

Squarylium Dyes: Structural Factors Pertaining to the Negative Third-Order Nonlinear Optical Response

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Abstract: Off-resonant electric field induced second harmonic generation (EFISH) and resonant third harmonic generation (THG) measurements of two squarylium dyes are reported. The magnitude of γ is large for both processes. The EFISH measurement clearly shows that the off-resonant third-order polarizability is negative, a consequence of the dominance of a non-two-photon mechanism. This unusual result is in agreement with our earlier reports on two other squarylium dyes. Resonant THG measurements strongly suggest that the two-photon contribution, while smaller than the one-photon contribution, is not negligible and cannot be entirely ignored when defining the overall third-order optical susceptibility. Consequently, the squaryliums are best qualitatively described by a three-level model that truncates to two dominant perturbation terms. Also reported is the isomeric distribution of squaryliums. Proton NMR results are interpreted by way of molecular mechanics to show that the squaryliums can readily exist as a mixture of isomers. The possible effects on nonlinear optical (NLO) measurements via an orientational contribution to the EFISH γ are discussed. An X-ray structure for the squarylium dye TSQ is presented and interpreted. The X-ray structure clearly suggests that the squarylium dyes are extensively bond delocalized with relatively little bond length alternation.

Introduction

Negative third-order polarizabilities (γ for the molecular property and $\chi^{(3)}$ for the bulk) are relatively uncommon. Such all-optical nonlinearities are self-defocusing, rather than self-focusing, eliminating the concern of the nonlinear optical auto-optical annihilation of a potential all-optical device. Negative γ s have recently also been instrumental in helping define the family of microscopic electronic mechanisms which can contribute to γ .^{1,2} Additionally, the few negative γ s that have been measured are relatively large in absolute magnitude compared to molecules with positive γ . These large magnitudes have been the consequence of relatively small contributions from two-photon states and have led to the hope of increasing the magnitude of γ considerably beyond those reported in the past. We report here some new measurements on squarylium dyes, as well as verify the presence of a non-negligible two-photon state. We report linear-optical and proton NMR spectral details suggesting that the dyes ISQ and BSQ exist as a mixture of isomers and provide some interpretation of the impact of this on the optical properties.

Structural concerns such as relative bond length alternation³ are becoming important in optimizing structures for nonlinear

optics. We have determined the crystal structure of the squarylium dye TSQ and show, by way of analysis of its crystal structure and calculated structures, that this dye shows significant bond delocalization, as evidenced by its reduced bond length alternation.

Theory

Defining the mechanisms which contribute to the electronic γ has been a nontrivial undertaking. Early work in the field identified two-photon contributions as being an important element.⁴ This has required the implementation of models which require at least three states, one of which must be a two-photon state. In addition, in the absence of relatively sophisticated nonlinear spectroscopy or calculations, the two-photon state remains a mysterious unknown contribution for the materials chemists who have been undertaking the optimization of molecules for all-optical applications. The consequent frustratingly slow development of new molecules has prompted a pessimistic prediction for all-optical organic devices.⁵

With the experimental problems and theoretical restrictions in mind, we¹ and others^{6,7} attempted to define a limited model which should provide the necessary qualitative and semiquantitative behaviors. Such a model would be useful in providing materials chemists with the structure–property guidelines to systematically enhance γ . The development of this model involved starting with the relatively complex one-dimensional

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nine-term three-level model⁸ and choosing an approximation path that reduced it to a simpler and more intuitive one-dimensional three-term three-level model

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

where $\gamma_c = -K\mu_{01}^4 D_{11}$, $\gamma_n = K\mu_{01}^2 (\Delta\mu_{01})^2 D_{111}$, $\gamma_{tp} = K\mu_{01}^2 \mu_{12}^2 D_{121}$, μ_{01} is the transition moment to the significant one-photon state, μ_{12} is the transition moment between the one-photon and significant two-photon state, $\Delta\mu_{01}$ is defined as $\mu_{11} - \mu_{00}$, D_{lm} and D_{lmn} are dispersion terms which have been defined earlier,⁸ and K is a constant defined by the optical process. The constant K is always positive, as are D_{lm} and D_{lmn} when all resonant interactions contributing to the process $\gamma(\omega_4; \omega_1, \omega_2, \omega_3)$ are off resonance and to low energy of the electronic excitation manifold. In the notation used by Garito,⁶ γ_c is a type I term, γ_{tp} is a type II term, and γ_n is a type III term. In Pierce's notation,⁷ γ_c is identified as "G", γ_{tp} is identified as "X", and γ_n is identified as "D".

Under the circumstances defined above, there are three optimization approaches to eq 1. The simplest optimization is to consider centrosymmetry, requiring that γ_n . This reduces the model to

$$\gamma \approx \gamma_c + \gamma_{tp} \quad (2)$$

Note here that γ_c and γ_{tp} are opposite in sign but contain a cross term, μ_{01} , that makes them compete. Thus, if the magnitude of μ_{01} is greater than μ_{12} , γ is negative, while if it is smaller, γ is positive. This will always be true under the resonant conditions defined above as long as the two-photon state is higher in energy than the one-photon state (i.e., $D_{111} \geq D_{121}$). In general, as a presumption, the magnitude of μ_{12} has commonly been larger than μ_{01} , which may have been influenced by the one-photon and two-photon energy difference, E_{12} , which is commonly smaller than the ground and one-photon energy difference, E_{01} . This latter realization about E_{01} and E_{12} has recently¹⁰ been used to reveal excited state optical nonlinearities of large magnitude. The condition of $|\mu_{12}| > |\mu_{01}|$ typically is more significant than $D_{111} \geq D_{121}$ (or $D_{11} \geq D_{121}$) so that most third-order optical nonlinearities are dominated by the two-photon state and are positive. Normally, the condition $|\mu_{12}| > |\mu_{01}|$ can be so dominant that even great differences in energy (increasing the ratio $D_{11} \geq D_{121}$) between the one- and two-photon states cannot allow for negative γ s. This, in combination with an experimental habit of two-photon *resonant* measurements means that most molecules will only reveal themselves as positive optical nonlinearities, γ . Thus, finding negative γ required us to specifically look for it. The important main search criteria were centrosymmetry, a molecule with its oscillator strength concentrated in one significant μ_{01} , as well as perhaps a measurement process that did not bias two-photon resonances over one-photon or three-photon resonances. The earlier reported work of Stevenson et al. showed that free-electron structures could display negative γ s, even in the absence of strict centrosymmetry, though some structures also displayed positive γ s.¹¹ At the time, in the absence of Marder's bond length alternation studies, which work toward rationalizing such

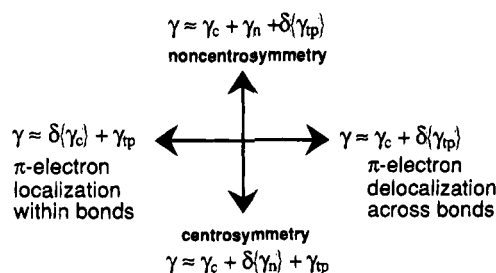


Figure 1. Optimization neumonic for the third-order nonlinear optical response. Note that $\delta\{\}$ signifies a less important contributing term.

behavior, it was necessary for us to apply strict centrosymmetry criteria to optimize for a negative nonlinearity.

The choice¹² of the free-electron-delocalized squaryliums with their narrow intense isolated low-energy transitions and the creation¹³ of a specialized quadratic electro-optic measurement follow from the previous arguments. The QEO process involves an optical frequency probe ω modulated by a much lower frequency Ω . The contributions from one- ($\omega_0 - \omega$) and three-photon resonances ($\omega_0 - \omega - 2\Omega$) are large, being close to the significant transition frequency (ω_0), while two-photon resonance ($\omega_0 - 2\Omega$) contributions are always minimized. This permitted the comparison of the measured electro-optic γ_{QEO} to that obtained by calculating γ_c from linear spectroscopic results. As it may be, the squarylium dye we first investigated possessed a significant negative nonlinearity so that biasing the measurement with the QEO process was unnecessary.

Given the above discussion, it is also relevant to examine the theoretical consequence of noncentrosymmetry. Under this restriction, one can argue that molecules with large dipole changes could lead to a situation where the magnitude of γ_n is much greater than the magnitude of γ_c . Since the moments contribution to the two-level model for β is embedded in γ_n , it is clear that optimization of γ_n can proceed by way of optimization of β , though with some possible deviation from maximum due to the extra $\Delta\mu$ factor. Further, the shift in state symmetries upon moving from a centrosymmetric to an extreme noncentrosymmetric system should lead to a decline in the magnitude of γ_{tp} . We have recently shown that the QEO γ for molecules with large hyperpolarizabilities, β , can be rationalized in just this manner.¹⁴ A similar conclusion has been reached by Garito et al.¹⁵ Thus, γ reduces to

$$\gamma \approx \gamma_c + \gamma_n \quad (3)$$

The above arguments define an optimization mnemonic (Figure 1) which involves either shifting symmetry or electron localization. In this context, shifting symmetry involves modifying the structural atomic positions, while shifting electron localization involves adjusting the relative donor and accepting capabilities of substituents. It is important to recognize that, in the discussion of symmetry, we strictly are referring to nuclear coordinate symmetry, though, in principle, a molecule which is nuclear coordinate acentric could be electronically nearly symmetric. Marder's recent results² thus can be interpreted and made to suggest that negative γ nonlinearities could be obtained in a polar molecule by reducing the electronic asymmetry and increasing the electron delocalization (reducing bond length alternation). This is important because it could represent a

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(9) In this regard, states 1 and 2 are relative, and not absolute. In other words, there may be nonessential states between 0 (ground) and 1 or between 1 and 2 which may be unimportant for the four-wave mixing scattering process.

