designing thin film systems that incorporate the group II metals, silicon, and oxygen.

Summary

Ternary phase diagrams have been determined for the M-Si-O systems, where M = Mg, Ca, Sr, and Ba. These phase diagrams can be used to explain previous experimental results for reactions between SrO films on Si and to predict what can happen at the interfaces between M-containing compounds and either Si or SiO_2. These phase diagrams are not difficult to determine, yet they are important in providing guides in designing experiments and in selecting chemically stable materials for thin-film structures.

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Registry No. Mg, 7439-95-4; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3; Si, 7440-21-3; O_2, 7782-44-7.

Use of Thiazole Rings To Enhance Molecular Second-Order Nonlinear Optical Susceptibilities

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It is shown that the appropriate replacement of benzene-ring structures by thiazole rings in polar donor-acceptor molecules will result in an increase of the microscopic scalar second-order nonlinear optical quantity, $\mu_0\beta$, of up to a factor of ≈ 3. Electric field induced second harmonic generation (EFISH) results are presented for two species of this type and compared to the corresponding benzenoid structures. In general, the results show the increases in $\mu_0\beta$ to be largely due to dispersion, with smaller effects seen in dipole and transition moments. There is a significant narrowing of the transition band from $2\Gamma \approx 3530$ cm^{-1} to $2\Gamma \approx 2110$ cm^{-1} upon replacement of benzene by thiazole, thus keeping the effects of damping relatively constant and permitting ready application of these dyes for electrooptic device applications in the near IR ($\gtrsim 1300$ nm). Scalar $\mu_0\beta$ as large as ≈ 5300 D cm^5 esu^{-1} ($\lambda_{2\omega} = 789.5$ nm; $\lambda_{max} = 645$ nm; $\Gamma = 1057$ cm^{-1}, the half-width at half-maximum) are observed for a (dicyanovinyl)thiazole azo dye.

Introduction

It is well-known that five-membered conjugated heterocycles (furan, thiophene, thiazole, etc.) possess considerably less aromatic stabilization than benzene, although they are considerably more stable than the acyclic butadiene analogues.[1,2] Thus, while the cost in energy to break the aromatic delocalization is less than in benzene, substantial thermodynamic stability remains. This observation is important for organic electronic and optical materials. Electrically conducting doped polythiophene[3] is a stable compromise between the air-unstable polyacetylene and the more poorly conducting polyphenylene analogues.[4] The relatively poor conductivity and greater stability of polyphenylene can be attributed to localization of electrons in each aromatic ring. Since the characteristics of nonlinear optical (NLO) materials depend on the intramolecular transfer of electron density, it could be argued that similar replacement of benzene moieties will lead to enhancements in the NLO susceptibilities. This will bring the susceptibilities closer to those of the donor-acceptor conjugated dienes, though the molecule will retain much of its stability and all of its planarity, and extended conformation, relative to those containing benzene rings. Zhao et al.[5] and independently Fichou et al.[6] have demonstrated large third-order susceptibilities, γ, in thiophene oligomers. Kaino et al.[7] have shown poly(2,5-thienylenevinylene) to possess a higher bulk third-order nonlinearity, $\chi^{(3)}$, than the phenylene analogue. Despite the promise of larger second-order nonlinearities in compounds containing heterocycles in place of benzene, there have apparently been no great successes reported in the literature for such compounds.

The second-order microscopic nonlinearity, β, is approximately given by a two-level model:[8]

$$\beta = K(\Delta\mu_{01})(\mu_{01})^2F(\Omega_{01},\omega_1,\omega_2) \qquad (1)$$

where K is a constant that depends on the optical process, μ_{01} is the scalar magnitude of the transition moment vector ($\int \Psi_0 e\mathbf{r}\Psi_1 \, d\tau$, where Ψ_0 and Ψ_1 are the ground- and excited-state wave functions, and $d\tau$ represents the integral over all space), $\Delta\mu_{01}$ is the change in dipole moment between the ground and first excited state (given by $\mu_{11}-\mu_{00}$),

