Chem. Mater. **1993,** *5,* 733–737

Quadratic Electrooptic Effect in Molecules with Large Optical Hyperpolarizabilities

Carl W. Dirk* and Noel Caballerro

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968-0513

Mark G. Kuzyk

Department of Physics, Washington State University, Pullman, Washington 99164-2814

Received November 24, 1992. Revised Manuscript Received March 10, 1993

We report quadratic electrooptic derived third-order optical polarizabilities, γ, on two thiazole azo dyes that we have previously demonstrated to possess large optical hyperpolarizabilities, β. We demonstrate that the data are consistent with our previously introduced restricted three-level model for γ. Specifically we show that the susceptibility can be accounted for by two perturbative terms and that we are also possibly observing the predicted enhancement in γ for molecules with large β when the peak narrows. We also suggest that this mechanism offers an approach to systematic improvements for the ratio $\mathrm{Re}[\gamma]/\mathrm{Im}[\alpha]$.

Introduction

There is considerable interest in the nonlinear optical properties of organic molecules and polymers due to possible applications in electrooptic and all-optical signal processing.[1] The lowest order nonlinear optical tensor, β, is well understood in a structure–property sense, primarily due to a simple two-level model[2,3] which seems to explain the behavior of all molecules with large β. More and more sophisticated chemical interpretations of the two-level model are leading to both a better understanding and more improvements in β.[4] It is likely that broad-band gigahertz range electrooptic modulators will be commercially available in less than 5 years, based on such materials.

All-optic signal processing, the kind that would power an optical computer (possibly up to 10^6 times faster than present electronic computers), is based on the four-wave mixing tensor γ. Such an application is demanding since it requires both a large γ and a small loss ($\mathrm{Im}[\alpha]$) in the frequency region of operation. While some organic materials minimally meet these restrictions,[5,6] no recent improvements have been reported. Indeed, it has been claimed that further improvements in the ratio $\mathrm{Re}[\gamma]/\mathrm{Im}[\alpha]$ are not readily obtainable.[7]

The search for better γ materials has been severely hampered by the inability of chemists to define the critical structure–property factors that lead to large γ, let alone the consideration of $\mathrm{Re}[\gamma]/\mathrm{Im}[\alpha]$. Due to the contribution of two-photon resonances, in addition to one-photon states, a simple two-level model is not applicable for γ. A complete three-level description involves nine terms that are interrelated through a number of quantities that cannot be easily measured or intuitively grasped. There has been recent considerable success at accurate quantitative calculation of γ,[8,9] though accurate calculations of individual systems have been less helpful with regard to a broader structure property understanding. There has also been considerable success at empirical modification of a given structural motif such as the benzothiazole,[10] though it is not clear whether γ arises from the same mechanism (vide infra) for the variants of the structural motifs. Still, there is value in such calculational and empirical approaches, since some of what is learned is transferable to other systems regardless of the mechanism behind the nonlinear optical process.

We have recently made considerable progress toward a mechanistically oriented structure/property model for the molecular third order optical nonlinearity, γ.[11] The basis for this model is a restricted perturbation series three-level model, the basis of which bears some conceptual resemblance to the very successful two-level model for β. The three-level model we've proposed[11] presumes three significant contributing terms for γ:

$$\gamma \approx \gamma_c + \gamma_n + \gamma_{tp} \qquad (1)$$

where $\gamma_c = -(\mu_{01})^4 D_{11}$, $\gamma_n = +(\mu_{01})^2(\Delta\mu_{01})^2 D_{111}$, $\gamma_{tp} = +(\mu_{01})^2(\mu_{12})^2 D_{121}$, μ_{rs} is a transition moment, $\int(\Psi_r \mathbf{e}\cdot\hat{\mathbf{r}}\Psi_s)\,d\tau$, $\Delta\mu_{01}$ is the change in dipole moment, $(\mu_{11} - \mu_{00})$, and D_{lm} and D_{lmn} are dispersion factors, which are defined here for the QEO process:[11,12]

