, 0.025 mol), 2-methylpyrazine (2.35 g, 0.025 mol), and potassium hydroxide (5.61 g, 0.1 mol) in 15 mL of DMSO were stirred at room temperature for 18 h and poured into 250 mL of water. The precipitated solid was filtered, air dried, and purified by chromatography on silica

gel using toluene as the eluent. Recrystallization from hexane gave a 67% yield, mp 92–93 °C. Calcd for $C_{10}H_8N_2S$: C, 63.82; H, 4.28; N, 14.89; S, 17.00. Found: C, 63.87; H, 4.26; N, 14.79; S, 16.93; EIMS (70 eV) 188 (M^+ , 100).

2-(2-Thienyl)-1-(2-quinoxalyl)ethene (IV): A solution of sodium methoxide was prepared by reacting 0.80 g of sodium with 25 mL of absolute methanol. To this solution was added 1.8 g (0.025 mol) of 2-methylquinoxaline and 3.0 g (0.025 mol) of 2-thiophene carboxaldehyde, and the resulting mixture heated at reflux for 2 h. The reaction mixture was cooled to room temperature, and the resulting solid filtered and air dried. The crude product was purified by column chromatography on silica gel using 1:1 cyclohexane–ethyl acetate as the eluent followed by recrystallization from hexane–ethyl acetate to give a quantitative yield of compound IV mp 103–104 °C; lit.¹¹ mp 98–99 °C. Calcd for $C_{14}H_{10}N_2S$: C, 70.57; H, 4.23; N, 11.76; S, 13.43. Found: C, 70.55; H, 4.07; N, 11.68; S, 13.42. EIMS (70 eV) 238 (M^+ , 100).

1-(2,2'-Bithienyl)-1-(2-pyrazinyl)ethene (V): This compound was prepared using the procedure previously described for compound III using 2,2'-bithiophene-5-carboxaldehyde^{12,13} and 2-methylpyrazine as starting materials. The crude product was purified by column chromatography on silica gel using 1:1 cyclohexane–ethyl acetate as the eluent followed by recrystallization from hexane–ethyl acetate to give a 52% yield of III. Anal. Calcd for $C_{14}H_{10}N_2S_2$: C, 62.22; H, 3.73; N, 10.37; S, 23.68. Found: C, 62.31; H, 3.68; N, 10.39; S, 24.02. EIMS (70 eV) 270 (M^+ , 100).

Characterization of Nonlinear Optical Properties.

The measured values of μ , $\mu\beta$, β_{μ} , and λ_{\max} of the same representative compounds are also given in Figure 2 along with the theoretically calculated values.

The dipole moment measurement was carried out following the standard procedure.¹⁴ A series of dilute solutions of each compound were prepared and their dielectric constant ϵ and refractive index n were measured. The dipole moments were derived from the slopes of the plots of ϵ and n^2 against concentration by using the expression given by Smith.¹⁵ Nonpolar *p*-xylene was used as solvent.

The $\mu\beta$ values were obtained using the electric-field-induced second harmonic generation.^{16–18} In this experiment, one measures an effective third-order nonlinearity Γ_{EFISH} for a solution containing the compound of interest, which is related to $\mu\beta$ by

$$\Gamma_{\text{EFISH}} = f_0 f_{\omega}^2 f_{2\omega} \{ N[\gamma(-2\omega; 0, \omega, \omega) + \mu\beta/5kT] + N_s \gamma_s^{\text{eff}} \} \quad (3)$$

where f_0 is the Onsager local field factor, f_{ω} and $f_{2\omega}$ are Lorentz–Lorentz local field factors, N is the number density of the chromophore, $\gamma(-2\omega; 0, \omega, \omega)$ is the contribution from electronic motion, and the last term is the contribution from solvent. We estimated $\gamma(-2\omega; 0, \omega, \omega)$ from $\gamma(-\omega; \omega, \omega, -\omega)$, the result of degenerate four-wave mixing (DFWM) analysis.¹⁹ Fundamental beams of 1064 and 602 nm were employed for EFISH and DFWM, respectively. Chloroform was used as the solvent as well as in the internal standard, assuming Γ_{EFISH} (chloroform) = 0.88×10^{-13} esu¹⁶ and $\chi_{\text{DFWM}}^{(3)}$ (chloroform) = 0.81×10^{-13} esu.²⁰

UV–visible spectra in chloroform were recorded on a Shimadzu UV-3101PC spectrometer.

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Results and Discussions

PNA has a large dipole moment and in the crystalline form is centrosymmetric showing no second-order activity. The crystal is yellow. In contrast, compound I has a small dipole, a larger β value, is almost colorless in the crystalline form, and shows a strong second-order activity (powder SHG) indicating a noncentrosymmetric crystalline form. The noncentrosymmetric crystallization will be favored by the small dipole moment. When compounds IV and V are compared to compound III and compound II is compared to compound I, they show the same trend as predicted by the theory. To experimentally gain an insight into the angle between μ and β , we employed eq 1 to calculate μ_{CT} and θ , the angle between μ and the long axis X , from the net dipole moment measured and the direction and magnitude of the component dipole moments,^{21,22} as is illustrated in Figure 3. The results are also listed in Figure 2.

The use of this method to calculate θ predicts that for compound II, the direction of the dipole will be at an angle of about 114° with respect to the largest component of β assumed to be along the long axis. This angle will yield a very small negative $\mu \cdot \beta$, in accordance with the almost vanishing EFISH signal observed experimentally. Considering the influence of the angle, one may expect β to be comparable to that of I, namely, not much affected by the linkage position. This is supported by our theoretical calculation as discussed above.

Hyper Rayleigh scattering has been used in the past to measure β . In this method one measures β^2 and thus the modulus of the β tensor (its largest component).²³ Our preliminary results of hyper Rayleigh scattering also indicate a close value of β for both structures I ($\beta = 14 \times 10^{-30}$ esu*) and II ($\beta = 19 \times 10^{-30}$ esu). The measurements were carried out in chloroform, assuming

$$\beta \text{ (chloroform)} = -0.49 \times 10^{-30} \text{ esu.}^{23}$$

Conclusions and Future Directions

Both the theoretical and the experimental studies show the new class of chromophores described to have large β values but small ground-state charge transfer compared to PNA. The dipole moment vector can be manipulated by changing the position and number of nitrogen atoms in the heterocyclic ring.

The largest β component is along the long axis of the molecule and can be amplified by use of oligomeric units or fused rings. These two ways of manipulation of dipole moment and nonlinearity are almost independent. The optical transparency window is broadened toward higher frequency because of the reduced color of these materials when compared with type I chromophores with equivalent values of β .

The ability to manipulate μ and β independently offers great flexibility in designing new chromophores with finely tailored properties to better match the necessary requirements for various applications. The ability to substitute the ring positions of the heterocycles offers the possibility of easily incorporating these types of materials into polymers or sol-gel matrices. Because of the large aromatic character, better compatibilities are expected with highly aromatic thermoplastics having high glass transition temperatures.

The use of "all aromatic" units offers additional advantages in improved chromophore thermal stability as well as reduced chromophore toxicity, both of which are currently under investigation in our laboratories.

The versatility associated with heteroaromatic structures thus offers tremendous opportunities in developing and optimizing NLO materials properties at both the molecular and bulk levels.

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