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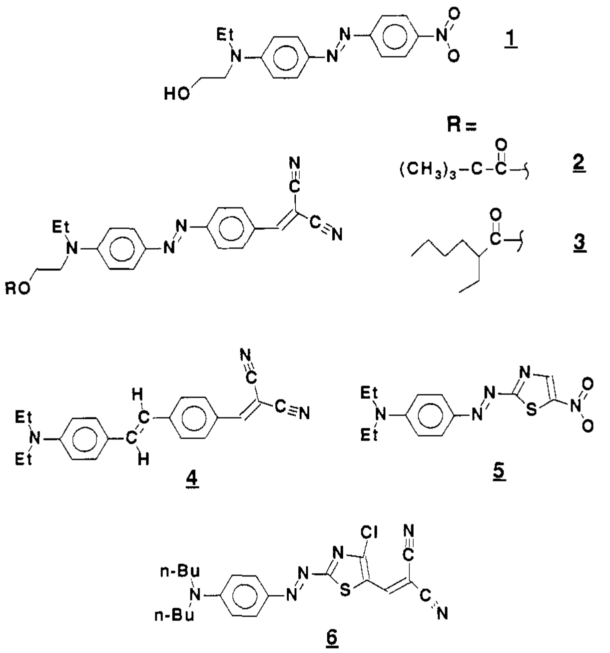
Chart I



and $F(\Omega_{01},\omega_1,\omega_2)$ (defined by eq 3) is the frequency dependence of the nonlinear optical dispersion. Under this approximation, β can be increased in three ways.

The least desirable method is to shift the excited state closer in frequency to either incident frequency, ω_1 or ω_2, or to either the sum, $\omega_1 + \omega_2$, or difference, $\omega_1 - \omega_2$, frequencies. While this can result in a great increase in β, it is often accompanied by increases in absorption or damping,[9] which, in turn, can result in either optical damage or attenuation of the nonlinearity. Note, however, if one simultaneously also narrows the electronic transition sufficient to offset absorption and damping, the use of resonance can lead to large *useful* increases in the nonlinearity. The difficulty of this approach is in elucidating a rational way to narrow electronic resonances.

The two most desirable approaches to experimentally optimize eq 1 involve increasing either the transition moment, μ_{01} (proportional to the square root of the integrated absorption) or the change in dipole moment, $\Delta\mu_{01}$. Typically, the transition moment and dipole moment have most easily been increased by increasing the conjugation length between the donor and acceptor moieties or by incorporating better donors or acceptors, though both of these approaches usually also red-shift the electronic transition. It is proposed here to maintain a roughly constant conjugation length but replace benzene moieties with thiazole. The aim is to reduce the "resisting" aromatic delocalization with the hope of increasing electron transmission between donor and acceptor and thereby increase both μ_{01} and $\Delta\mu_{01}$.

To test this hypothesis we have prepared the compounds given in Chart I and measured the electric field induced second harmonic (EFISH) $\mu_0\beta$, ground-state dipole moments, μ_0, and ground to first excited state transition moments, μ_{01}.

Experimental Section

Solvents and starting materials were obtained from Aldrich Chemical Co. and used without further purification. Compound **1** was obtained from Aldrich and purified by dissolving it in methanol, filtering, and reducing to dryness. Compounds **2** and **3** were prepared by using established methods[10] and gave satisfactory analyses. Compounds **4**[11] and **5**[12] were prepared as previously described. Compounds **2** and **3** were combined in a 1:1 molar ratio to increase solubility for dielectric solution studies being reported elsewhere.[13] Since the alkyl group remote to the chromophore is expected to have little effect on the electronic properties, a known mixture is adequate to characterize the chromophore optical properties. This mixture is hereafter referred to as **2–3**. The *N*,*N*-diethyl analogue of compound **6** has been reported.[14] The *N*,*N*-dibutyl derivative, **6**, used here was prepared in the following manner:

2-Amino-4-chloro-5-(β,β'-dicyanovinyl)thiazole[15] (5.91 g, 33.1 mmol) is added to 2.31 g (33.5 mmol) of $NaNO_2$ dissolved in a mixture of 20 g of concentrated H_2SO_4 and 40 mL of 85:15 (v/v) acetic acid/propionic acid at 0–5 °C. The reaction proceeds with heat evolution (maintain below 10 °C), yielding a reddish brown solution. After 15–25 min of stirring, this is added to 7.48 g (36.4 mmol) of *N*,*N*-dibutylaniline in 150 mL of 85:15 acetic acid/propionic acid at ≈5 °C. The resulting blue-brown solution is stirred for 15–20 min and then poured into a solution of 150 g of sodium acetate in a mixture of 1 L of H_2O and 750 mL of ice, with rapid stirring. The purple precipitate is collected by filtration, washed on the filter with water, allowed to dry, taken up in CH_2Cl_2, dried over Na_2SO_4, filtered, and vacuum reduced to 45–55 mL. This solution was streaked onto 35 2-mm silica gel preparatory TLC plates, first eluted two times with 5% ethyl acetate in hexane and then four times with 10% ethyl acetate/hexane. The product was isolated by cutting the blue band from the plate, dissolving in CH_2Cl_2, filtering, and vacuum reducing to dryness, yield 828 mg (≈9% based on chromatography of 65% of the crude product); 360-MHz ^1H NMR ($CDCl_3$ solvent and standard) δ 0.99 (t, J = 7 Hz), 1.40 (br m), 1.67 (br m), 3.47 (t, J = 8 Hz), corresponding to the butyl groups, 6.73 (d, J = 9 Hz), 7.8–8.1 (br s), corresponding to the phenyl protons (presumably, the latter signal corresponds to a doublet being broadened by the azo group lone pair), and 7.93 (s), presumably the dicyanovinyl proton. Anal. Calcd for $C_{21}H_{23}N_6ClS$: C, 59.08; H, 5.43; N, 19.68; Cl, 8.30; S, 7.51. Found: C, 59.57; H, 5.67; N, 20.49; Cl, 8.11; S, 7.83.