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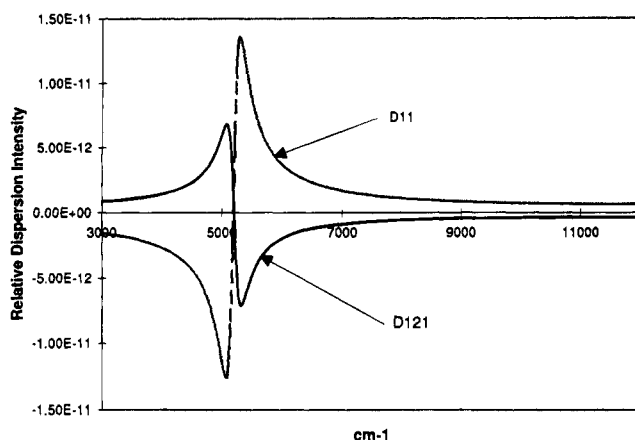
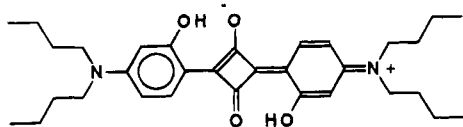


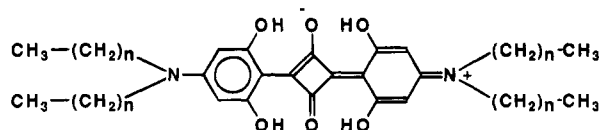
Figure 2. Plot of the calculation of the dispersion terms D_{11} and D_{121} for the THG process as a function of the THG fundamental frequency presuming λ_{\max} of 640 nm for the one-photon state and 333 nm for the two-photon state and approximating the theoretical Lorentzian damping as the experimental peak width $2\Gamma_G$ of 704 cm^{-1} of TSQ. The presumed two-photon energy comes from the work of Garito et al.¹⁶

systematic path to negative γ nonlinearities which do not require nuclear coordinate centrosymmetry. It is important to recognize that Marder's bond length alternation results approach provides the mechanics to generate the details for the smooth transition between two positive γ optimized structures (one corresponding to positive β and the other negative β) and the one negative optimized structure. We had earlier suggested that such a smooth transition must exist, as well as correctly predicted the nature of the maxima (positive γ) and minima (negative γ).

Our past work¹ implied that the two-photon contribution was small for the squaryliums, though we were not able to determine the true magnitude of γ_{tp} . Garito and co-workers have investigated the mechanisms that determine the sign and the magnitude of γ in the squaryliums and have suggested that a two-photon contribution is significant.¹⁶ Consequently we chose to undertake a third harmonic generation measurement of BSQ



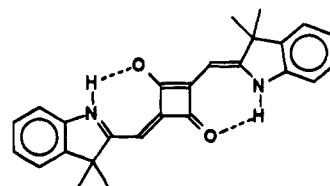
and another dye, TSQ ($n = 3$)



This measurement was chosen to yield a third harmonic embedded in the absorption spectrum of the dye near where a two-photon state might be expected to exist. Under such circumstances, a positive third-order nonlinearity would suggest that γ is being mostly influenced by γ_c , and that the nearest relevant two-photon state was very high in energy relative to the significant singlet ground state. A negative nonlinearity would suggest a significant two-photon contribution. This is obvious if one examines Figure 2, where the one-photon and two-photon dispersion terms, D_{11} and D_{121} , of γ_c and γ_{tp} respectively, are illustrated as a function of THG fundamental frequency. It can be seen that, in the absence of a γ_{tp} (D_{121}) contribution, the off-resonant negative nonlinearity should

become positive as the three-photon resonance passes through the one-photon state excitation energy. The presence of a significant γ_{tp} contribution can lead to a significant negative nonlinearity under the same circumstances. The negative and positive contributions compete, though depending on the relative magnitudes of the transition moments, μ_{01} and μ_{12} , a γ_{tp} contribution is necessary for the observation of a negative γ above the one-photon transition, when a negative γ is observed below the one-photon transition.

Comparisons are also made to ISQ:



Both ISQ and BSQ can exist as sets of cis-trans isomers. We explore this possibility, and show how this isomerization can affect and complicate the interpretation of third-order nonlinear optical polarizations.

Experimental Section

Reagent chemicals and solvents were used as purchased without further purification. Calculations were performed with PCMODEL V4.0 (Serena Software) or HYPERCHEM (Autodesk Software) on an Intel 80486 based machine or using SPARTAN (Wavefunction Software) and SYBYL (Tripos) on a Silicon Graphics Indigo or Indigo-2 workstation. CNDO singly and doubly excited configuration electronic spectral calculations were performed with an adaptation of the QCPE program CNDUV99 (QCMP062) on an Intel 80486 based personal computer.

To make calculations computationally more manageable for the sometimes limited hardware, we eliminated methyl groups (CNDO calculation of ISQ isomers) or shortened longer alkyl chains to methyl groups (AM1 and PM3 calculations of TSQ, BSQ, and HSQ: N -alkyls \rightarrow N -methyls). All AM1 and PM3 calculations were performed by utilizing the default SCF conditions and parameters inherent to MOPAC.

Finite field calculations of γ were performed using AM1 MOPAC 5.0 by utilizing the "POLAR" option following full SCF AM1 single configuration geometry optimization. Calculations of γ were performed using the induced dipole approximation¹⁷ on both the single configuration calculations of this optimized geometry and the configuration interaction calculations based on this geometry. Configuration interaction calculations were performed using the 100 lowest energy configurations derived from all excitations from the seven highest occupied orbitals to the seven lowest unoccupied orbitals (MOPAC keyword "C.I. = 7").

The preparation of the squarylium dye ISQ follows the procedure outlined for indoliniums.¹⁸ BSQ is a known dye whose preparation is outlined in the literature.¹⁹ Dyes such as TSQ and HSQ ($n = 5$) were prepared using the general procedure outlined below:

TSQ. To a 250 mL round bottomed flask containing 150 mL of benzene and 15 mL of n -butanol is added 3.7 g (0.0286 mol) of dibutylamine and 5.10 g (0.0314 mol) of 1,3,5-trihydroxybenzene dihydrate. A Dean-Stark trap, water cooled condenser, and nitrogen bubbler inlet are affixed, and the reaction is refluxed for 48–72 h with azeotropic distillation of water. The solution is cooled briefly, and 1.63 g (0.0143 mol) of 1,2-dihydroxy-1-cyclobutene-3,4-dione is added. Refluxing is resumed and continued for 5–6 days, during which period water is azeotropically removed. The resulting blue solution is reduced in volume, removing the benzene. Butanol is removed by azeotropic

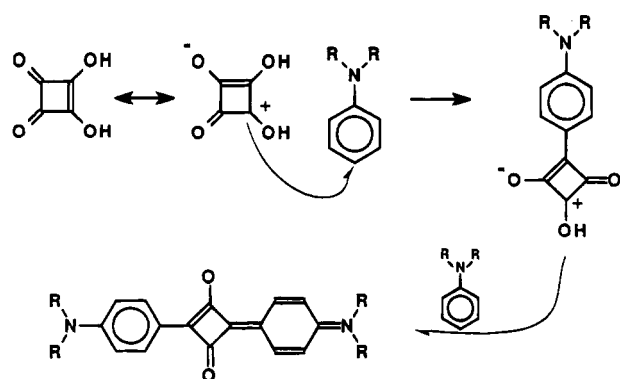
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Scheme 1



distillation with cyclohexane, at which point the final cyclohexane solution of 15–20 mL is allowed to cool to promote crystallization. After the solution is cooled, the crystalline product is filtered and washed with cold 5:95 ethyl ether/hexane, yield 4.33 g (36%). By NMR, the product is typically >99% pure. Further purification of small quantities can be achieved by low-pressure liquid chromatography on silica gel (eluent: ethyl acetate mixtures with hexane).

