Electronic Structure and Linear and Nonlinear Optical Properties of Symmetrical and Unsymmetrical Squaraine Dyes

Fabienne Meyers, Chin-Ti Chen, Seth R. Marder, and Jean-Luc Brédas*

Abstract: In this theoretical study, we investigate the molecular and electronic structures of symmetrical and unsymmetrical squaraine dyes. Such dyes can be represented by the formula D–A–D, where D is a donor group and A an acceptor moiety. We analyze the evolution in geometric structure that results from changing both donor substituents simultaneously or from varying only one donor group to produce an asymmetrical system. The changes in geometric and electronic structures are compared and found to be consistent. The trends in linear and nonlinear optical properties, and in particular in second-order polarizabilities, are investigated in several ways. The two-state model appears to be inadequate in describing the second-order polarizability, β. Consequently, we are unable to deduce simple structure/property relationships that might help in the design of quadrupolar compounds for nonlinear optics. Finally, a series of unsymmetrical squaraines with OH substitution and enol–ketone isomerism are investigated; the calculated nonlinear properties follow a similar trend to the experimental results: the OH substitution and isomerization contribute to increasing the ground-state polarization.

Keywords
nonlinear optics · quadrupolar compounds · quantum-chemical calculations · semiempirical calculations · squaraines

Introduction

The basic structure of the squarylium dye can be described as a 1,3-dioxygenated cyclobutene ring that is substituted at the 2 and 4 positions by electron-rich aromatic groups (Figure 1). Squaraine-type molecules are well known for their narrow and intense absorption bands in solution with molar extinction coefficients on the order of $10^5\,\text{M}^{-1}\text{cm}^{-1}$ and λ_{max} values in the visible to near-IR region, depending on the nature of the donor substituents on the aromatic rings.[1–4] Such large molar extinction coefficients suggest that there is extensive charge delocalization along the squaraine backbone D–A–D (where D is a donor and A a π electron acceptor). This system is quadrupolar in terms of its charge distribution. In an earlier theoretical paper, it was shown that the electronic distribution of the NMe_2/NMe_2 squaraine (see Figure 1 for definition of this notation) is highly polarized, as expected for the general formula D–A–D (here, D = anilino moieties and A = central C_4O_2 unit).[5] Furthermore, the charge transfer during the electronic transition between the ground state (S0) and the first excited state (S1), S1←S0, is found to be mostly confined within the C_4O_2 unit, with little charge being transferred from the anilino moieties to the C_4O_2 unit. Owing to significant intermolecular interactions, the squaraines exhibit a panchromatic absorption in the solid state (compared to that in solution, the absorption is broader and red-shifted). These dyes have been mostly studied in the context of organic semiconductors and photoconductors, with a view to applications in xerographic photoreceptors (e.g., as infra-red photoreceptors in diode laser printers), organic solar cells, or optical recording media.[6]

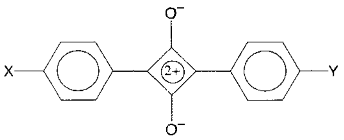

Figure 1. Squaraine-type molecule. X and Y are donor groups, such NMe_2 or OMe, or simply H. In this paper the general notation used for the molecule shown is X/Y; squaraines are referred to as symmetrical when X and Y are identical and unsymmetrical when X and Y are different.

In recent years, a renewed interest in squaraine-type molecules has arisen in the field of organics for nonlinear optics (NLO). Symmetric squaraines (i.e., X = Y in Figure 1) have been identified as prototypical structures displaying negative and unusually large third-order polarizabilities γ.[7] The origin of the negative sign of γ has been investigated by means of the so-called three-term model expression.[8–14] Contrary to some

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of the early proposals, the first excited state is not the only one that contributes to the third-order response, but its *negative* contribution to γ appears to be more important than the significant *positive* contributions from higher-lying two-photon excited states (i.e., states that possess the same symmetry as the ground state).