Due to a side reaction of the Vilsmeier formylation, which leads to the starting material,[15] compound **6** possesses a chlorine on the 4-position of the thiazole ring. Its certain effect will be to modestly increase the ground-state dipole moment of **6**. Other resonance and steric interactions are uncertain, so that when comparing results for **6** to those of **2–3** (vide infra), there is potentially some extra uncertainty to contend with. The derivative without the chlorine atom is not readily accessible.

Electric field induced second harmonic generation (EFISH) and dipole moment measurements were done as previously described,[16] except the solvent methylene chloride was substituted for dimethyl sulfoxide (DMSO) for EFISH measurements because of the solvolytic instability of some of the cyano compounds in DMSO. Dipole moments were measured in dioxane and extrapolated to values in methylene chloride by using established methods.[16]

All linear optical spectra were determined in methylene chloride unless specified otherwise.

Calculations

Transition moments, $|\mu_{01}|$, are calculated from the integrated absorption by using the following expression:

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$$|\mu_{0n}| = \left[\left[\frac{\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu}{\nu_{0n}}\right]\frac{3\ \ln\ (10)hc\epsilon_0}{2\pi^2 N_\mathrm{A}}\right]^{1/2} \tag{2}$$

where $\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu$ is the integrated absorption of the electronic spectrum, $\epsilon_\nu^{(n)}$ is the absolute molar absorptivity of state n at wavenumber ν, ν_{0n} is the wavenumber of the absorption maximum of state n, h is Planck's constant, c is the speed of light, ϵ_0 is the permittivity of free space, and N_A is Avogadro's number. This is an adaptation of Herzberg's[17] adaptation of Mulliken's expression.[18] The calculated transition moment consists of an anisotropic one-dimensional component (x) that is presumed to arise from an integrated absorption due to an isotropically averaged one-dimensional oscillator. In units of debye, the constants can be evaluated: $|\mu_{0n}|^2 = 9.1862 \times 10^{-3}\ (\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu/\nu_{0n})\mathbf{D}^2$, where the experimental value of $\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu/\nu_{0n}$ has been determined in units of L mol^{-1} cm^{-1}.

To avoid a numberical integration, a Lorentzian peak shape has previously been assumed, permitting an analytical two-point integration.[19] This yields $\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu = \pi\epsilon_\mathrm{max}\Gamma$, where Γ is taken as the half-width at half-maximum, and ϵ_max is the value of $\epsilon_\nu^{(n)}$ at the peak maximum, ν_{0n}. This approach is valid if the broadening is dominated by the uncertainty mechanism or if inhomogeneous broadening is not significant. This will normally not be the case, and the Lorentzian approximation will usually lead to transition moments ≈20%[20] too large.

Doppler broadening, usually more significant than uncertainty broadening, leads to Gaussian-shaped peaks. Under this approximation, $\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu = \pi^{1/2}\epsilon_\mathrm{max}\Gamma_\mathrm{G}$, where Γ_G is given by $|\nu_{0n} - \nu_{\epsilon_\mathrm{max}/e}|$ and $\nu_{\epsilon_\mathrm{max}/e}$ is the frequency at which ϵ_max has been reduced by $1/e$ ($e = 2.71828...$).

Usually, the most significant broadening mechanism is due to collisions. This is physically complex and leads to peak shapes that cannot be trivially described as Gaussian or Lorentzian.[21] Because of this uncertainty, the integrated absorption, $\int \epsilon_\nu^{(n)}\,\mathrm{d}\nu$, is best determined by numerical integration of the measured electronic spectrum. We do this by integrating from ϵ_max, toward the low-energy side of the peak, to a frequency ν at which $\epsilon_\nu^{(n)} = 0.01\ \epsilon_\mathrm{max}$ and doubling to obtain the full area under the peak. This half integration is done to avoid using the high-energy side of the peak, which may have a weak shoulder or may be influenced by the tail of a higher energy excitation. Table IV supplies the transition moments derived from this numerical integration ($|\mu_{01}|$) and compares them to transition moments obtained from the Lorentzian ($|\mu_{01}|_\mathrm{L}$) and Gaussian ($|\mu_{01}|_\mathrm{G}$) definitions provided here. Note that the Gaussian approximation is the best fit to the numerical integration for the data presented here. However, previous work has shown that "anomalous" Lorentzian fits are possible.[22] Thus, neither approximation can be used with impunity.