$$D_{1m1}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hat{\mathbf{I}}_{1,2,3}\{[(\Omega_{1g} - \omega_\sigma)(\Omega_{mg} - \omega_1 - \omega_2) \times (\Omega_{1g} - \omega_1)]^{-1} + [(\Omega^*_{1g} + \omega_3)(\Omega_{mg} - \omega_1 - \omega_2)(\Omega_{1g} - \omega_1)]^{-1} + [(\Omega^*_{1g} + \omega_1)(\Omega^*_{mg} + \omega_1 + \omega_2)(\Omega_{1g} - \omega_3)]^{-1} + [(\Omega^*_{1g} + \omega_1)(\Omega^*_{mg} + \omega_1 + \omega_2)(\Omega^*_{1g} + \omega_\sigma)]^{-1}\}$$

---

(1) Marder, S. R.; Sohn, J. E.; Stucky, G. D.; Materials for Nonlinear Optics: Chemical Perspectives; *ACS Symposium Series No. 455,* (American Chemical Society, Washinton DC 1991.)

(2) Oudar, J. L. *J. Chem. Phys.* 1977, *67,* 447.

(3) Lalama, S. J.; Garito, A. F. *Phys. Rev. A.* 1979, *20,* 1179.

(4) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* 1991, *252,* 103.

(5) Kuzyk, M. G.; Paek, U. C.; Dirk, C. W. *Appl. Phys. Lett.* 1991, *59,* 902.

(6) Kuzyk, M. G.; Andrews, M. P.; Paek, U. C.; Dirk, C. W. *SPIE Proc.* **1991,** *1560,* 44.

(7) Greene, B. I.; Orenstein, J.; Schmitt-Rink, S. *Science* **1990,** *247,* 679.

(8) Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F. *Phys. Rev. B.* 1988, *38,* 1573.

(9) Soos, Z. G.; Ramasesha, S. *J. Chem. Phys.* **1989,** *90,* 1067.

(10) Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1990,** *2,* 660.

(11) Dirk, C. W.; Cheng, L.-T.; Kuzyk, M. G. *Int. J. Quantum Chem.* **1992,** *43,* 27.

(12) Kuzyk, M. G.; Dirk, C. W. *Phys. Rev. A.* **1990,** *41,* 5098.

0897-4756/93/2805-0733$04.00/0

$$D_{11}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hat{\mathbf{I}}_{1,2,3}\{[(\Omega_{1g} - \omega_\sigma)(\Omega_{1g} - \omega_3) \times (\Omega_{1g} - \omega_1)]^{-1} + [(\Omega_{1g} - \omega_3)(\Omega^*_{1g} + \omega_2)(\Omega_{1g} - \omega_1)]^{-1} + [(\Omega^*_{1g} + \omega_\sigma)(\Omega^*_{1g} + \omega_3)(\Omega^*_{1g} + \omega_1)]^{-1} + [(\Omega^*_{1g} + \omega_3)(\Omega_{1g} - \omega_2)(\Omega^*_{1g} + \omega_1)]^{-1}\}$$

where $\hat{\mathbf{I}}_{1,2,3}$ is an operator that permutes the indexes 1, 2, 3 and Ω_{1g} is defined as the complex absorption frequency $(\omega_{01} + i\Gamma_{01})$, with a complex conjugate Ω^*_{1g}.

We have concluded that eq 1 can be optimized on any of the three major terms.