Symmetrical squaraines are, a priori, of no interest in terms of a second-order response, since these molecules are centrosymmetric, a feature that leads to vanishing even-order polarizabilities. However, a large second-harmonic generation (SHG) signal has recently been detected from an ultra-thin Langmuir–Blodgett film made of symmetrical squaraine species;[15, 16] the appearance of a second-order response has been attributed to a significant intermolecular charge transfer resulting in the formation of a noncentrosymmetric supramolecular unit (such as a dipolar dimer or higher aggregate).

Unsymmetrical squaraines (i.e., containing two different donor groups) are currently being investigated as a novel class of compound with interesting second-order NLO properties.[17, 18] Depending on the nature of the donor groups, the second-order polarizability can be tuned between positive and negative. In particular, EFISH (electric field induced second harmonic) measurements on systems with more extended conjugation (formed by replacing one benzene ring by a stilbene unit) indicate a $\mu\beta$ value that is roughly eight times larger than that of 4-*N*,*N*-dimethylamino-4′-nitrostilbene (DANS), a traditional (dipolar) D–A compound for second-order applications.[18]

At the present time, the relationship between structure and nonlinear optical properties is not well defined for quadrupolar D–A–D compounds. In contrast, structure/property relationships have been proposed for the more traditional D → A compounds, which have proved to be useful tools to guide the design of organic chromophores with optimized second- and third-order optical nonlinearities.[19–22] Based on quantum-chemical studies and backed by numerous experimental data, these relationships for the first-, second-, and third-order polarizabilities can be summarized in the form of Figure 2. The molecular structure (represented by the x axis of Figure 2) is directly related to the ground-state polarization (which itself depends on the degree of charge separation between donor and acceptor). In a polymethine-type dye, the relevant structural parameter is the degree of bond-length alternation (BLA, defined as the average difference in bond length of adjacent carbon–carbon bonds along the polyene segment). In our previous calculations, the changes in ground-state polarization were simply modeled by applying an external static electric field to the molecule;[21] in practice, the ground-state polarization can be tuned by 1) controlling the donor and the acceptor strength, 2) changing the topology of the conjugated segment between the donor and acceptor end groups, and 3) varying the solvent polarity.[22] The NLO properties were then evaluated for the whole range of possible BLA values, and relationships between BLA and the molecular polarizabilities were proposed.

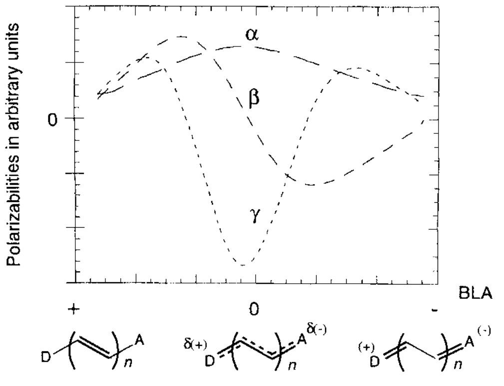


Figure 2. Qualitative evolution of the first- (α), second- (β), and third-order polarizabilities (γ) as a function of the ground-state polarization, measured in terms of bond-length alternation (BLA) for a generic push (donor, D)/pull (acceptor, A) polyene.[21]

The structure/property relationships reported in Figure 2, even though deduced for dipolar compounds, inspired our study of unsymmetrical squaraines for second-order properties. A standard approach for optimizing β in push–pull polyenes is to increase the strength of the donor and acceptor substituents; this corresponds to moving along the left-hand section of the β curve in Figure 2, starting at the polyene limit and decreasing the (positive) BLA value, thereby increasing β. In unsymmetrical squaraines the approach was different; rather than starting near the polyene limit (and decreasing the magnitude of BLA by searching for stronger donor or/and acceptor groups), we started from a highly polarizable cyanine-like structure, that is, a structure that results from an equal mixture of the neutral and charge-transfer resonance forms and possesses zero BLA (and vanishing β). In fact, a symmetrical squaraine can be represented by a mixture of the equivalent resonance forms shown in Figure 3, which translate into the highly symmetrical so-called cyclobutenediylium form (as represented in Figure 1). This form is thus comparable to a cyanine-like structure. When two different donor groups are introduced, the system becomes asymmetric, and the degree of ground-state polarization departs from the cyanine limit; consequently, non-zero (positive or negative) β values should be expected and have indeed been observed experimentally.[17, 18]

