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Syntheses and Linear and Nonlinear Optical Properties of Unsymmetrical Squaraines with Extended Conjugation

Chin-Ti Chen,[†] Seth R. Marder,*[†,‡] and Lap-Tak Cheng[§]

Molecular Materials Resource Center
The Beckman Institute, 139-74
California Institute of Technology
Pasadena, California 91125
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91109
DuPont Central Research and Development
Wilmington, Delaware 19880-0356

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Squaraine dyes are known to exhibit sharp and intense absorptions (molar extinction coefficient ~ 10^5 cm^{-1} M^{-1}) in solution with λ_{max} ranging from the visible to the near-IR region.[1] Due to the optical features, squaraines are attractive candidates for a number of applications, such as photoreceptors in solar cells,[2] photoconductors for xerography,[2] and media for diode laser optical recording.[3] Recently, it has been demonstrated that symmetrical and unsymmetrical squaraines have large second (γ)[4] and substantial first (β)[5] molecular hyperpolarizabilities. The synthesis of unsymmetrical squaraines involves the preparation of monosubstituted precursors followed by condensation with a second donor. Thus, by using precursors, such as 1-[4-(dimethylamino)phenyl]-2-hydroxycyclobutene-3,4-dione[6] and 1-[(alkyloxy)phenyl]-2-hydroxycyclobutene-3,4-dione,[5,7] three types of unsymmetrical squaraines have been synthesized. To date, for both symmetrical and unsymmetrical squaraines, five- or six-membered aromatic or *exo*-methylidene quaternary heterocyclic rings that are limited to six atoms or less in length (from the donor functionality to the C_4O_2 central ring) have been used. Here we report the synthesis and the linear and nonlinear optical properties of a new unsymmetrical squaraine with extended conjugation, [4-[3,5-dihydroxy-4′-(*N*,*N*-dibutylamino)]stilbenyl]-[4″-(isopentyloxy)phenyl]squaraine (**3**), which is 12 atoms in length from the dibutylamino donor of stilbene to the central C_4O_2 acceptor ring.

We designed and synthesized 4-(*N*,*N*-dibutylamino)-3′,5′-dihydroxystilbene (**1**) as the donor for squaraines with the intent of extending the conjugation length and consequently generating a near-IR absorbing squaraine with large molecular hyperpolarizabilities. To direct the condensation of 1-[4-(isopentyloxy)-phenyl]-2-hydroxycyclobutene-3,4-dione (**2**) with **1** to the para position of the phenyl ring away from the amino donor in **1**, two hydroxy donor groups were introduced on meta positions of the remote phenyl ring. In addition, the dibutylamino substituent on **1** and isopentyl on **2** were incorporated to render the resulting squaraines soluble. The synthesis of **1** consists of a three-step procedure.[8] The condensation between **1** and **2** was performed in a procedure analogous to that developed by Law *et al.*,[7] and the product of **3** was purified by recrystallization from dichloromethane.[9] The β-value (measured by electric-field-induced second-harmonic generation, EFISH, in chloroform using 1.907-μm fundamental radiation[10]) and its zero frequency form $\beta(0)$ (corrected for dispersive enhancement using a two-state model[11]) for **3** are shown in Table 1, together with the data of optical absorption maximum (λ_{max}), molar extinction coefficient (ϵ), bandwidth at half-height ($W_{1/2}$), and the dipole moment (μ). The shorter unsymmetrical squaraines **4** and **5** were synthesized,[12] and their linear and nonlinear optical data are also included in Table 1 for comparison.

Table 1. Optical Data of Unsymmetrical Squaraines **3–5** Measured in Chloroform Using 1.907 μm as Fundamental Radiation

no.	λ_{max} (nm)	$W_{1/2}$[a] (cm^{-1})	ϵ (10^4 M^{-1} cm^{-1})	μ (10^{-18} esu)	β (10^{-30} esu)	$\beta(0)$ (10^{-30} esu)
3	732	2650	5.7	8.1	481	170
4	570	1230	14	6.5	–53	–31
5	572	2280	9.0	7.4	–62	–36

[a] $W_{1/2}$ denotes the bandwidth at the half-height of the absorption band at λ_{max}.

With extended conjugation, λ_{max} of **3** is at 732 nm, red-shifted more than 160 nm from 570 and 572 nm of **4** and **5**, respectively. Accompanying this bathochromic shift is a weakening and broadening of the absorption band (Table 1). The nonlinear optical properties of **3–5** exhibit some interesting behavior. As expected, both μ and the magnitude of β for **3** are considerably larger than those for **4** and **5**, with $\mu\beta$, which is of interest in poled polymer applications, being about 8 times greater than that of the prototypical stilbene compound 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS) ($\mu\beta = 482 \times 10^{-48}$ esu).[10b] The magnitude of $\beta(0)$ is about 5–8 times that of its shorter analogs **4** and **5**, but *opposite* in sign. Within the context of the two-state model,[11] the sign of the β is related to the difference between the excited-state (μ_{ee}) and ground-state (μ_{gg}) dipole moments. The negative sign of β for **4** and **5** suggests that the magnitudes of their ground-state dipole moments are greater than those of their excited-state dipole moments, in contrast to **3**, whose positive β implies that its μ_{ee} is greater than its μ_{gg}. Thus, this positive β value for **3** is consistent with the observed positive solvatochromism (λ_{max} appears at 684 nm in hexanes, 696 nm in diethyl ether, and 726 nm in acetone). In contrast, **4** and **5** have smaller negative β values and exhibit slightly negative solvatochromism (λ_{max} of **5** appears at 570 nm in hexanes, 566 nm in diethyl ether, and 562 nm in acetone). The nuclear magnetic resonance (NMR) spectra provide further insight into the differences among the electron distributions in **3**, **4**, and **5**. In particular, there is a significant change in the chemical shift (see Figure 1) of the carbon (and its associated hydrogens) α to the amino nitrogen upon going from aniline derivatives (**6** and **7**) to squaraines (**4** and **5**), whereas there is very little change for the corresponding chemical shifts in going from **1** to **3**. In addition, the *trans* ^1H–^1H coupling

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[†] Molecular Materials Resource Center, The Beckman Institute, California Institute of Technology.