Optimization of γ_{tp}

$$\gamma \approx \gamma_c + \gamma_{tp} \tag{2}$$

occurs for centrosymmetric molecules dominated by a two-photon contribution and can give large positive susceptibilities. In this case, γ_c is negative while γ_{tp} is positive. Cancellation occurs, but γ_{tp} dominates, leading to large positive susceptibilities. It appears the π bond-localized oligoenes and ene-ynes are optimized in this manner. This has been verified by recent calculation and "essential states" analysis of oligoenes.[13]

Centrosymmetric non-two-photon-dominated systems are based on a susceptibility dominated by γ_c:

$$\gamma \approx \gamma_c \tag{3}$$

and have large negative third-order susceptibilities. It should be emphasized that γ_{tp} never disappears but apparently declines sufficiently to permit γ_c to be dominant. Presently, it appears the π-bond delocalized free-electron polymethine systems fall into this class with the squaryliums being an especially good example. Pierce has recently verified this approach by calculation of a series of polymethines, and verifies the implication of eq 3 regarding the length dependence of γ.[14] The reasons behind the circumstance of $|\gamma_c| > |\gamma_{tp}|$ have not yet been elucidated.

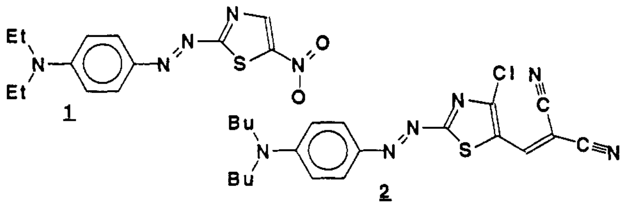
Molecules optimized on γ_n

$$\gamma \approx \gamma_c + \gamma_n \tag{4}$$

are also optimized through β, since the two-level expression for β is embedded in γ_n. The term γ_{tp} has been dropped because as the molecule becomes more asymmetric, the states which supported a large μ_{12} undergo symmetry transformations so that they are no longer purely symmetric or antisymmetric. In particular, the two-photon state (here defined as 2) becomes more asymmetric as the molecule becomes more asymmetric. In this instance, the dipole operator is asymmetric, and state 1 is asymmetric, with the consequence that the transition moment μ_{12} becomes smaller. Thus μ_{12}, and consequently γ_{tp}, decline in magnitude. As discussed above for systems dominanted by γ_c, the term γ_{tp} will likely never disappear and potentially will represent an occasional necessary quantitative correction. However, it may not affect the overall trend in a qualitative structure–property sense, especially for molecules with large γ_n. In the limit where γ_{tp} is ignored, note again that γ_c and γ_n cancel. However, large $\Delta\mu$'s (i.e., large β) will lead to a situation where γ_n dominates with consequent large positive susceptibilities. Thus, larger β's should lead to larger molecular γ's.[15]

In addition, narrowing the electronic absorption could possibly result in an enhancement for molecules with large γ based on γ_n. This occurs because the ratio of the dispersion contributions for γ_n (D_{111}) and γ_c (D_{11}), D_{111}/D_{11}, increases with decreasing natural peak width, Γ. This simultaneously lowers $\mathrm{Im}[\alpha]$, so that considerable increases in the electronic $\mathrm{Re}[\gamma]/\mathrm{Im}[\alpha]$ may be possible. This absorption narrowing enhancement mechanism is strictly true when damping is due solely to the natural linewidth. Inhomogeneous broadening will complicate the issue greatly with regard to this enhancement mechanism so that there may be optimum inhomogeneous peak widths (dependent on the microscopic molecular inverse radiative lifetime) to maximize the ratio $\mathrm{Re}[\gamma]/\mathrm{Im}[\alpha]$.

We report here a quadratic electrooptic study on two dyes, 1 and 2, with especially large β, and demonstrate by way of linear optical results, solvatochromism, and use of previous nonlinear optical measurements of β that the quadratic electrooptic susceptibility, γ_{QEO}, can be rationalized in terms of eq 1. We further examine the effect of the inhomogeneous peak widths with regard to a possible peak-narrowing enhancement mechanism.