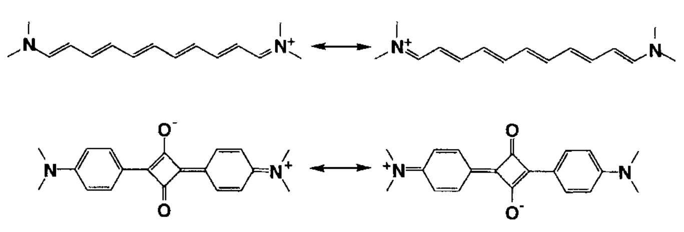


Figure 3. Canonical resonance structures for a cyanine compound (top) and a squaraine (bottom).

In the present work, we aim to test whether our previous analysis of the structure/NLO property relationships for dipolar systems can be extended to molecules that display a two-directional D–A–D charge-transfer (quadrupolar) character. We have undertaken a theoretical study of the geometric structures, electronic properties, and first- and second-order polarizabilities for a series of symmetrical (NMe_2/NMe_2, OMe/OMe, H/H) and related unsymmetrical squaraines (NMe_2/OMe, NMe_2/H, OMe/H). Squaraines with hydroxy substituents on a phenylene ring are also considered.

Methodology

The geometries of all molecules investigated in the present study are optimized at the semiempirical Hartree–Fock AM1 level.[23] This method is known to afford accurate geometry estimates for organic molecules. Since no environmental effects are included in the determination of the molecular structures, the (hyper)polarizabilities calculated for these structures cannot strictly be compared to the experimental values. However, in this study, our main goal is to contrast the behavior of quadrupolar molecules (in this case, squaraine dyes) with that of the more traditional dipolar compounds.

The transition energies, state dipole moments, and transition dipole moments were calculated with the INDO Hamiltonian coupled to configuration interaction (CI).[24] Here, the CI consisted of single (S) excitations between all π molecular orbitals (SCI calculation). Finally, the calculation of the molecular polarizabilities was based on the sum-over-states (SOS) approach, that is, on the perturbation expansion of the Stark energy of the molecule.[25] Within the SOS approach, the expressions of the static first- and second-order polarizabilities are given by Equations (1) and (2), where $\Delta\mu$ is the difference between the dipole moments in the excited state (e) and the ground state (g), E_{ge} the transition energy between e and g, and μ_{ge} the corresponding transition dipole moment. The state e' refers to higher excited states. The first term in expression (2) corresponds to the so-called two-state model, which only includes the contribution of the ground state and the main charge-transfer excited state (generally the lowest one).[26, 27]

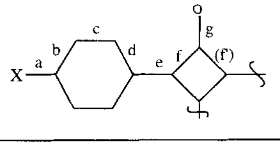
$$\alpha \propto \sum_{e \neq g} \frac{\mu_{ge}^2}{E_{ge}} \tag{1}$$

$$\beta \propto \sum_{e \neq g} \frac{\mu_{ge}^2 \Delta\mu}{E_{ge}^2} + \sum_{e \neq g} \sum_{e' \neq g \neq e} \frac{\mu_{ge}\mu_{ee'}\mu_{e'g}}{E_{ge}E_{ge'}} \tag{2}$$

Results and Discussion

Ground-State Structures—Geometry and Charge Distributions: The molecular structures of all symmetrical and unsymmetrical squaraines were fully optimized at the AM1 level. In every case, a planar structure is observed to be the most stable conformation. Some typical bond lengths are reported in Table 1 and compared to the geometry of corresponding D–A compounds previously studied. The parameter that best expresses the influence of the donor end group is found to be the degree of bond-length alternation within the phenylene ring, Δr; here Δr is defined as the average sum of the absolute value of the bond-length differences between the bond involving *ortho* carbons and the adjacent two bonds (see Table 1). In a purely aromatic system, Δr is zero (for example, in benzene all the carbon–carbon bond lengths are calculated to be 1.395 Å at the AM1 level); it gradually increases with increasing quinoidal character. In Table 1, the structures of the symmetrical squaraines H/H, OMe/OMe, and NMe_2/NMe_2 are compared to those of *para*-nitroaniline (PNA), characterized by a dominant aromatic character, and diaminodicyano-*para*-quinodimethene (PQ), characterized by a quinoidal character. From these geometries it can be seen that the phenylene ring in the squaraines has a predominant aromatic character, which evolves, as expected, towards a more quinoidal structure with increasing donor strength of the end group X. The geometric changes inside and adjacent to the squaraine ring upon substitution are small; the maximum change is in the bond length *e* (0.007 Å, from 1.409 Å in H/H to 1.402 Å in NMe_2/NMe_2; Table 1).