The procedure for calculating the "dispersionless" β_0 has been previously outlined.[16,23] This modified susceptibility is still weighted by the excitation frequency of the first excited state. In effect, some of the frequency dependence remains in β_0. We define a potentially more useful quantity, $\beta_\mathrm{I} \equiv \beta/2KF(\Omega_{01},\omega_1,\omega_2)$ where $F(\Omega_{01},\omega_1,\omega_2)$ (F_Γ in Table III) is given by

Table I. Linear Optical Results Determined in Methylene Chloride and DMSO[a]

compd	λ_max, nm	ϵ, M^{-1} cm^{-1}	Γ, cm^{-1}	Γ_G, cm^{-1}
1	480	31 700	1960	2320
2–3	513	46 600	1760	2060
4	485	37 680	2020	2440
5	579	44 200	1280	1490
6	645	58 000	1060	1260
	664[b]	50 100[b]	1230[b]	1440[b]

[a] Γ is the peak half-width at half-maximum. Γ_G is defined in the text. [b] Determined in DMSO.

$$F(\Omega_{01},\omega_1,\omega_2) = I_{1,2} = \left[\frac{1}{(\Omega_{01} - \omega_1 - \omega_2)(\Omega_{01} - \omega_1)} + \frac{1}{(\Omega_{01} - \omega_2 - \omega_1)(\Omega_{01} - \omega_2)} + \frac{1}{(\Omega^*_{01} + \omega_2)(\Omega_{01}^* + \omega_1 + \omega_2)} + \frac{1}{(\Omega^*_{01} + \omega_1) = (\Omega^*_{01} + \omega_2 + \omega_1)} + \frac{1}{(\Omega^*_{01} + \omega_2)(\Omega_{01} - \omega_1)} + \frac{1}{(\Omega^*_{01} + \omega_1)(\Omega_{01} - \omega_2)}\right] \tag{3}$$

Equation 3 is the two-level dampled frequency dispersion for a general second-order nonlinear optical process as determined from eq 43b of Orr and Ward.[24] The quantities Ω_{01} ($\omega_{01} + i\Gamma/2$) and Ω^*_{01} ($\omega_{01} - i\Gamma/2$) are the complex absorption frequencies of the first excited state, where ω_{01} and Γ are, respectively, the transition frequency and inverse radiative lifetime for the first excited state. The operator $I_{1,2}$ permutes and averages the sub indices of ω_1 and ω_2. Note that when $\omega_1 = \omega_2 \equiv \omega$ and $\Gamma = 0$ (i.e., undamped second harmonic generation, SHG), this equation reduces to $3\omega_{01}^2(\omega_{01}^2 - \omega^2)^{-1}(\omega_{01}^2 - 4\omega^2)^{-1}$, which is the standard[16] SHG frequency doubling two-level dispersion. For second harmonic generation, the constant K is normally set equal to $^1/_2$ to account for the frequency degeneracies.[24] Note that this implies an undamped SHG two-level model given by $\beta = {}^3/_2(\mu_{01})^2\Delta\mu_{01}\omega_{01}^2(\omega_{01}^2 - \omega^2)^{-1}(\omega_{01}^2 - 4\omega^2)^{-1}$, which would be in agreement with expressions reported by many earlier workers.

The value of Γ is experimentally taken as the peak half-width at half-height (hw-hh).[25] This definition of Γ presumes Lorentzian peak shapes, although when broadening is inhomogeneous (the usual case for liquids and solids near room temperature), peak shapes will normally be Gaussian and are somewhat more narrow than implied by the Lorentzian peak hw-hh. For the purposes of dispersion corrections using eq 3, all experimental Γ's in this investigation are approximated as if from Lorentzian-shaped peaks.

Insofar as the two-level model applies, the quantity β_I is the frequency-independent "intrinsic" *moments* contribution to β; in other words it is considered proportional to $\mu_{01}^2\Delta\mu_{01}$, where μ_{01} is the transition moment and $\Delta\mu_{01}$ is the change in dipole moment. This parameter provides

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(20) Assuming a pure Lorentzian when actually a pure Gaussian results in a constant actual error of $(\pi \ln (2))^{1/4} = 1.214769...$ in the transition moment, about 20% too large.