1

2

Experimental Section

Molecules 1 and 2 were prepared as previously described.[16] Quadratic electrooptic measurements were performed on dye-doped PMMA (poly(methyl methacrylate)–ITO (indium tin oxide) glass sandwiches as previously described.[17,18] Compound 1 was measured with a HeNe laser probe at 632.8nm, while compound 2 was measured with a Kr laser probe at 799nm.[19]

Solvatochromism results were calculated as previously described[20] using the solvatrochromism equation

$$\bar{\nu}_g - \bar{\nu} = A\left[\frac{n^2-1}{2n^2+1}\right] + B\left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right] \tag{5}$$

$$B = (1/hc\epsilon_0 a^3)\mu_g(\mu_g - \mu_e) \tag{6}$$

with one modification: The molecular volumes a^3 were approximated as $\{\ell + 1.9\}^3$ where ℓ is the internuclear length in angstroms. This is different than the parametrization ($\{k\ell\}^3$; $k = 0.7$) described by Paley et al.[20] but seems more intuitive in light of consideration that the van der Waals extension (1.9 Å chosen here based upon a fit to the data of Paley et al.) to a molecular dimension is mostly constant and does not depend on the molecular length. Aside from this conceptual rationalization, it is trivially relevant to note that if a component ($k^3\ell^3$) of a cubic polynomial is used for a parametrization of a molecular volume, then a full cubic polynomial ($\{\ell + a\}^3 = \{\ell^3 + 3a\ell^2 + 3a^2\ell + a^3\}$) will normally provide a better parametrization.

The internuclear lengths, ℓ, used in this study were as follows: 1 (11.7 Å), 2 (14.4 Å); they are based on structures optimized through the *mmx* feature of PCMODEL. The lengths were

---

[13] Dixit, S. N.; Guo, D.; Mazumdar, S. *Phys. Rev. B.* **1991**, *43*, 6781.

[14] Pierce, B. M. *SPIE Proc.* **1991**, *1560*, 148.

[15] Garito, A. F.; Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O. *SPIE Proc.* **1988**, *971*, 2.

[16] Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater.* **1990**, *2*, 700; **1991**, *3*, 207.

[17] Kuzyk, M. G.; Dirk, C. W. *Appl. Phys. Lett.* **1989**, *54*, 1628.

[18] Kuzyk, M. G.; Dirk, C. W.; Sohn, J. E. *J. Opt. Soc. Am. B* **1990**, *7*, 842.

[19] Dirk, C. W.; Caballerro, N.; Tan, A.; Kuzyk, M. G.; Cheng, L.-T.; Katz, H.; Schilling, M. a preliminary report in *SPIE Proc.*, in press.

[20] Paley, M. S.; Harris, J. M.; Looser, H.; Baumert, J. C.; Bjorklund, G. C.; Twieg, R. J. *J. Org. Chem.* **1989**, *54*, 3774.

Table I. Linear Optical Results. Note That the PMMA Results Were Not Used in the Solvatochromism Fit

	λ_{max},[a] nm	
	1	2
PMMA	581	640
acetone	582	640
benzene	560	620
acetonitrile	588	644
methylcyclohexane	522	594
pentane	510	582
DMSO	610	658

	peak half-widths, cm^{-1}	
	1	2
Γ(PMMA)[b,c]	1720	1563
Γ_G(PMMA)[b,d]	1951	1795

[a] ±0.5 nm. [b] ±12 cm^{-1}. [c] The peak half-width at half-height. [d] The peak half-width at height 1/*e*.

Table II. Solvatochromism Results Obtained by Least-Squares Fit of the Linear Spectroscopic Data in Table I to Eq 5

	1	2
A, cm^{-1}	−26930	−15690
B, cm^{-1}	−3483	−2167
$\bar{\nu}_g$, cm^{-1}	24360	19910
$\Delta\mu$(solvato),[a] D	16	15
$\Delta\mu$(EFISH),[b] D	16	16

[a] ±≈10–15%. [b] Reference 16; ±≈10–15%.