Table 1. AM1-optimized bond lengths (in Å) of symmetrical squaraines H/H, OMe/OMe, and NMe_2/NMe_2, and of D-benzene-A compounds, *para*-nitroaniline (PNA; $D = NH_2$, $A = NO_2$) and diaminodicyano-*para*-quinodimethene (PQ; $D = (NH_2)_2C$, $A = C(CN)_2$). The bond-length alternation (Δr) is given by $1/2[|b-c| + |d-c|]$.



	a	*b*	*c*	*d*	*e*	*f*	*g*	Δr
X = H	1.101	1.397	1.390	1.412	1.409	1.476	1.228	0.014
X = OMe	1.374	1.404	1.383	1.415	1.405	1.475	1.229	0.026
$X = NMe_2$	1.384	1.425	1.381	1.413	1.402	1.475	1.231	0.038
PNA	1.370	1.423	1.383	1.407	1.477			0.032
PQ	1.422	1.435	1.359	1.443	1.377			0.080

In Figure 4 the Δr results for the unsymmetrical squaraines are summarized and compared to those for their parent compounds (i.e., the related symmetrical squaraines); for example, in the case of NMe_2/H, the Δr values for the phenylene rings attached to NMe_2 and H are compared to those of NMe_2/NMe_2 and H/H, respectively. It can be seen from Figure 4 that the unsymmetrical substitutions introduce deviations from the structures of the parent symmetrical compounds. The stronger donor substituent induces a more pronounced quinoidal character in the phenylene ring to which it is attached, while the weaker donor substituent induces a less quinoidal (i.e., more aromatic) character. The amplitude and sign of the deviations in the unsymmetrical squaraines (i.e., the difference between the Δr value in a given phenylene ring and that in the related symmetrical squaraine) depend on the difference in strength between the two donor substituents. For example, in NMe_2/H, the deviation is larger and positive (+ 0.008 Å) in the phenylene ring connected to NMe_2, and smaller and negative (− 0.002 Å) in the phenylene ring connected to H. NMe_2/H thus appears to be "more unsymmetrical" than, for example, the OMe/H molecule, which has smaller deviations in both rings (+ 0.002 and −0.001 Å).

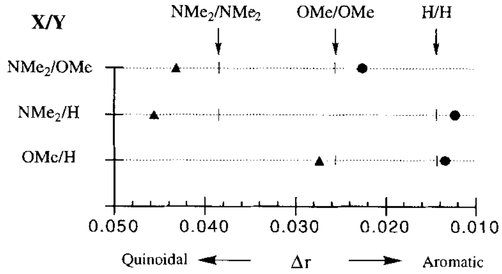


Figure 4. Bond-length alternation (Δr, in Å) in the phenylene rings of unsymmetrical squaraines compared to the related symmetrical parent squaraines. Each horizontal line represents one compound. ▲ = Δr in the ring substituted by X in X/Y; | = equivalent value in X/X (Y/Y); ● = Δr in the ring substituted by Y in X/Y.

The geometry of the squaraine ring of the unsymmetrical compounds is little affected; the carbon–carbon bond length varies at most from 1.464 to 1.484 Å, while in symmetrical systems, this bond length remains at 1.475 Å (bond *f*, Table 1).

In order to understand the geometric evolutions in the symmetrical and unsymmetrical squaraines, we investigated qualitatively the π-charge distributions, provided by the Mulliken populations (Figure 5). Calculations were performed at the INDO-CI level based on the AM1 geometries.