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(25) Presuming a first-order rate decay with lifetime τ ($1/\Gamma$), one arrives at the Lorentzian peak shape, via Fourier transform, with the half-width at half-maximum being given by $1/\tau$ (Γ). See: Flygare, W. H. *Molecular Structure and Dynamics*; Prentice-Hall: New York, 1978; Chapter 7.

Table II. Dipole Moment[a] and Nonlinear Optical Results[b]

compd	$\beta\mu_0$, 10^{-30} D cm^5/esu	$\beta_I\mu_0$,[b] 10^{-22} D cm^3/esu ($\equiv D^4$)[c]	β, 10^{-30} cm^5/esu	β_0,[23] 10^{-30} cm^5/esu	β_I,[b] 10^{-22} cm^3/esu ($\equiv D^3$)[c]	μ_0, D	$\Delta\mu_{01}$,[27] D
1	800	680 (2670)	90	51	76 (300)	8.9	13
2–3	1880	1260 (4970)	190	98	126 (500)	10.0	15
4	1470	1200 (4740)	180	101	147 (580)	8.2	19
5	2190	900 (3500)	260	104	105 (410)	8.5	16
6	5320	1230 (4860)	530	147	123 (490)	10.0	16

[a] $\mu_0 \pm 10\%$; determined in dioxane, extrapolated to methylene chloride as previously shown.[16] [b] Determined in methylene chloride by using the EFISH process; fundamental wavelength 1.579 μm. Note that β, β_0, and β_I are the "undressed" local field corrected[16] quantities, while $\Delta\mu_{01}$ is "dressed". [c] Note that results for $\beta_I\mu_0$ and β_I have been presented in a mixed set of units (D cm^3 esu^{-1} and cm^3 esu^{-1}, respectively), which are directly related to $\beta\mu_0$ and β, respectively, through F_Γ^{SHG} (Table III), and in the more familiar units of debye (D^4 for $\beta_I\mu_0$ and D^3 for β_I).[26] Note the following uncertainties: $\beta\mu_0$ ($\pm15\%$); $\beta_I\mu_0$ ($\geq15\%$); β_I ($\geq\pm25\%$); $\Delta\mu_{01}$ ($\geq\pm30$–35%).

Table III. Damped (F_Γ) and Undamped ($F_{\Gamma=0}$) Two-Level Dispersion Factors for Second Harmonic Generation (SHG) and the Electrooptic Effect (EO) and Corresponding Damping Corrections ζ^{SHG} and ζ^{EO}[a]

compd	F_Γ^{SHG}, 10^{-7} cm^2	$F_{\Gamma=0}^{SHG}$, 10^{-7} cm^2	F_Γ^{EO}, 10^{-7} cm^2	$F_{\Gamma=0}^{EO}$, 10^{-7} cm^2	ζ^{SHG}	ζ^{EO}
1	0.1184	0.1208	0.085	0.0865	0.981	0.992
2–3	0.1494	0.1528	0.0945	0.095	0.978	0.993
4	0.1224	0.1251	0.0875	0.0885	0.978	0.991
5	0.2453	0.2514	0.128	0.129	0.976	0.994
6	0.4321	0.4505	0.169	0.170	0.960	0.994

[a] The fundamental wavelength for both processes is taken as 1.579 μm.

Table IV. Experimental Transition Moments[a] Determined in Methylene Chloride

compd	$\lvert\mu_{01}\rvert$	$\lvert\mu_{01}\rvert_G$	$\lvert\mu_{01}\rvert_L$
1	7.5	7.6	9.3
2–3	9.0	8.9	11.0
4	8.5	8.5	10.3
5	7.9	7.9	9.7
6	8.7	8.8	10.7
	8.7[b]	8.8[b]	10.9[b]

[a] Moments (units of debye) have been calculated by numerical integration ($\pm5\%$) unless specified as from the Gaussian ($\lvert\mu_{01}\rvert_G$) or Lorentzian ($\lvert\mu_{01}\rvert_L$) analytical approximations. [b] Determined in DMSO.