Table III. Nonlinear Optical Results

	1	2
$\lvert\mathrm{Re}[s_{1133}]\rvert$, M^2/V^2	8.5×10^{-22}	1.9×10^{-21}
$\lvert\mathrm{Re}[\gamma_{QEO}]\rvert$,[a] cm^7/esu^2	14×10^{-34}	36×10^{-34}
$\mathrm{Re}[\gamma_c]$,[b] cm^7/esu^2	-8×10^{-34}	-8×10^{-34}
$\mathrm{Re}[(\gamma_n)_s]$ (solvato $\Delta\mu$),[c] cm^7/esu^2	$+12 \times 10^{-34}$	$+53 \times 10^{-34}$
$\mathrm{Re}[(\gamma_n)_{EFISH}]$ (EFISH $\Delta\mu$),[d] cm^7/esu^2	$+12 \times 10^{-34}$	$+62 \times 10^{-34}$
$\mathrm{Re}[\gamma_c] + \mathrm{Re}[(\gamma_n)_s]$, cm^7/esu^2	$+4 \times 10^{-34}$	$+45 \times 10^{-34}$
$\mathrm{Re}[\gamma_c] + \mathrm{Re}[(\gamma_n)_{EFISH}]$, cm^7/esu^2	$+4 \times 10^{-34}$	$+54 \times 10^{-34}$

[a] ±10–15%. [b] ±≈10–20%. [c] ±≈30%. [d] ±≈20–35%.

defined to include only the conjugated atoms of the molecular framework. Ground-state dipole moments, μ_g, used to calculate $\Delta\mu$ ($\Delta\mu = \mu_e - \mu_g$) from the solvatochromism B, have been previously determined.[16]

In eqs 5 and 6, n and ϵ are the solvent refractive index and dielectric constants, respectively, $\bar{\nu}_g$ is the gas-phase excitation energy in cm^{-1}, $\bar{\nu}$ is the solvent excitation energy in cm^{-1}, h is Plancks constant, c is the speed of light, ϵ_o is the permittivity of free space, and μ_e is the excited state dipole moment. The constants $\bar{\nu}_g$, A, and B are determined by least-squares fits of eq 5 to the solution data in Table I.

Transition moments, μ_{01}, of **1** and **2** have been previously determined in methylene chloride.[16] Local field corrections of the transition moments from the CH_2Cl_2 environment to the PMMA environment were not performed. Even if the standard correction of $(n^2 + 2)/3$ is applied, it will result in a change of less than 10% on going from methylene chloride to PMMA. Making the correction may add approximately 15–20% to the values of γ_c and γ_n reported in Table III.

The quadratic electrooptic coefficients, s_{1133}, in units of m^2/V^2 were converted[18] to the molecular γ_{QEO} (units of cm^7 esu^{-2}) by multiplying by $9 \times 10^8 n^4/12\pi$ cm^4 V^2 esu^{-2}, where n is the refractive index (approximately 1.5), and then dividing by the molar concentration, M_d, of the dye in the PMMA polymer thin film. Here, the molar concentration was approximated as $M_d = 10N_A \times \mathrm{wt}\ \% \times \rho/M_w$, where N_A is Avogadro's number, wt % is the percentage weight of the dye in the PMMA, ρ is the material density (approximated as the density of pure PMMA, $\rho = 1.188$ g/cm^3, for low dye concentrations), and M_w is the molecular weight of the dye. The concentrations for the QEO measurements of the two samples reported here were 3.1% (**1**) and 3.85% (**2**).