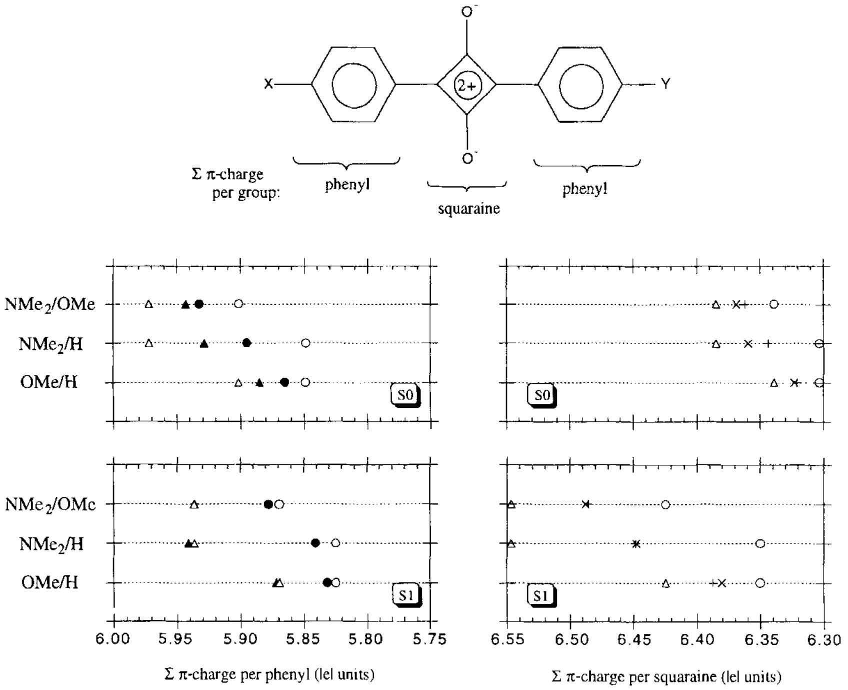


Figure 5. The total (INDO-SCI//AM 1) π-charge distribution in the two phenylene rings (left) and in the central squaraine ring (right) for the unsymmetrical squaraines in the ground state S0 (top) and in the first excited state S1 (bottom). For the phenylene π-charge analysis, the charges in the ring substituted by X in X/Y (▲) and the ring substituted by Y in X/Y (●) are compared to those for the corresponding symmetrical molecules X/X (△) and Y/Y (○), respectively. The charge in the squaraine ring of X/Y (×) is compared to the values observed in X/X (△) and Y/Y (○), and to the average of these two values (+).

The analysis provides evidence that, in the ground state of the symmetrical squaraines, the donor substituents mainly affect the adjacent phenylene ring and to a smaller extent the central squaraine ring, with both entities gaining π-electron charge upon substitution. The total π charges for each phenylene ring are reported in Figure 5; they lie between the 5.85|e| in H/H and 5.97|e| in NMe_2/NMe_2; in the central moiety, the total π charges lie between 6.30|e| in H/H and 6.38|e| in NMe_2/NMe_2. The increase in π charge in the phenylene rings and in the central squaraine ring depends, as expected, on the strength of the donor substituents ($NMe_2/NMe_2 > OMe/OMe > H/H$).

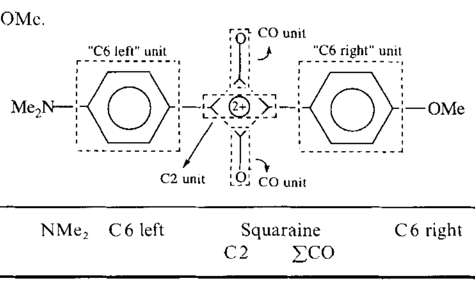
The π-charge distributions in the unsymmetrical squaraines are also given in Figure 5. In comparison to the related symmetrical parent compounds, it is interesting to note that, upon unsymmetrical substitution, the ring next to the strongest donor substituent (i.e., following our convention, the ring on the left-hand side in Figure 5) appears to give more charge to the adjacent ring. The opposite is calculated for the other ring, which exhibits a weaker donor character, with respect to its symmetrical parents. This behavior is in qualitative agreement with the trend observed in the geometric structures (i.e., more and less quinoidal character, respectively, for the rings on the left-hand and right-hand sides).