[‡] Jet Propulsion Laboratory, California Institute of Technology.

[§] DuPont Central Research and Development.

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(9) **3** was obtained with 36% yield and characterized by FAB-MS, ^1H and ^{13}C NMR, UV–visible, IR, and elemental analysis. Anal. Calcd for $C_{37}H_{45}NO_6$ ($3 \cdot H_2O$): C, 74.09; H, 7.56; N, 2.34. Found: C, 74.29; H, 7.55; N, 2.34.[8]

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(12) **4** and **5** were synthesized by condensing **2** with appropriate donors, **6** and **7**, respectively.[7] As analytically pure **4** was precipitated from the reaction solution, **5** was further purified by recrystallization from dichloromethane. **4** and **5** were isolated with 70 and 52% yields, respectively.[8]

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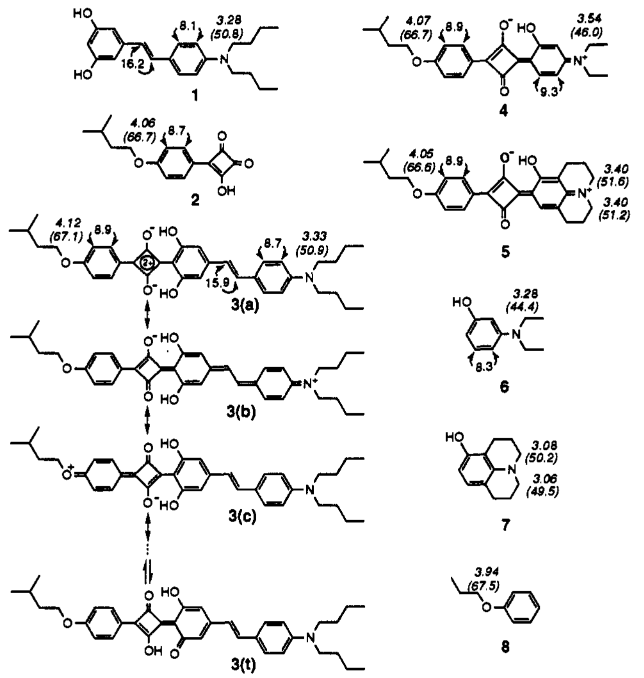

Figure 1. Structures of **1**–**8**, including canonical structures **3(a)**, **3(b)**, and **3(c)**; tautomeric structure **3(t)**, with selected nuclear magnetic resonance spectroscopic data. The italic numbers are ^{1}H and ^{13}C (in parentheses) chemical shifts (ppm relative to TMS in $CDCl_3$) for α-hydrogens and α-carbons of alkyl groups. The numbers sandwiched by a pair of curved arrows are the coupling constants (in Hz) between hydrogen atoms on adjacent carbons.

constant of central carbon–carbon double bond decreases only by 0.3 Hz from **1** to **3** (see Figure 1). These data imply that the structure of the stilbenyl moiety in **3** is only marginally perturbed from that in **1**. The downfield chemical shifts observed in **4** and **5**, in contrast, are suggestive of a significant increase in positive charge on the amino nitrogen.[13]

It is possible to rationalize both the NMR spectroscopic and the nonlinear optical results in terms of differences in the relative contributions of various canonical resonance structures to the ground state. Thus, for example, if a charge-transfer resonance structure (such as **3(b)**) dominates the ground state of **3**, then a negative β would be expected (we believe this to be the case for **4** and **5**). In contrast, if a canonical structure such as **3(a)** is most important, then **3** could be considered as a stilbene type compound with a strong acceptor and would be expected to have a positive β. Since, in its charge-transfer form, **3** has two six-membered rings that lose aromatic stabilization, whereas in **4** and **5** only one ring loses aromatic stabilization, it is possible that the ground-state structure of **3** is dominated by **3(a)**, whereas **4** and **5** have charge-transfer resonance forms corresponding to **3(b)** that contribute more to the ground-state structure. Such an explanation is fully consistent with the observed linear and nonlinear optical properties as well as the NMR spectra. However, it should be noted that a referee suggested that **3** may actually exist as a tautomeric structure, **3(t)**. Although we cannot exclude this interesting explanation with available spectroscopic data, we note that it would be possible for **4** and **5** to also adopt such a structure, in which they too would be expected to have positive β, which was not observed.

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Supplementary Material Available: Synthetic scheme for the synthesis of stilbene **1**, including the reaction conditions, and spectroscopic and analytical data for **2** and unsymmetrical squaraines **3**–**5** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[13] From NMR data (Figure 1), there is no substantial difference in the chemical shifts of the α-carbon and its associated hydrogens of the isopentyloxy moiety in **2**–**5** and the butyloxy group in **8**. In addition, the coupling constants between the phenylene hydrogens of 4-(isopentyloxy)phenyl in **3**–**5** are essentially the same. These data imply that the charge on the 4-(isopentyloxy)phenyl donor of **3**–**5** is similar.