The dispersion contributions to $\mathrm{Re}[\gamma_c]$ and $\mathrm{Re}[\gamma_n]$, $\mathrm{Re}[D_{11}]$ and $\mathrm{Re}[D_{111}]$, respectively, are calculated from eq 43c of Orr and Ward's[21] perturbation expressions, where the summation is carried out over the l, m, n indexes of Orr–Ward such that $l = m = n = 1$, and correcting[22] for the isotropic average for the QEO process by multiplying by 1/15. Note that the constant K in the Orr–Ward publication,[21] which defines the process, was chosen to be equal to 3, implying the process $\gamma(-\omega;\omega,0,0)$. The quadratic electrooptic measurement used here is formally the process $\gamma(-\{\omega+2\Omega\};\omega,\Omega,\Omega)$, however, the modulation frequency is extremely small ($\Omega = 4000$ Hz) relative to the probe frequency (4.7×10^{14} Hz), and has been approximated as essentially zero. This does result in a factor of four difference in K, though we consider the approximation justified and demanded given the great differences in frequency, as well as taking into consideration the laser linewidth and natural linewidth for the molecular electronic process. Note that the peak half-width at half-height in PMMA, Γ (Table I), was substituted into eq 43c of Orr and Ward to ad hoc correct for damping.[21] Comparison of QEO results to other third-order nonlinear optical measurement processes has been discussed earlier.[11,18,22]

Results

Linear optical results are displayed in Table I. Solvatochromism results are displayed in Table II. Nonlinear optical results are displayed in Table III.

Solvatochromism versus EFISH $\Delta\mu$. The solvatochromism derived parameter B is used to calculate $\Delta\mu$ ($\Delta\mu = 1.5808 \times 10^{-5}\, Ba^3/\mu_g$, where $\Delta\mu$ is in units of debye, B is in units of cm^{-1}, a^3 is in cubic angstroms and parametrized as defined earlier, and μ_g is the ground-state dipole moment in debye). These results are consistent with previously determined EFISH two-level derived $\Delta\mu$s.[16] The rationale for checking the EFISH-derived $\Delta\mu$s with solvatochromism arises from the consideration that a two-level analysis of β *is* an approximation. Calculation of $\Delta\mu$ directly from β using the two-level approximation involves using quantitites like the transition moment (μ_{01}), λ_{max}, and peak width at half-height (2Γ), each of which has an associated experimental error. Additionally, damping corrections are ad hoc at best, considering the Orr and Ward *definition* of the use of Γ. Also, in the case of an asymmetric electronic absorption or an EFISH measurement necessarily too close to resonance, an unambiguous determination of a damping correction may not be possible. Furthermore, there is the consideration of the all electronic third-order contribution to the EFISH measurement (usually ignored or guessed), as well as local field corrections. This series of approximations and sources of error can make tenuous the determination of $\Delta\mu$ from the EFISH β. Thus, in many cases, it may be more desirable to calculate the $\Delta\mu$ for γ_n from properly length parameterized (vide supra) solvatochromism data than from EFISH data. For this investigation, the good fit between EFISH and solvatochromism $\Delta\mu$s was facilitated by the modification in the parameterization of the molecular volume, the modification to a Gaussian calculation of the transition moment,[16] and the recognition of the difference in definitions[23] for the solvatochromism and EFISH β's. In calculating the intrinsic β_I (a completely frequency-independent parameter) from which we calculate $\Delta\mu$, we have taken liberty in making the necessary factor of two correction in the EFISH results, $\beta_I \equiv \beta/\{(2KF(\Omega_{01},\omega)\}$, where

---

(21) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.
(22) Dirk, C. W.; Kuzyk, M. G. *Chem. Mater.* **1990**, *2*, 4.
(23) Willets, A.; Rice, J. E.; Burland, D. M. *J. Chem. Phys.* **1992**, *97*, 7590–7599.

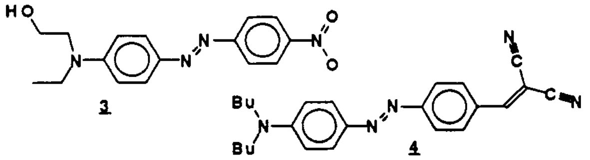
K is the permutation symmetry factor defined by Orr and Ward, and $F(\Omega_{01},\omega)$ is the two-level dispersion function involving the laser fundamental at frequency ω and the complex absorption frequency Ω_{01}.