We also prepared TSQ by another procedure:

TSQ. To a 250 mL round bottomed flask containing 140 mL of benzene and 7 mL of *n*-butanol is added 6.43 g (0.0397 mol) of 1,3,5-trihydroxybenzene dihydrate and 2.26 g (0.0198 mol) of 1,2-dihydroxy-1-cyclobutene-3,4-dione. A Dean–Stark trap, water cooled condenser, and nitrogen bubbler inlet are affixed, and the reaction is refluxed for 48 h with azeotropic distillation of water. The solution was cooled, followed by addition of 5.23 g (0.0397 mol) of dibutylamine. Refluxing and azeotropic distillation is continued for 4–7 days, yielding a dark blue solution. Benzene is removed by distillation followed by removal of *n*-butanol by azeotropic distillation using cyclohexane. The volume is reduced to 20 mL, then cooled to promote crystallization of the product. The product is filtered and washed with hexane or a 5:95 mixture of ethyl ether/hexane, yield 2.2 g (20%).

This second procedure worked well once, but was not generally reproducible to give high yields, and so was not further pursued.

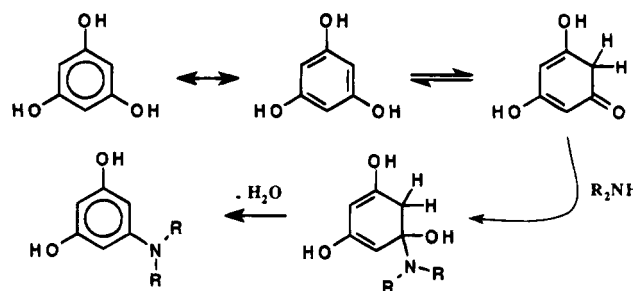
Dyes were verified by elemental analyses,²⁰ NMR and/or UV–visible spectroscopy. A typical proton NMR spectrum of TSQ and relevant proton NMR spectral regions of ISQ are provided in the supplementary material.

It is possible to purify the long alkyl chain anilinium squarylium dyes by low-pressure liquid chromatography on silica gel (eluent: mixtures of ethyl acetate and hexane). Nonforced gravity columns typically lead to some decomposition, possibly due to slow hydrolysis. Because TSQ traveled relatively slowly down the low-pressure column, using the same synthetic procedures outlined above, we lengthened the alkyl chains to six carbons (using dihexylamine) to give the molecule HSQ. HSQ proved relatively easy to obtain pure by chromatography in larger quantities than TSQ, so that quantitative electronic absorption measurements were made on this molecule (*vide infra*). Nonquantitative (unspecified concentration) measurements were performed on TSQ (as well as BSQ and ISQ) to obtain λ_{max} s and peak width data as a function of solvent.

Synthesis

The synthesis of squarylium dyes is relatively straightforward, involving a double electrophilic attack by squaric acid on the electron-rich substrates. Preparation of the TSQ family of dyes, possessing four hydroxys ortho to the squarate, is facilitated by recognition of the tautomerization of phloroglucinol to permit nucleophilic attack by a secondary amine.²¹ The resulting

Scheme 2



aminoresorcinol reacts readily with squaric acid to yield the TSQ family of dyes. HSQ was synthesized by substituting dihexylamine for dibutylamine. These latter dyes were prepared because the longer alkyl groups improved the ability to purify the dyes by low-pressure liquid chromatography. The dyes TSQ and HSQ display no apparent differences in their linear absorption spectra. Nonlinear optical measurements were initially performed on purified samples of TSQ, though subsequent quantitative linear optical measurements were made on HSQ.

Linear and Nonlinear Optical Results. An EFISH measurement (Table 1) of TSQ in methylene chloride at 1.907 μm supplied a value of $-9.5 \times 10^{-34} \text{ cm}^2/\text{esu}^2$ for γ . This is the largest magnitude negative nonlinearity measured to date for a squarylium dye. For molecules possessing γ s dominated by γ_c , γ is expected to be proportional to the square of the integrated absorption of the main electronic transition. TSQ possesses an EFISH γ that is 1.27 times that of the EFISH γ for BSQ. This implies that the integrated absorptions would differ by 13%. This prompts a quantitative comparison of the linear electronic spectra of the two dyes.

We have prepared another dye HSQ (*n*-hexyls substituted on the nitrogens), which only differs in the lengths of the alkyl chains relative to those of TSQ (*n*-butyls substituted on the nitrogens). This dye was carefully purified by low-pressure liquid chromatography, and its electronic absorption spectrum was measured quantitatively in methylene chloride, supplying an extinction coefficient, ϵ , of $284\,000 \text{ L M}^{-1} \text{ cm}^{-1}$. Given the anticipated negligible effect of the alkyls on the electronic structure of the molecule, TSQ would be expected to possess a similar absorption coefficient. Thus, the nonquantitative electronic absorption spectrum for TSQ, otherwise identical to that of HSQ, was renormalized by the HSQ extinction magnitude for the purposes of further analysis presented here.

Comparison of the spectra of BSQ and TSQ (HSQ) shows that TSQ possesses approximately 19% greater integrated absorption. CNDO-SCI-DCI calculations predict an opposite effect, with the TSQ transition intensity predicted to be slightly lower in intensity.

For the CNDO calculation of TSQ, the main transition is at 484.1 nm, which is considerably different than the pentane spectrum λ_{max} of 635 nm, though one must recall that even the pentane environment is different than a “gas phase” calculation. A solvatochromism extrapolated gas phase value (*vide infra*) is close to the CNDO calculated value. There is another CNDO calculated singlet transition located at 419.2 nm with an isotropic dipole transition intensity of 0.9 D, which could conceivably contribute to the γ_c term, which might contribute to the observed difference in nonlinearities. The electronic absorption spectrum of TSQ does reveal a significant shoulder to higher energy of the main peak. Neither isomer (*vide infra*) of BSQ shows a similar significant calculated transition near the lowest singlet, though the experimental spectrum of BSQ shows (supplementary material) a weak (weaker than in TSQ) shoulder. Possibly some

(20) BSQ. Calcd: C, 73.80; H, 8.53. Found: C, 73.86; H, 8.50. TSQ. Calcd: C, 69.53; H, 8.04. Found: C, 69.60; H, 8.07. ISQ. Calcd: C, 78.75; H, 6.11. Found: C, 78.80; H, 6.13. HSQ. Calcd: C, 72.24; H, 9.11. Found: C, 71.97; H, 9.12. Further characterization by sealed quartz capillary DSC provided melting points: ISQ, 148 °C; BSQ, 188 °C; TSQ, 233 °C; HSQ, 204 °C.

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Table 1. Experimental and Calculated Nonlinear Optical Coefficients^a

molecules measd	EFISH γ^b	THG γ^c	molecules calcd	$\gamma(0)^{d,e}$	$\gamma(0)^{d,f}$ (CI)
ISQ	$-3.5 \times 10^{-34} g$		ISQ4	-11.3×10^{-34}	-27.3×10^{-34}
BSQ	$-7.5 \times 10^{-34} g$	-8.98×10^{-34}	ISQ6	-17.1×10^{-34}	-53.9×10^{-34}
			BSQ-T	-7.12×10^{-34}	-33.2×10^{-34}
			BSQ-C	-7.41×10^{-34}	-37.7×10^{-34}
TSQ	-9.5×10^{-34}	-37.45×10^{-34}	TSQ	-7.69×10^{-34}	-20.6×10^{-34}

^a Units of esu. ^b Fundamental of 1907 nm, in methylene chloride. ^c Fundamental of 1390 nm, in chloroform. ^d Zero-frequency MOPAC AM1 finite field calculation from MOPAC AM1 optimized structures. Note that the $1/6$ permutation correction has not been applied. ^e Based on single configuration AM1 finite field calculations. ^f Based on AM1 CI finite field calculations. ^g From ref 1.

Table 2. Calculated Transition Wavelengths and Oscillator Strengths versus Experimental Extinction Coefficients

	$\lambda_{\max}(\text{exptl})$ nm, CH ₂ Cl ₂	$\lambda_{\max}(\text{exptl})$ nm, pentane	AM1-CI ^a γ (nm) ^b	CNDO SCI+DCI ^c γ (nm)	CNDO isotropic ^d transition moment, D	$\epsilon(\text{exptl})^e$ L M ⁻¹ cm ⁻¹	CNDO based calculation of ϵ^{CNDO} , L M ⁻¹ cm ⁻¹ ; pure isomers	CNDO based calculation of ϵ^{CNDO} , L M ⁻¹ cm ⁻¹ ; isomer mixtures
ISQ4			537.1	472.6 ^f	6.8 ^f	177 000	226 000 ^g	187 000 ^{h,i}
ISQ6	655	658	529.3	502.0 ^f	7.4 ^f		253 000 ^g	168 000 ^{h,j}
BSQ-C			552.3	515.8	7.5	232,000	273 000 ^k	289 000 ^{h,i}
BSQ-T	649	640	552.5	514.8	7.5		274 000 ^k	289 000 ^{b,h}
TSQ ^m	650	635	543.8	484.1	7.0		274 000 ^h	
HSQ ^m						284,000		