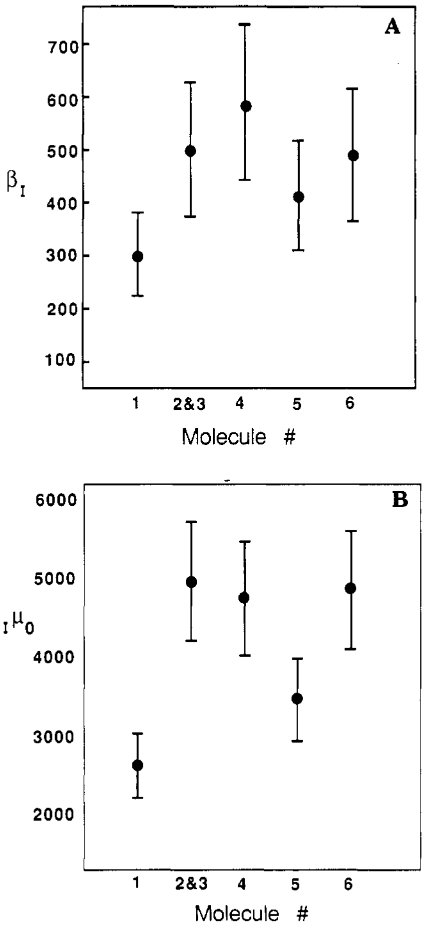

Figure 1.

a direct frequency-independent measure of the magnitude of molecular charge reorganization in the SHG process. The parameter β_0 is a useful figure of merit for optimizing molecules for applications that involve processes that are relatively far off resonance. The parameter β_I is useful to determine whether a molecule's given β_0 is as large as it could have been independent of its λ_{max}.

The damping correction, ζ, is defined as $F(\Omega_{01},\omega_1,\omega_2/F(0,\omega_1,\omega_2)$ ($F_\Gamma/F_{\Gamma=0}$; see Table III). When the effect of damping is negligible, ζ will be equal to or near unity. Note that the peaks dealt with here are Gaussian in shape, so that the Lorentzian presumption of the definition of Γ results in an overestimate of the effects of damping on ζ. The actual ζ's will be somewhat closer to unity than those calculated here.

Results and Discussion

Linear optical data are reported in Table I. Nonlinear optical data and ground-state dipole moments are reported in Table II.

Linear Optical Data. Upon replacement of the benzene ring in either **1** or **2–3** with the thiazole group, the lowest energy excitation is significantly red shifted—3560 cm^{-1} for **5** relative to **1** and 3990 cm^{-1} for **6** relative to **2–3**—and there is a pronounced increase in the molar absorptivity, ϵ, at λ_{max}. However, in both cases, the peak narrows considerably, so that the integrated absorption and transition moments (Table IV) remain relatively constant. Changes in ground-state dipole moments are also slight (Table II). Thus, in the absence of nonlinear optical measurements, one might expect any differences (comparing corresponding benzene- and thiazole-substituted molecules) in second-order nonlinear optical behavior to be dominated by the effects of dispersion, unless there are significant differences in excited-state dipole moments.

Nonlinear Optical Data. It is clear that there are significant improvements in β and $\beta\mu_0$ when the second benzene ring of either **1** or **2–3** is replaced with a thiazole ring. However, there are significant differences in λ_{max} for all compounds, and the second harmonic ($\lambda_{2\omega}$ = 789.5 nm) of the measurement frequency is relatively close to these state energies, and, as implied by the linear optical data, resonance effects are a crucial concern.

The quantities β_I and $\beta_I\mu_0$ have been corrected for all resonance effects, including damping,[9] at least to a two-level approximation. Within experimental error the values of β_I are the same for compounds **2–6** (Figure 1a). Thus, despite the large differences in β, the intrinsic "moments" nonlinearity of β_I seem to vary much less.

The projection of β_I onto the dipole moment is given by $\beta_I\mu_0$. The weighting by this additional moment (μ_0) further levels the dispersionless "moments" nonlinearities, but in two distinct groups (Figure 1b), due to the smaller experimental error (≈±15%). It is clear that the nitro- and dicyanovinyl-substituted molecules are different. These $\beta_I\mu_0$ results suggest that the dicyanovinyl-substituted dyes are *intrinsically* superior to the nitro-substituted dyes for poled polymer applications. Thus, given a SHG or electrooptic (EO) materials application where the nonlinearity comes from poling of dye molecules, compounds **2**–**3**, **4**, and **6** are intrinsically very similar and probably significantly superior to nitro-substituted dyes. Also, comparison of the error bars for **5** and **1** suggests that when using the nitro acceptor, the thiazole moiety might be improving the intrinsic moments nonlinearity of the $\beta_I\mu_0$ parameter. It is the relative difference between the excited-state and fundamental operating frequencies that dictates how much of the moments nonlinearity will be projected out through dispersion. For the dicyanovinyl compounds, less of a dispersion "projection" is necessary than for the nitro compounds, and when using the nitro group, the thiazole may still be intrinsically superior to a benzene.