QEO Results. Note that the quadratic electrooptic method we've used readily supplies the absolute value of the real part of the quadratic electrooptic coefficient, s_{1133}, at least when the imaginary contribution is small. When close to resonance, both QEO and electroabsorption need to be performed to correctly determine the real part of s_{1133}.[24] For these measurements, the HeNe (λ = 632 nm) QEO probe of compound 1 was in the tail of the absorption and so experienced some loss. Instead of performing an electroabsorption measurement to correct γ_{QEO}, we approximately corrected the appropriate γ_c and γ_n by use of the adhoc damping parameter, Γ, introduced by Orr and Ward.

The issue of orientational versus electronic contributions is critical for comparison of a measured γ_{QEO} to γ_c and γ_n, which, the latter, by the nature of their source, are purely electronic. Our earlier QEO and microscopic elastic response work suggested that the orientational contribution was no larger than 25–40%.[18] More recently, Poga et al. have demonstrated by the angular dependence of tensor ratios of electroabsorption measurements of a squarylium dye that the orientational contribution is no larger than approximately 12% in PMMA, at least for the centrosymmetric dye that was measured.[25] Noncentrosymmetric dyes, such as 1 and 2 experience two *cancelling* orientational contributions, one involving molecular dipole reorientation convolved with an electrooptic process, and the other involving an α-mediated induced dipole which couples with the field to reorient the birefringent molecule.[18] This suggests that the total orientational contribution to the dyes measured here are no larger than 12% and are likely smaller. Thus the measured γ_{QEO} reported in Table III likely represent at least 90% electronic contribution. Whether, the actual purely electronic value is slightly larger or smaller than the magnitudes of γ_{QEO} in Table III depends on which orientational contribution dominates.

In Table III, one can compare the measured γ_{QEO} to the sum $\gamma_c + \gamma_n$, using either the γ_n derived from either the EFISH $\Delta\mu$ or the solvatochromism $\Delta\mu$. The EFISH and solvatochromism γ_n do not deviate significantly from one another, so that the sums are similar. More importantly, the comparison of γ_{QEO} with either sum suggests a relatively close qualitative fit, within the limits of the experimental errors and unquantified artifacts such as orientational contributions and residual two-photon contributions. It is perhaps relevant to note that because γ_c and γ_n are opposite in sign and close in magnitude, the error for the sum $\gamma_c + \gamma_n$ can be quite large. Thus experimental uncertainties alone could nearly account for the deviation between the observed γ_{QEO} and the sum $\gamma_c + \gamma_n$. Besides experimental uncertainty as a source of deviation, it is possible that a small negative orientational predominance could account for the differences between γ_{QEO} and the sum $\gamma_c + \gamma_n$. It is also possible that the two-photon contribution is not negligible, though due to the positive sign for γ_{tp}, this argument could perhaps be most reasonable only for 1.

The decline of the γ_{tp} term has been predicted[11] based on the argument that the state symmetries are no longer purely symmetric or antisymmetric in a concentrosymmetric dye, leading to a decline in the magnitude of μ_{12}, relative to a centrosymmetric system. These results are consistent with that prediction. Additionally, these results are consistent with an earlier[26] analysis we performed on two other dyes:


3

4

3: $|\mathrm{Re}[\gamma_{QEO}]| = 7.1 \times 10^{-34}$ cm^7/esu^2, $\{\mathrm{Re}[\gamma_c] + \mathrm{Re}[\gamma_n]\} = +7.1 \times 10^{-34}$ cm^7/esu^2. 4: $|\mathrm{Re}[\gamma_{QEO}]| = 29 \times 10^{-34}$ cm^7/esu^2, $\{\mathrm{Re}[\gamma_c] + \mathrm{Re}[\gamma_n]| = +38 \times 10^{-34}$ cm^7/esu^2) with large β.