^a This calculation was used to calculate the AM1-CI finite field $\gamma(0)$ s presented in Table 1; MOPAC 5.0 within the TRIPOS program SYBYL; keyword: "C.I. = 7". ^b This calculated extinction coefficient presumes 79% BSQ-T and 21% BSQ-C and is shown in Figure 4. ^c Includes singly excited and doubly excited configurations; starting structures based on PCMODEL mmx/SCF π -electron optimized structures. ^d Transition moment vectors were isotropically averaged to represent the true relative intensity seen experimentally in solution. Recall that the electronic absorption area is proportional to the square of this value. ^e Determined in dichloromethane. ^f These molecules were calculated with the methyl groups removed since the size of these molecules exceeded the capabilities of the computer presently being used for the CNDO calculation. ^g Calculated using Gaussian peaks and a $1/e$ peak width of 794 cm⁻¹ taken from the experimental determination of ISQ in dichloromethane. ^h Calculated using Gaussian peaks and a $1/e$ peak width of 704 cm⁻¹ taken from the experimental determination of TSQ in dichloromethane. ⁱ This calculated extinction coefficient presumes 64% ISQ6 and 36% ISQ4 and is shown in Figure 6. ^j This calculated extinction coefficient presumes 36% ISQ6 and 64% ISQ4 and is shown in Figure 6. ^k Calculated using Gaussian peaks and a $1/e$ peak width of 744 cm⁻¹ taken from the experimental determination of BSQ in dichloromethane. ^l This calculated extinction coefficient presumes 21% BSQ-T and 79% BSQ-C and is shown in Figure 4. ^m Note that TSQ and HSQ differ only in the length of alkyl groups attached to the nitrogens.

of the shouldering in BSQ (as well as TSQ) is vibronic in origin. However, in a relative sense, the differences in calculated transition intensity, as well as in the EFISH NLO behavior can probably not be considered significant.

Third harmonic generation (THG) measurements on both BSQ (-8.98×10^{-34} esu) and TSQ (-37.45×10^{-34} esu) were performed in CHCl₃ at 1.39 μ m. This places the third harmonic at 463 nm, well below the main absorptions near 640 nm. Both results are large negative nonlinearities, indicating, as suggested above, that a significant two-photon state is likely to be present. Thus, at least for measurements for which one resonant frequency is embedded in the excitation spectrum, one must model the nonlinearity as

$$\gamma \approx \gamma_c + \gamma_{\text{tp}}$$

The calculations of Garito et al. support this.¹⁶ This might help put into the perspective the observed difference between the γ_c determined from linear optical quantities and the quadratic electro-optic γ measured at 799 nm.¹

The similarity between the EFISH results and the dissimilarity between the THG results is problematic. Our own finite field calculations (Table 1) verify the negative nonlinearity behavior in all of the squaryliums and agree well (single configuration AM1 MOPAC finite field γ) with EFISH measurements which could be considered nearly off-resonant. On-resonant measurements, such as the THG measurement reported here, might be expected to show more significant differences if the relative two-photon contribution varies or if higher excited states contribute (i.e., not a three-level system).

Interestingly, nonlinear optical calculations (Table 1) suggest that ISQ should possess a significantly larger γ than either BSQ

Table 3. X-ray Crystallographic Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for the TSQ molecule^a

	x	y	z	U(eq)
O(1)	11074(4)	11816(2)	4054(1)	54(1)
O(2)	6812(4)	13285(2)	4788(1)	54(1)
O(3)	4402(4)	9355(2)	6785(1)	54(1)
N	-1075(5)	13329(2)	7033(2)	44(1)
C(1)	10468(6)	10809(3)	4583(2)	40(1)
C(2)	8260(6)	10525(2)	5312(2)	36(1)
C(3)	5912(5)	11230(2)	5735(2)	37(1)
C(4)	5241(6)	12593(3)	5467(2)	38(1)
C(5)	2976(6)	13274(3)	5884(2)	41(1)
C(6)	1177(6)	12670(3)	6609(2)	39(1)
C(7)	1822(6)	11324(3)	6888(2)	42(1)
C(8)	4068(6)	10634(2)	6469(2)	38(1)
C(9)	-2055(6)	14697(3)	6699(2)	53(1)
C(10)	-2360(7)	15482(3)	7509(2)	59(1)
C(11)	170(7)	15484(3)	7865(3)	74(2)
C(12)	-219(10)	16279(3)	8661(4)	137(3)
C(13)	-2880(6)	12679(3)	7799(2)	47(1)
C(14)	-2062(6)	12339(3)	8850(2)	53(1)
C(15)	-3875(8)	11611(4)	9599(3)	86(2)
C(16)	-3162(9)	11277(4)	10639(3)	102(2)

^a Space group $P\bar{1}$, $a = 5.2600(10)$ \AA , $b = 10.965(3)$ \AA , $c = 13.786(4)$ \AA , $\alpha = 77.14(2)^\circ$, $\beta = 80.08(2)^\circ$, $\gamma = 77.15(2)^\circ$.

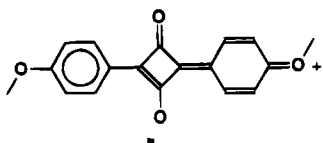
or TSQ in contradiction with the experimental results. These discrepancies are dealt with further below.

Crystallographic Results

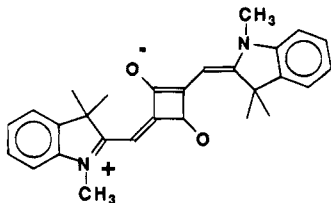
Atomic coordinates for TSQ are supplied in Table 3, with additional data available in the supplementary material.

Prior to this work, there were four previously known crystallographic structures of squarylium dyes: one phenolinium

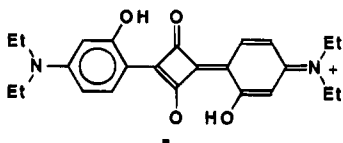
(Cambridge Crystallographic Data Base REFCODE: MXP-BUQ)²²



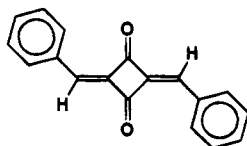
one indolinium (CCD REFCODE: DONXEJ)²³



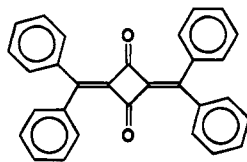
and two crystal morphs of an anilinium squarylium dye (CCD REFCODES: VAYSET and VAYSET01)²⁴



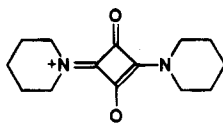
Structures VAYSET and VAYSET01 are analogous to molecule BSQ, allowing us, with the present determination of TSQ, to make a comparison between two significant squarylium dyes. Further comparison to MXPBUQ, DONXEJ, and other 1,3-cyclobutanedione structures, two of which can be considered fairly localized (CCD REFCODE: BERGAG)²⁵



and (CCD REFCODE: BERGEK)²⁶



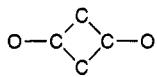
and the delocalized structure (CCD REFCODE: DEDSEK)²⁷



reveals (Table 4) relevant structural features pertaining to the electronic properties of TSQ.

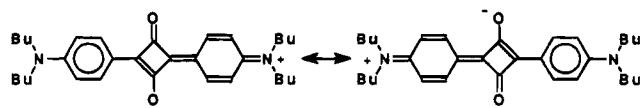
The present structure (Figure 3) of TSQ is centric and essentially planar. Structures MXPBUQ, VAYSET, and VAYSET01 are centrosymmetric and essentially planar, while structure DONXEJ is significantly twisted out of planarity and is noncentric. We have usually formulated and considered our squarylium structures as cross conjugated fully delocalized cyanine and oxonol-type structures. Such a polymethine-type formulation presumes these molecules to be free-electron like. A typical characteristic of such structures is the relatively even

Table 4. Comparison of X-ray and Calculated Structural Parameters of Squarylium Dyes and Related Structures^a

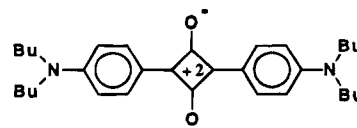
			conjugated carbon chain		
	mean squate C—O length (Å)	mean squate C—C length (Å)	conjugation path ^b	mean C—C length (Å)	std dev (Å)
TSQ X-ray ^c	1.253	1.447		1.414	0.029
TSQ AM1	1.241	1.477		1.426	0.031
TSQ PM3	1.235	1.472		1.422	0.031
VAYSET	1.249	1.461	a	1.407	0.036
			b	1.401	0.045
VAYSET01	1.248	1.462	a	1.414	0.031
			b	1.417	0.036
BSQ-T AM1	1.235	1.476	a	1.422	0.028
			b	1.421	0.037
BSQ-T PM3	1.226	1.474	a	1.420	0.029
			b	1.418	0.036
BSQ-C AM1	1.242 ^d	1.466 ^d	a	1.421	0.026
	1.229 ^e	1.485 ³	b	1.423	0.037
BSQ-C PM3	1.243 ^d	1.457 ^d	a	1.417	0.023
	1.211 ^e	1.492 ^e	b	1.421	0.042
MXPBUQ	1.230	1.482		1.411	0.043
DONXEJ	1.224	1.471		1.413	0.046
BERGAG	1.213	1.492		1.409	0.051
BERGEK	1.208	1.501		1.419	0.054
DEDSEK	1.240	1.456			