Concluding this section, it appears that we are seeing a saturation in the intrinsic moments nonlinearity, β_I of ≈(120–130) × 10^{-22} cm^3 esu^{-1} (≈480–510 D^3),[26,27] across this series of molecules. There must be a limit to how much charge reorganization can be supported in an organic molecule, and it is possible that the product of the square of the transition moment and change in dipole moment is about as big as it can get for virtual excitations for molecules of this size. This result is also suggested by Cheng et al. on a study of donor–acceptor substituted benzenes and stilbenes.[28] Using the data in that reference, β_I for 4-(dimethylamino)-4′-nitrostilbene (a molecule of the same size and type considered here) is calculated to be 117 × 10^{-22} cm^3 esu^{-1} (463 D^3), in agreement with the results presented here. On the other hand, while examination of the $\beta_I\mu_0$ parameter suggests a further leveling, this leveling occurs only within groups having the same donor and acceptor, so that a distinct preference exists for the dicyanovinyl acceptor. The dicyanovinyl group does result in a modest lengthening of the molecule, which should lead to correspondingly higher transition and dipole moments.

Effects of Damping. If other system restrictions (i.e., normal optical transmission frequencies) dictate a fixed SHG or EO fundamental frequency in the near IR, normally between 1300 and 1500 nm, then the compound with the transition closest in resonance to the SHG or EO fundamental frequency will produce the largest nonlinear effect. In this case, $\beta\mu_0$ and β are relevant quantities, and compound **6** is now clearly the best. However, the lower molecular excitation energy now raises questions about the effects of absorption and damping. Will the tail of the molecular electronic excitation lower the nonlinearity because of damping and increase the absorption loss beyond a tolerable level?

For a fundamental wavelength of 1.579 μm, absorption would clearly be a problem for SHG for compound **6**, especially in a concentrated solution or for long path lengths. However, for an electrooptic device operated at that wavelength or even as low as 1.3 μm, the absorbance of vibrational overtones will be more of a concern than the electronic excitation tail. Damping effects on 1.579 μm SHG (Table III) are relatively insignificant, even for compound **6**, primarily due to the narrowing (Γ; see Table I) of the excitation as the molecular first excitation energy is shifted to the red upon replacement of benzene by thiazole. Because of this extreme narrowing, damping effects on 1.579-μm EO may be very slightly less for **5** and **6** than for the *higher* excitation energy **1**! As noted in the Experimental Section, the damping corrections, ζ, represent *upper* estimates for the effect of damping. The true ζ's represented by the Gaussian peak shapes should be closer to unity. Thus the red shift of **6** has been sufficiently offset by the narrowing of the excitation that the longer nonlinearity can be effectively sampled for the EO process.

Aromatic Delocalization, λ_{max}, and β. Aromatic delocalization energies for benzene, thiophene, and furan are thought to be 36, 29, and 16 kcal/mol (1.56, 1.26, and 0.694 eV), respectively.[1,2,29] Oxazole, the oxygen analogue of thiazole, is thought to be less aromatic than furan.[30] We may then expect that thiazole will have an aromatic delocalization less than thiophene but greater than furan. Previous discussion has shown that the major difference in β between **1** and **5** or between **2**–**3** and **6** is confined to dispersion and therefore reflected in the differences in λ_{max}. Thus if the major difference between the thiazole and analogous phenyl azo dyes is the energy cost for *localization* of the electrons in each ring upon excitation from the "benzenoid" aromatic ground state to the "quinoid" excited state, the differences in λ_{max} could perhaps be interpreted as the difference in aromatic delocalization energy between the thiazole and benzene rings. The difference in excited-state energies between **1** and **5** is 10.2 kcal/mole (0.442 eV), while the corresponding difference for **6** and **2**–**3** is 11.4 kcal/mol (0.494 eV). Presuming that the donor (p-R$_2$NPhN=N) and acceptor (NO$_2$ or CH=C(CN)$_2$) moieties affect the thiazole and benzene ground and excited states in the same way, this would imply an aromatic delocalization of 24.6–25.8 kcal/mol (1.07–1.12 eV) for thiazole, which is in agreement with the inference provided above. This result may be entirely coincidental, and further *linear* extrapolation may not hold, but it would imply that a more red-shifted dye, with incidently higher β, could be prepared by replacing the thiazole in **5** or **6** with oxazole.