It may be significant to note that 4 was measured by a HeNe laser probe 3210 cm^{-1} off resonance, while 2 was measured by krypton laser probe 3110 cm^{-1} off resonance. Thus, one would expect that the respective values of γ_c are similar (4: $\mathrm{Re}[\gamma_c] = -6.8 \times 10^{-34}$ cm^7/esu^2), if the transition moments are similar (differ by only 4%[16]), and they are. The intrinsic β_I[16] (proportional to $\Delta\mu\{\mu_{01}\}^2$) are similar (differ by less than 3%[16]) for both 2 and 4, but the EFISH-derived γ_n (proportional to β_I) are quite different (4: $\mathrm{Re}[\gamma_n] = +45 \times 10^{-34}$ cm^7/esu^2), as are the γ_{QEO}. The main difference, is the great disparity in peak widths between the two dyes (Γ, the peak half-width at half-height for 4 in PMMA is 1888 cm^{-1}).[17] We are possibly seeing the effect of narrowing peak width; resulting in an increasing ratio of D_{111}/D_{11} with decerasing Γ, as described earlier. We must cautiously consider the problems that can render this a spurious observation and conclusion. The theoretical and supposed experimental *enhancements* in $\mathrm{Re}[\gamma]$ due to the difference in peak widths are probably within the experimental uncertainty. In addition, the difference between the theoretical and experimental enhancement in $\mathrm{Re}[\gamma]$ is possibly equivalent to the magnitudes of the orientational contributions, though the net orientational contributions for each molecule could be expected to be systematic, of the same magnitude, and in the same direction with regard to sign. There is also the uncertainty regarding the difference in relative contribution of γ_{tp} to either molecule, which depends on the relative energy difference and overlap between the one- and two-photon states, quantities that are unknown here. The main complication is the consideration of the effect of inhomogeneous broadening. Given these mitigating factors, we cannot positively assert that the narrowing mechanism is the source of the increase in γ_{QEO}. The present observation is intriguing, and will require comparison of dyes with even greater differences in peak width, as well as a more complete theoretical and experimental description of the two-photon states within these molecules.

---

(24) Kuzyk, M. G.; Poga, C. Quadratic Electrooptics of Guest-Host Polymers. In *Molecular Optoelectronics*: Materials, *Physics and Devices*; Zyss, J., Ed.; Academic Press: New York, in press.

(25) Poga, C.; Kuzyk, M. G.; Dirk, C. W. Quadratic electro-optic studies of molecular reorientational and electronic mechanisms in polymers. *SPIE Proc.*, in press.

(26) Dirk, C. W.; Kuzyk, M. G. Materials for Nonlinear Optics: Chemical Perspectives. *ACS Symposium Series No. 455*; Marder, S. R., Sohn, J. E.; Stucky, G. D., Eds.; American Chemical Society: Washington DC, 1991; pp 687–703.

Conclusions

We have verified the mechanistic prediction of large γ in molecules with large β. More importantly, we have again demonstrated that the γ_n optimization mode of eq 1 is valid, since our results are consistent with a decline in magnitude of γ_{tp} in the presence of a large magnitude for γ_n. These results are not meant to suggest that the two-photon contribution vanishes in molecules dominated by γ_n, but that the relative importance of such a term dimishes in defining the overall γ. As suggested above, part of the deviation from the comparison of Re[γ_{QEO}] to the sum Re[γ_c] + Re[γ_n] may arise from the contribution of a small but not insignificant two-photon contribution.

Our results also possibly show for the first time the predicted enhancement of γ_n-dominated γ by narrowing of peak width, though a variety of uncertainties make this mechanistic assignment fairly tenous at this time. If correct, the implications could be important with regard to possible future increases in electronic Re[γ]/Im[α], and possibly for the consequent feasibility of third order nonlinear optical devices.

Acknowledgment. This work was supported in part by a UTEP University Research Initiative Grant, the NIH MARC Program (Grant GM 08048), the Texas Advanced Research Program (Grant 003661-012), and the Petroleum Research Fund.