^a The conjugation path, a or b, is a defined in the text. BSQ structures that are "trans" are indicated by the letter "T", while "C" indicates "cis". PM3 and AM1 optimized structures are from SPARTAN. ^b Defined in the text. ^c See Figure 3. ^d The carbonyl syn with both OH. ^e The carbonyl anti with both OH.

bond lengths between conjugated carbons. Thus, the average bond length should be between that of a single bonded C—C and a double bonded C=C. The average CC length in the TSQ structure is 1.414 Å with a standard deviation of 0.029 Å. Other squarylium dyes as well as calculated structures (to be discussed, *vide infra*) illustrate similar average lengths, suggesting there is extensive delocalization throughout the molecule. A considerable amount of double bond character evidently exists between all conjugated carbons. As expected, a quinone contraction exists between carbons C(7) and C(8) (1.365 Å) or carbons C(4) and C(5) (1.366 Å), implying the contribution of the quinone resonance form inherent to the squarylium polymethine resonance structures. The most significant deviation toward single bond character exists in the squarate ring itself. Thus, while the net molecular carbon—carbon bond order lends itself toward equilibrating delocalized cross conjugated cyanine/oxonol structures



the squarate still possesses cyclobutadienyl dication character



Thus, the true resonance structure must be a complex mixture of these two basic resonance forms. The cyclobutadienyl ring is most contracted in the TSQ squarylium structure. This may be occurring due to the hydrogen bonding stabilizing the anionic oxygen. Either structure should display long carbonyl

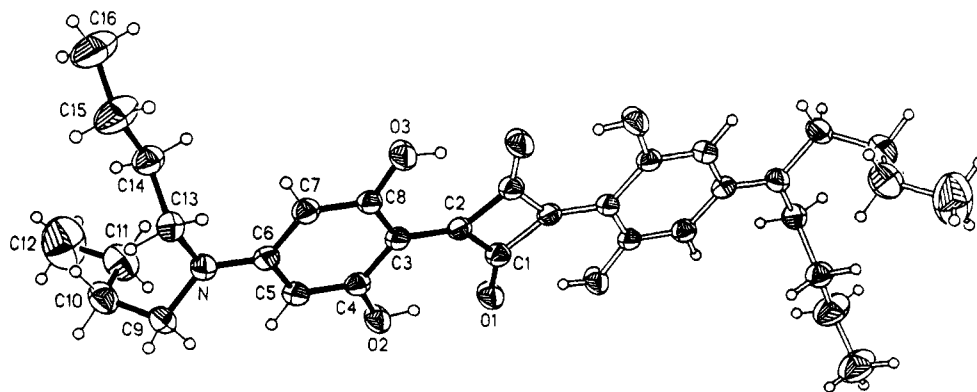


Figure 3. Molecular structure of TSQ from X-ray crystal structure determination. Atomic coordinates are provided in Table 3.

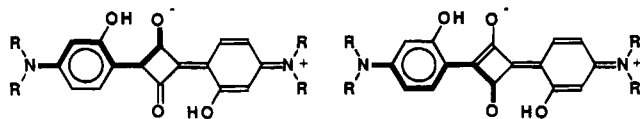
Table 5. Comparison of Calculated and NMR-Derived Experimental Isomer Ratios for ISQ and BSQ

	ISQ6/ ISQ4	ISQ6: ISQ4	BSQ-C/ BSQ-T	BSQ-C: BSQ-T
PCMODEL				
based on <i>mmx</i>	0.680	40:60	0.455	31:69
based on ΔH°_f	0.095	9:91	0.538	35:65
PM3				
based on ΔH°_f	0.446	31:69	1.328	57:43
AM1				
based on ΔH°_f	0.832	45:55	0.548	35:65
expt, ref 19				24:76 ^a
expt, this work	0.57 ^{b,c}	36:64 ^{b,c}	0.27 ^c	21:79 ^{c,d}
	0.52 ^{a,b}	34:66 ^{a,b}		
	0.69 ^{a,e}	41:59 ^{a,e}		

^a CDCl₃. ^b Based on integration of N-H protons. ^c CD₂Cl₂. ^d Based on integration of the aromatic protons ortho to the squarate. ^e Based on integration of olefinic protons.

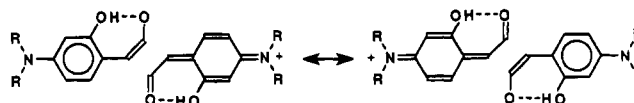
carbon–oxygen bonds. All of the zwitterionic squaryliums display long carbonyl bonds, with TSQ possessing the longest of any reported to date. By contrast, the localized cyclobutadiones (BERGAG and BERGEK) display considerably shorter carbonyl bonds. The delocalized DEDSEK displays a long carbonyl bond.

The effect of the ortho hydroxys is of interest since these moieties may be influencing the overall bond delocalization. We compare two distinct conjugation paths (Table 4)



one involving conjugation on the side with the hydroxy and the other on the side without the hydroxy. Standard deviations for the averages of these conjugation paths are significantly different with the standard deviation along the hydroxy side being comparable to that for TSQ. This is seen in the crystal structures of the VAYSET and VAYSET01, as well as in calculations (both AM1 and PM3) of BSQ. The hydroxy evidently helps further polarize the squarate carbonyl, and it is clear that this is enhanced in TSQ relative to BSQ (or VAYSET and VAYSET01). Under this influence, the squaryliums in

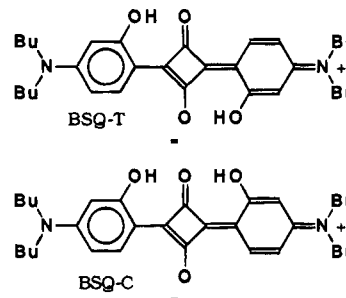
some sense could also be viewed as an antiparallel system of two donor–acceptor substructures within the molecule.



This assessment is similar to that reached by Garito and co-workers.¹⁶

Isomeric Squarylium Dyes

There is a report in the literature on the NMR analysis of BSQ.¹⁹ Proton NMR distinctly suggests that BSQ exists as a mixture of two isomers, in the proportion of 24:76 in favor of the centrosymmetric structure:



We had suspected the presence of an isomer mixture for ISQ when attempts at deconvolution of the electronic spectra consistently suggested the presence of at least two distinct vibronic absorption manifolds. The presence of a polar isomer has some implications with regard to the third-order optical polarization. It could possibly lead to contributions of a significant γ_n term and could also greatly perturb the EFISH γ due to an orientational contribution via the hyperpolarizability, β , projected on the dipole moment. Presuming a positive orientational contribution, this would reduce the negative nonlinearity further beyond the cancellation due to the γ_{ip} term. In order to further clarify this isomerism issue, we have investigated the proton NMR of ISQ, BSQ, and TSQ.

Investigation of BSQ primarily consisted of verifying the earlier study of Kazmaier et al.¹⁹ Proton NMR spectra collected in CD₂Cl₂ reveal ortho (to the squarate) aromatic doublets at 7.92 and 7.81 ppm ($^3J = 9.2$ Hz) with relative intensities in good agreement (Table 5) with the CDCl₃ spectrum of Kazmaier et al. The meta protons, more distant from the squarate, appear at 6.10 ppm ($^4J = 2.3$ Hz) and 6.36 ppm ($^3J = 9.2$ Hz, $^4J = 2.3$ Hz).

(22) Farnum, D. G.; Neuman, M. A.; Suggs, W. T., Jr. *J. Cryst. Mol. Struct.* **1974**, *4*, 199.

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(26) Gatehouse, B. M. *Cryst. Struct. Commun.* **1982**, *11*, 369.

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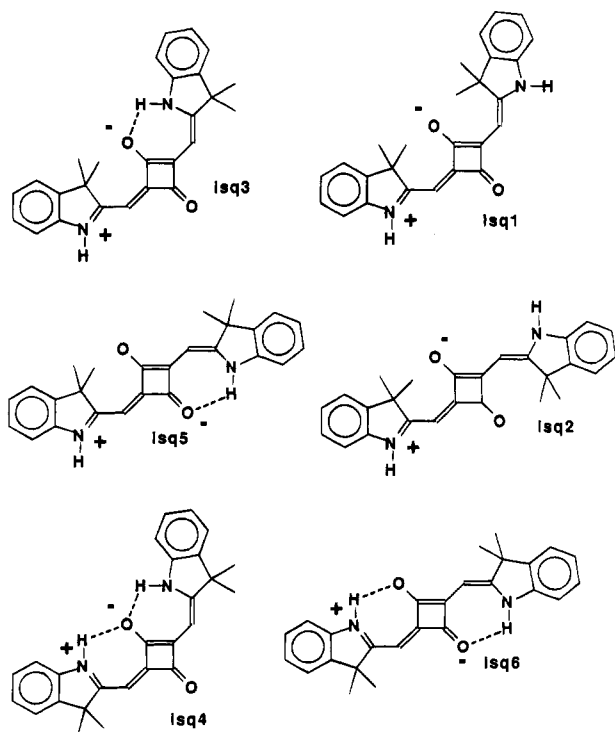
Table 6. Calculated Heats of Formation, Strain Energies, and Dipole Moments for the Isomers of ISQ and BSQ^a