Conclusions

We report here a useful method for establishing a new class of dyes for second-order nonlinear optics utilizing the thiazole heterocyclic moiety. Both β and $\beta\mu_0$ are increased substantially, though these increases seem to be largely due to dispersion, particularly for the (dicyanovinyl)thiazole dye, **6**. Hence, our initial hope to increase the moments contribution to β was thwarted. However, the thiazole moiety greatly narrows the molecular electronic excitation so that the increases in the nonlinearity should not be accompanied by significant increases in absorption or damping. It is possible that these latter deleterious effects might slightly decrease, relative to the analogous benzene–substituted compounds, in electrooptic modulation applications. Thus, these new dyes, when incorporated in

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(26) The more familiar units of Debye are obtained by multiplying by $(4\pi\epsilon_0)^2$ (≡3.9461 × 10^{-32} esu^4) and then multiplying by 1 × 10^{54} D^3 cm^{-3} esu^{-3}. ϵ_0 is the permittivity of free space.

(27) Note that from β_I and the experimentally determined transition moments, $|\mu_{01}|$ (Table IV), one can obtain a "two-level" change in dipole moment, $|\Delta\mu_{01}|$ ($\equiv f^3\beta_I|\mu_{01}|^{-2}$), where f equals $(n^2 + 2)/3$ as a simple Lorenz–Lorentz local field correction. See Table II.

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"poled polymers", may be particularly attractive for electrooptic applications where $\beta\mu_0$ and the width of the absorption band are critical characteristics.

For this work, the thiazole ring was chosen over other heterocycles because of the availability of starting materials, ease of synthesis, and an anticipated higher stability of intermediates and final products. Presumably other heterocycles could be used and may result in further redshifting and hopefully further narrowing of the absorption.

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Permeability of Methyl Methacrylate Grafted Cellulose Triacetate Membrane

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Methyl methacrylate (MMA) was grafted onto a porous cellulose triacetate membrane by applying the radiation-induced graft polymerization technique in the vapor and liquid phases. Comparison of the pure water flux between the MMA-grafted membrane prepared by vapor-phase or liquid-phase grafting shows that the membrane prepared by vapor-phase grafting exhibited higher flux than the membrane prepared by liquid-phase grafting with the same amount of grafted polymer branches. The apparent specific volume of the graft phase was determined as a function of the degree of grafting from the measurement of the flux and dimensions of the resulting membrane. When vapor-phase grafting is employed, the graft chains are considered to enter the amorphous domain in the trunk polymer, which agrees with the morphological observations of the membrane.

Introduction

A filtration membrane can be easily modified by radiation-induced graft polymerization.[1] The hydrophilic group[2] and ion-exchange group[3] or chelating group[4] were introduced into existing microfiltration membranes. Since the grafted polymer branches fill the pores of the starting polymer, the introduction of the functional group induces flux decrease. Therefore, the density of the functional group and the water flux are trade-off factors. In a previous paper,[5] vinyl monomers such as acrylonitrile, styrene, vinyl acetate, and acrylic acid were grafted onto a polyethylene microfiltration membrane by the preirradiation grafting technique. The reaction of the monomer vapor with the trapped radical formed in the trunk membranes was found to be a superior method in that the flux decrease was repressed.

The objectives of our study were 2-fold: (1) to prepare the methyl methacrylate grafted membrane by vapor- and liquid-phase grafting; (2) to compare the morphological change and flux of the resulting membranes. In this study, we selected a porous cellulose triacetate membrane as the trunk polymer and examined the permeability change accompanied by radiation-induced grafting by considering the location of the grafted branches.

Experimental Section

Materials. A commercially available porous cellulose triacetate (CTA) membrane (FM22, Fuji Film Co., Ltd., Japan) was used as the trunk polymer for grafting. This flat membrane has been industrially used for microfiltration. The diameter and thickness of the membrane were 47.4 and 0.179 mm in a wet state, respectively. The membrane has nominally 0.22-μm-diameter pore size and 70% porosity. Technical-grade methyl methacrylate (MMA, Wako Pure Chemical Ind., Japan), from which the inhibitor and plasticizer were previously removed, was used.

Preparation of MMA-Grafted Membrane. The CTA membrane was irradiated with an accelerator operating at a beam energy of 2.0 MeV and current of 1 mA at room temperature in a nitrogen atmosphere. The dose was 200 kGy. The graft polymerization was performed by introducing MMA vapor or liquid MMA to the reaction ampule. In vapor-phase grafting, irradiated CTA membrane reacted in MMA vapor. In liquid-phase grafting, irradiated CTA membrane was immersed in liquid MMA. After predetermined periods, the membrane was removed from the ampules and washed thoroughly with benzene to remove residual MMA and poly-MMA homopolymer from the membrane. The MMA-grafted membrane was dried under reduced pressure, and the weight was measured.

The degree of grafting (dg), defined in eq 1, ranged from 10

$$\mathrm{dg} = [(W_1 - W_0)/W_0]100 \qquad (1)$$

to 100%, where W_0 and W_1 are the weights of the starting and MMA-grafted membranes, respectively. The MMA-grafted

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