	PC MODEL			PM3		AM1	
	mmx strain, kcal/mol	ΔH_f° , kcal/mol	$ \vec{\mu}_0 $, D	ΔH_f° , kcal/mol	$ \vec{\mu}_0 $, D	ΔH_f° , kcal/mol	$ \vec{\mu}_0 $, D
ISQ1	93.58	185.20	1.24				
ISQ2	93.08	184.85	0.22				
ISQ3	76.26	168.76	3.14				
ISQ4	60.12	153.28	5.69	54.780	4.149	95.126 ^b	3.666 ^b
ISQ5	76.57	168.85	4.41				
ISQ6	60.35	153.31	0.01	55.298	0.020	95.236 ^b	0.020 ^b
BSQ-T	49.13	128.54	0.74	-45.544	1.760	-12.758 ^c	2.842 ^c
BSQ-C	48.66	128.17	0.17	-45.375	0.029	-13.117 ^c	0.003 ^c

^a Not included in this table is the CNDO-SCI-DCI dipole moment for BSQ-C (1.67D). ^b Optimized under the AM1 version of SPARTAN. ^c Optimized under the AM1 version of HYPERCHEM.

Proton NMR spectra of TSQ were obtained in CD₂Cl₂ and CDCl₃. TSQ is symmetric, with meta aromatic protons appearing at 5.76 ppm (CD₂Cl₂) or 5.74 ppm (CDCl₃) as a singlet. The hydroxy protons were observed at 10.84 ppm (CD₂Cl₂) or 10.95 ppm (CDCl₃) as singlets. The hydroxy proton resonance is noticeably broader in CD₂Cl₂ than in CDCl₃. The presence of singlets for either resonance in either solvent verifies the presence of this molecule as a single isomer.

Proton NMR spectra of ISQ reveal two sets of amine protons (CD₂Cl₂, 12.82 and 12.57 ppm; CDCl₃, 12.81 and 12.52 ppm) and two sets of olefinic protons (CDCl₃, 5.50 and 5.43 ppm; CD₂Cl₂, solvent residual proton signal obscures signals). This suggests the presence of two different isomers. The molecule ISQ can exist as six obvious cis-trans isomers:



In order to determine which isomers are present, we have conducted a molecular mechanics investigation of BSQ and ISQ (Table 6). This first involved calculations based on the PCMODEL mmx force field augmented by a PPP type π -electron calculation inherent to the PCMODEL program. This permitted a first-order ranking of the possible isomeric structures. More time consuming PM3 and AM1 structure optimization calculations were then performed on each of the subsequent most likely structures. Each of these calculations provided free

energies of formation or strain energies for each of the possible isomers. On the basis of these calculations, it was concluded that there are two most likely isomers each for either BSQ or ISQ.

NMR ratios of the two BSQ isomers are compared to thermodynamic predictions based on the molecular mechanics calculations (Table 5). If one presumes that the minor NMR isomer is the cis isomer, then the AM1 and PCMODEL based predictions are reasonably close to the experimental results. The PM3 calculations predict a close equilibrium though biased against the trans isomer. We have examined the carbon atom charges in both optimized AM1 and optimized PM3 calculations in the hope of determining which NMR resonances can be assigned to either isomer. The more positively charged the carbon, presumably the more down-field would be the protons attached to the carbons. Both AM1 and PM3 calculations predict slightly more positively charged ortho carbons in the cis form (charges AM1: -0.012, PM3: 0.018) than in the trans form (charges AM1: -0.024, PM3: 0.017). This suggests that the more downfield protons may be assigned to the cis form, making it the minor isomer.

Proton NMR data collected for ISQ suggest the presence of two isomers, in agreement with the PCMODEL mmx force field calculations. All calculations suggest that the minor isomer should be ISQ6, the centrosymmetric structure, while the major isomer would be the very polar ISQ4. The major isomer N-H protons are shifted further downfield. Both PM3 and AM1 calculations resulted in identical nitrogen atom charges, precluding proton NMR assignments of the N-H protons based on atom charge differentials between the two isomers. The vinylic protons display an opposite chemical shift dependence with the minor isomer being shifted downfield. Calculations predict vinylic carbon atom charges: cis isomer—AM1 (-0.224), PM3 (-0.187); trans isomer—AM1 (-0.225), PM3 (-0.188). The vinyl carbons of the cis isomer are slightly more positive than those of the trans isomer, suggesting that the cis isomer vinyl protons would be shifted further downfield, making this the minor isomer. This contradicts all of the calculations. Because of the proximity of these protons to the squarate ring and its own ring current and polarization effects, it is probably safer to assume that the proton NMR resonances cannot be so trivially assigned. In any case, whichever is the major or minor isomer, the ratio inferred from NMR integration suggests that both isomer molecules exist as significant mole fractions. Finally, the most stable structures for ISQ are ISQ4 and ISQ6, though note that the crystal structure of DONXEJ would be comparable to the highest energy ISQ structure, ISQ2. While the most likely structures for ISQ are ISQ4 and ISQ6, simply substituting ISQ with an *N*-methyl group permitted isolation of a related high-energy form, albeit nonplanar. Thus, substituting ISQ with *N*-alkyl to improve solubility potentially creates yet another isomer distribution.

Solvatochromism and Spectral Simulation

Solvatochromism studies have been performed on TSQ and the isomeric mixtures of BSQ and ISQ (Table 7). Calculations (AM1, PM3, and CNDO) suggest that the two isomers of BSQ share resonance frequencies that differ little, at least in the gas phase, while the two ISQ isomers should possess significantly different γ_{max} s. Curiously, experimental spectra show that ISQ is most red-shifted relative to TSQ and BSQ, while CNDO calculations suggest that it is the most blue shifted. Solvatochromism gas phase extrapolated values, $\bar{\nu}_g$, agree well with the CNDO trend, though one must remember that both the BSQ and ISQ solvatochromism results are due to a mixture of

Table 7. Electronic Spectral and Solvatochromism Analysis Results for the Squarylium Dyes ISQ, BSQ, and TSQ, with λ_{\max} and Peak Half-Widths (Γ_G) at $1/e$ Assigned by Fits of the Low Energy Side of the Peak to a Gaussian Profile with the Indicated Standard Deviations, $\sigma_{\bar{A}}$ ^a

	ISQ			BSQ			TSQ		
	λ_{\max} (nm)	$\sigma_{\bar{A}}$	Γ_G (cm ⁻¹)	λ_{\max} (nm)	$\sigma_{\bar{A}}$	Γ_G (cm ⁻¹)	λ_{\max} (nm)	$\sigma_{\bar{A}}$	Γ_G (cm ⁻¹)
Electronic Spectral Results									
acetonitrile	650	0.016	417	645	0.014	437	644	0.014	421
pentane	658	0.020	350	640	0.017	282	635	0.043	277
dichloromethane	655	0.009	397	649	0.019	372	650	0.025	352
cyclohexane	662	0.020	351	637	0.016	290	640	0.042	288
isooctane	659	0.019	361	634	0.033	296	637	0.046	267
methylcyclohexane	661	0.007	364	636	0.011	308	639	0.010	291
chloroform	654	0.008	418	649	0.041	383	649	0.016	343
benzene	663	0.014	372	647	0.007	356	648	0.020	340
ethyl acetate	654	0.018	402	643	na	363	643	na	na
DMF	658	0.010	406	660	0.039	373	651	0.013	439
Solvatochromism Results									
A (cm ⁻¹)			-2540			-7880			-7150
B (cm ⁻¹)			207			-628			-437
$\bar{\nu}_g$ (cm ⁻¹)			15700			17300			17100

^a The constants A , B , and $\bar{\nu}_g$ (the extrapolated "gas phase" transition frequency) have been previously defined (see ref 14). Note that the Gaussian fits are good in contrast to our earlier^{1b} incorrect assignment of these peaks as Lorentzian.

isomers. TSQ typically displays the narrowest resonances, as might be expected for a single isomer. Thus, ISQ should show the broadest spectra with BSQ possessing spectra slightly broader than for TSQ. Generally, this is what is observed in most solvents. The solvatochromatic parameter B reveals the amount of dipolar character in both the excited and ground states, relative to the dipolar or induced dipolar nature of the environment. For all samples, the magnitude of this number is relatively small compared with that expected for a very polar dye¹⁴ with large hyperpolarizability β . It is noteworthy that the ISQ- B solvatochromism parameter is positive, which implies negative solvatochromism, or red shifting with decreasing polarity. This is unexpected and is best explained if one considers two possibilities: (1) The polar isomer may be blue shifting with decreasing polarity, while the centrosymmetric isomer remains essentially unchanged. It is then likely that the weighted average of the two peaks might appear to red shift since this centrosymmetric isomer peak would not be shouldering as much of the polar isomer peak. BSQ displays a smaller B parameter than TSQ, which might suggest that a similar effect is operable with this isomeric mixture, though slight enough so as to not lead to negative solvatochromism. (2) The other possibility is that the polar isomers of ISQ and BSQ display negative changes in dipole moment upon excitation from the ground to the excited state. This would lead to negative solvatochromism. The molecular hyperpolarizability, β , would then be negative, which would contribute to the negative γ as an orientational contribution to the EFISH γ . If this is occurring, then the true electronic γ would be somewhat smaller in magnitude than originally reported, for ISQ and possibly for BSQ. The significant difference in the THG γ s between BSQ and TSQ might support this contention, though it is more likely that the THG differences between BSQ and TSQ are due to differences in two-photon behavior.

Because of the isomer mixtures, short of complete vibronic deconvolution, it is not possible to use solvatochromism to assign excited state dipole moments to either ISQ4 or BSQ-C. Such an assignment would be useful since the magnitude and sign of the EFISH γ_n and orientational contributions could be estimated. Without such a correction, comparing calculated and measured γ s for either BSQ or ISQ could be treacherous (*vide infra*). Full vibronic deconvolutions are difficult and are presently being attempted.

As a further effort to characterize the isomeric behavior, the electronic spectra of ISQ, BSQ, and "TSQ" (HSQ) were

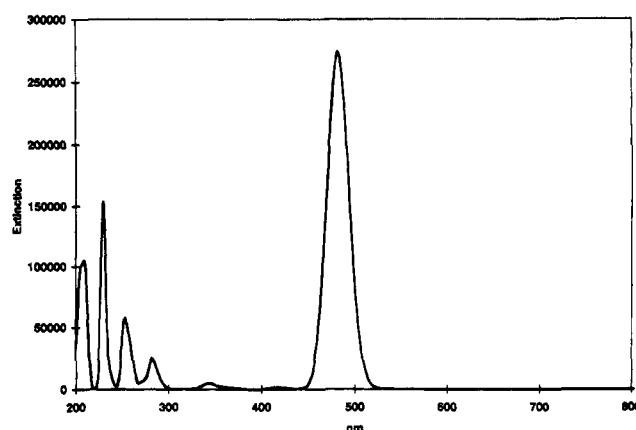


Figure 4. Calculated quantitative gas phase UV-visible electronic absorption spectrum of HSQ (TSQ). Structures actually calculated were slightly modified as detailed in the Experimental Section. Note that the experimental peak width of 704 cm⁻¹ (TSQ) of the maximum intensity resonance was assumed for all resonances. See Table 2.

simulated by calculating the spectral transitions by CNDO-SCI-DCI, fitting Gaussian peaks to each transition, and then in the case of the isomeric mixtures, linearly combining calculated spectra of the isomers using the weighting suggested by NMR. Electronic peak widths, which define the extinction maximum were set on the basis of the experimental peak widths. All peaks were defined to have the same peak width as the maximum absorption peak, though this is almost certainly not correct for all peaks and will likely lead to poorer quantitative fits for the higher frequency transitions. For the isomeric mixtures, the peak width of TSQ was used to generate each of the calculated spectra for the BSQ and ISQ isomers. This was done because TSQ, which is presumably not a mixture of isomers, would possess the only spectra where the peak width represents a system unperturbed by isomeric mixtures. Isomeric mixtures would normally possess wider peaks merely due to the combination of spectra of two or more compounds with different peak maxima. By examining Table 2 and Figures 4–7, one can easily see that extinction coefficients are predicted well, though transition wavelengths are blue-shifted as would be expected for "gas-phase" calculations. For ISQ, it is apparent that the smaller extinction coefficient is due to the mixture of two isomers, each of which individually would possess extinction coefficients comparable to TSQ or BSQ. The spectrum of ISQ is best reproduced when ISQ6 is calculated as the major

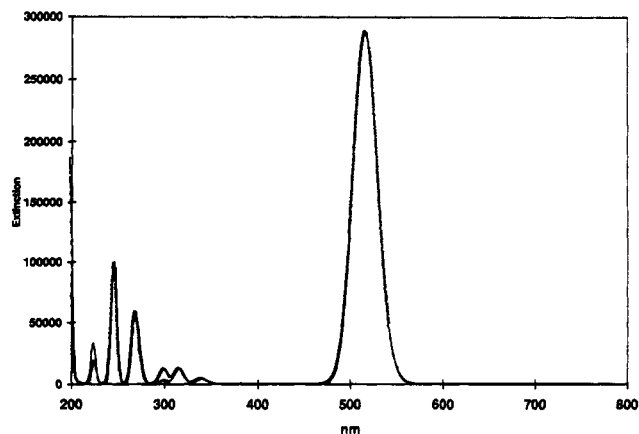


Figure 5. Calculated quantitative gas phase UV-visible electronic absorption spectrum of BSQ. Solid line: 21% BSQ-T and 79% BSQ-C. Dotted line: 79% BSQ-T and 21% BSQ-C. Structures actually calculated were slightly modified as detailed in the experimental section. Note that the experimental peak width of 704 cm^{-1} for TSQ was assumed. See text for details. See Table 2.

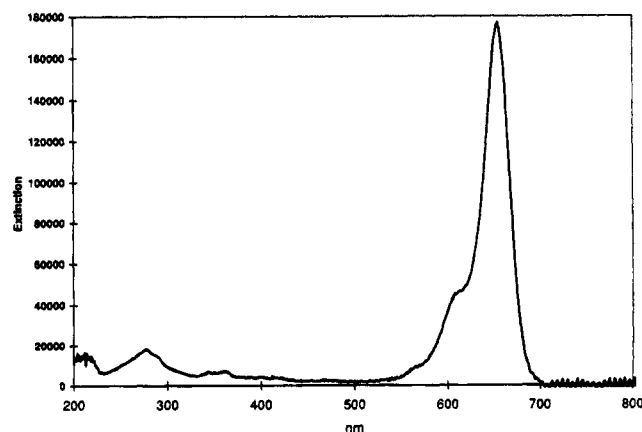


Figure 6. Experimental quantitative UV-visible electronic absorption spectrum of ISQ in methylene chloride. See Tables 2 and 7.

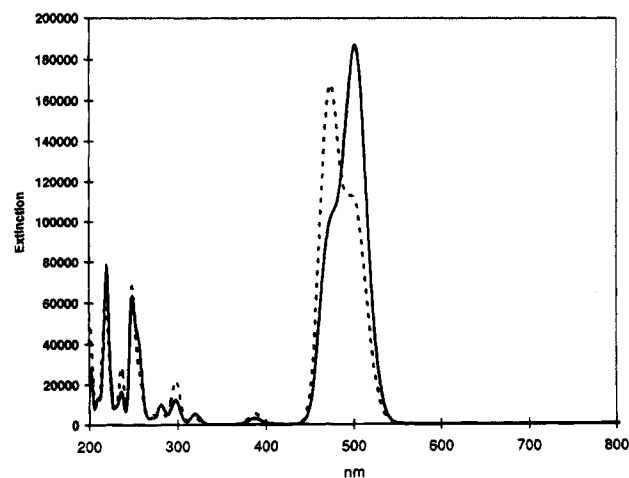


Figure 7. Calculated quantitative gas phase UV-visible electronic absorption spectrum of ISQ. Solid line: 64% ISQ6 and 36% ISQ4. Dotted line: 36% ISQ6 and 64% ISQ4. Structures actually calculated were slightly modified as detailed in the Experimental Section. Note that the experimental peak width of 704 cm^{-1} for TSQ was assumed. See text for details. See Table 2.

component, in contradiction to molecular mechanics and semiempirical quantum mechanical calculations.

The calculated spectrum (Figure 5) of BSQ is insensitive to the definition of the isomer mixture. Additionally, the calculated

extinction coefficient of BSQ appears too large. These two latter calculated observations suggest that BSQ may naturally possess broader peaks than TSQ and that isomerism does not seriously affect the electronic linear-optical properties of BSQ. Finite field calculations (Table 1) evidently suggest that the nonlinear optical properties also will differ little between BSQ-C and BSQ-T.

The calculated linear spectra of ISQ4 and ISQ6 are significantly different. The ISQ4 isomer also displays a significantly smaller (less negative) calculated γ , as might be expected due to the presence of a γ_n contribution. Additionally, the calculated γ s for both ISQ isomers suggest that both are expected to possess γ s bigger than or at least comparable to those for BSQ and TSQ. However, the opposite is observed experimentally. A reasonable explanation is that ISQ4 possesses a significant β which is negating the electronic γ of the isomeric mixture of ISQ4 and ISQ6 via a significant canceling positive γ_n contribution. The finite field calculations suggest that this alone is not enough cancellation since the ISQ4 isomer is still expected to possess a larger magnitude γ than either BSQ or TSQ. The discrepancy between the calculated (single configuration) and experimental EFISH trends of nonlinearities suggests that ISQ4 is likely also contributing a significant positive $\mu\beta$ orientational contribution. Finite field calculations for ISQ4 suggest that $\mu\beta_0$ is weakly positive ($+6.4 \times 10^{-30}\text{ D cm}^5\text{ esu}^{-1}$). However, even this small magnitude of $\mu\beta_0$ would correspond to an orientational γ_0^{or} of approximately $+1.5 \times 10^{-34}\text{ cm}^7\text{ esu}^{-2}$. Though this appears to be relatively small compared to the static electronic value of $\gamma_0 = -11.3 \times 10^{-34}$ (ISQ4) or $\gamma_0 = -17.1 \times 10^{-34}$ (ISQ6), one must keep in mind that β increases faster than γ as one approaches resonance. Thus it is likely the orientational γ_0^{or} would possess a larger canceling effect at the EFISH measurement frequency of $1907\text{ }\mu\text{m}$. The calculated $\mu\beta_0$ for BSQC of $50.7 \times 10^{-30}\text{ D cm}^5\text{ esu}^{-1}$ corresponds to an orientational γ_0^{or} of $+12.3 \times 10^{-34}$. Here the zero frequency canceling effect of the orientational contribution is predicted to be 65% greater than the electronic effect. The orientational contributions are estimates based on the presumption of

$$\gamma_0^{\text{or}} \approx \frac{\mu\beta_0}{5kT}$$

Given calculational uncertainties, the canceling effects for either ISQ4 or BSQC should be viewed as approximate. It is clear, however, that the canceling orientational effects could be significant.

Note that the predicted positive β suggests that the solvatochromism shifts must be positive (or red shifting with increasing solvent polarity).

Note that configuration interaction finite field calculations show some additional variation that the single configuration calculations did not display. With CI, BSQ is suggested to possess a larger γ than TSQ, while ISQ's γ , should be bigger yet, even as a mixture of isomers, both in contradiction to experiment. If the CI calculations are given more weight than the single configuration calculations, this supplies more credence for a canceling orientational γ_0^{or} for BSQC.

Conclusion

We have demonstrated that the molecules BSQ and ISQ can exist as a mixture of isomers. Our results are in good agreement with those of Kazmaier et al. for BSQ and with quantum mechanical and molecular mechanical calculations of the relative molecular strain energies or heats of formation. The squaryliums are clearly π -bond delocalized, as demonstrated by the

X-ray structure results and by optimization of structures by semiempirical calculations. Comparison to other structures indicates that the main role of the hydroxys is to stabilize the charge transfer from the amine nitrogens to the squarate oxygens.

We have also demonstrated again that the squaryliums generally appear to display large off-resonant *negative* third-order polarizabilities. Resonant third harmonic generation results clearly suggest the significant contribution of a two-photon state as predicted by Garito et al. Linear and nonlinear optical calculations suggest that γ should not differ significantly between BSQ and TSQ, at least far off resonance. Near resonance, the experimental resonant THG measurements suggest that the location of the two-photon state may differ significantly between BSQ and TSQ or that the three-level model effectively breaks down when in such a resonant interaction. Garito and co-workers have suggested the contribution of two or three significant two-photon states, which could contribute differently for BSQ and TSQ.¹⁶ Alternatively, there could be a significant positive γ_n contribution from the BSQ-C isomer. Such a contribution would be orthogonal to the main γ_c and γ_{tp} components. However, the isotropic CI finite field γ is larger (in negative magnitude) for BSQ-C than for BSQ-T, suggesting that such a contribution is not significant. It is more likely that BSQ-C possesses a canceling orientational contribution which cancels via a positive $\mu\beta$ contribution. This mechanism should be operative for the EFISH results and could rationalize the difference in trends between EFISH γ and the CI finite field trends. However, the orientational contribution cannot be used to explain the differences in THG γ , suggesting that the location of the two-photon states may be different between BSQ and TSQ.

Calculations of linear optical spectra clearly suggest that ISQ possesses an integrated absorption comparable to BSQ or TSQ, at least for the theoretical pure isomers. Calculated nonlinear optical results suggest that either isomer of ISQ should be superior to TSQ or BSQ. The noncentrosymmetric ISQ4 isomer component is significant in its mole fraction, and it probably possesses a significant dipole moment. There may be a significant orientation contribution to the EFISH γ , as well as a significant γ_n contribution which would contribute to the electronic γ in a positive sense. Quadratic electroabsorption studies suggest that ISQ in a PMMA matrix can be explained well by a three-level model, requiring only the contributions γ_c and γ_{tp} to explain the dispersion, which itself independently supports the presence of a significant two-photon state.²⁸ This might be thought to suggest that γ_n and EFISH orientational contributions would not be significant. However, the results presented here hint at a significant positive orientational contribution as well as perhaps a significant positive γ_n contribution from the noncentrosymmetric isomer ISQ4. This may not be incompatible with the electroabsorption results when considering that the electroabsorption studies have been conducted under conditions of a viscous polymer matrix which would impede motional contributions to γ . Also, the contributing quadratic electroabsorption dispersion of the γ_n term would probably be convolved with the quadratic electroabsorption dispersion of a γ_{tp} term. Due to the isomer complication, the story with regard to ISQ will remain complicated. Further work is necessary.

Overall, we arrive at a curious inference. The compound (TSQ) with apparently the largest experimental γ may actually

possess the smallest γ when correcting either BSQ or ISQ for orientational contributions.

It is possible, in light of Marder's bond length alternation results, that the observed contradictory variation in experimental and theoretical nonlinear optical behavior is due to solvent effects. In this regard, Law has suggested that in chlorinated hydrocarbons anilinium squaryliums with no stabilizing hydroxys can be considered essentially planar, though may be less so in other solvents.²⁹ The measurements reported here were made only in either chloroform or methylene chloride, and comparisons were confined largely within either of these solvents. Also, the presence of the hydroxys should lead to even more stability. Given their similar structures, it is unlikely that the molecules investigated here would have behaved significantly differently relative to one another with regard to their solvent interactions.

The experimental inference of a two-photon contribution to the squaryliums is significant. This observation rounds out and better defines a three-level model description for most molecules:

(1) Electron-localized molecules such as carotene, which display large positive nonlinearities. In the extreme of centrosymmetry, the model reduces to two terms

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

with γ_{tp} dominating.

(2) The extreme of noncentrosymmetry is represented by molecules with large β . Under these circumstances, γ_n is dominant, and the model is represented by

$$\gamma \approx \gamma_c + \gamma_n$$

The sign of β is irrelevant with regard to γ_n , so that molecules with either large positive or negative β s can produce large positive γ_n .

(3) The squarylium dyes, while displaying large negative γ s, evidently possess non-negligible γ_{tp} two-photon contributions. The model is then represented by

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

though with γ_{tp} being less significant. Optimization here tends toward molecules with free-electron character which are characterized by bond orders which do not deviate significantly along the backbone chain. Crystallographic evidence presented here supports this. However, bond orders alone are merely a symptom of an effect. The factor which evidently evened out the bond orders of TSQ relative to BSQ was the substitution of another pair of hydroxys.

Recent results of Mazumdar and co-workers³⁰ on polydiacetylene suggest that some molecules may require more than a three-level model to adequately quantitatively explain the third-order NLO behavior. However, the basic symmetry considerations should still hold for all terms, so that the NLO behavior mostly needs only to be considered in terms of additional higher order γ_c , γ_n , and γ_{tp} components (as also suggested by Garito and co-workers for the squarates),¹⁶ which should behave qualitatively the same as the first-order three-level components.

It must be recognized that the motivation for developing a restricted model such as the three-level model is not to improve quantitative fits, which by definition it can not accomplish, but to provide a simple structure/property tool to guide materials development. It has never been argued that the two-level model

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for β is quantitatively accurate. It is not, though it is inarguable that the two-level model for β has lead to systematic enhancement of β by allowing materials chemists to impose on it their intuitive insight regarding molecular electronic structure. It must further be recognized, as discussed here, that there are different mechanisms (electronic, orientational, etc., which each contribute *both* positive and negative components)³¹ contributing significant components to γ , especially for molecules with large γ . The *electronic* three-level model for γ helps categorize and distinguish the electronic positive and negative components—which are operating on a completely different temporal scale—from the orientational contributions, which also possess positive and negative components.

With regard to the isomer problem, more studies and some caution in interpreting past results are necessary. In particular, because of the centrosymmetry restriction on γ_n and the EFISH orientational contribution, molecules which naively may be presumed centrosymmetric, but which can possess other isomeric structures, must be dealt with carefully when interpreting third-order optical polarization results. For instance, variations in magnitude and sign of γ with varying environment may reflect, in some cases at least, a shift in conformational isomer structure and distribution. Also, unanticipated deviations from the three-level model may occur when failing to consider a γ_n

contribution in a supposed centrosymmetric dye which may contain a noncentrosymmetric component.

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Supplementary Material Available: Tables listing complete X-ray crystallographic data and figures showing UV–visible electronic absorption spectra of HSQ and BSQ, the proton NMR spectrum and electron absorption spectrum of TSQ, and proton NMR spectra for isomeric mixtures of ISQ (22 pages); observed and calculated structure factors for TSQ (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet access instructions.

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