In the squaraine ring, the total π charges change less than in the phenylene rings (the x axes in Figure 5 each cover 0.25|e|, in order to facilitate comparison). In the symmetrical squaraines, those with stronger donors have greater π charges within the central ring; in the unsymmetrical compounds, the π charge is calculated to lie between the limits found in the symmetrical parent molecules and to be slightly greater than the average of the latter two values (Figure 5). In absolute terms, the changes are small; this suggests that, in the ground state, there is no strong charge transfer from either donor moiety to the central acceptor squaraine ring. Similar conclusions have been reached in previous studies on donor–acceptor compounds,[28] such as diphenylacetylenes,[29] push–pull polyenes,[30] and 2H-pyrrole derivatives.[31]

Charge-transfer excited state: The π-charge distributions, obtained at the INDO/SCI level, on the basis of the AM 1 ground-state geometry, have also been analyzed in the lowest excited state, S1. The excited- and ground-state geometries are considered to be the same, since under optical frequencies, no geometric relaxation can occur. At the CI level the first excited state is found to mainly correspond to the one-electron transition between the HOMO and LUMO levels. In order to obtain a qualitative idea of the nature of the molecular orbitals, we report in Table 2, the sum per group (donor, phenylene, and squaraine rings) of the square of the HOMO and LUMO LCAO coefficients. If we consider a similar picture for a traditional dipolar compound, such as *para*-nitroaniline, the HOMO level is mainly localized on the donor/phenylene segment, while the LUMO level is mostly localized on the acceptor group. In contrast, the differences between the HOMO and LUMO levels in the squaraine compounds are mainly confined within the squaraine ring itself; the largest charge transfer upon excitation is from the CO moieties to the central C2 unit (the units are defined in Table 2). Since the wavefunctions are evenly spread over the donors, phenylene groups, and the acceptor center, a large transition dipole may be

Table 2. Contribution (in percent) of the units indicated below to the wavefunction of the HOMO and LUMO levels calculated for the unsymmetrical NMe_2/OMe squaraine and, for comparison, for a conventional D–A compound, *para*-nitroaniline.

a) NMe_2/OMe.



	NMe_2	C6 left	Squaraine		C6 right	OMe
			C2	ΣCO		
HOMO	7	26	16	25	24	2
LUMO	2	23	55	0	18	2

b) *para*-nitroaniline.

	NH_2	Phenylene	NO_2
HOMO	25	71	4
LUMO	3	44	53

0947-6539/97/0304-0533 $ 17.50+.50/0

expected, as well as a small difference between the state dipoles in the ground and first excited states.

In the first excited state, the sum of the π charges over the phenylene rings lie between 5.82|e| in H/H and 5.94 |e| in NMe_2/NMe_2 (Figure 5); this means that upon excitation both phenylene rings give more π charge to the central ring (on average 0.03|e| per phenylene ring, see Figure 5). A striking observation is that, in contrast to the distribution in the ground state, the unsymmetrical squaraines have π-charge distributions in their phenylene rings that are nearly identical to those in the related symmetrical parents.

In the central moiety, the total π charge spreads over a larger range of values, from 6.35|e| in H/H to 6.55|e| in NMe_2/NMe_2. The increase upon excitation is 0.05|e| in H/H and 0.17|e| in NMe_2/NMe_2. In the unsymmetrical squaraines, the π-charge increases upon excitation lie between these extremes, from 0.06|e| in OMe/H to 0.12|e| in NMe_2/OMe (they closely match the estimated average values of the charges evaluated for the parent molecules, see Figure 5).

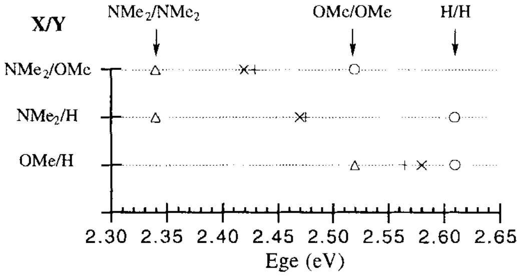


Figure 6. First transition energies (E_{ge}) for the squaraine compounds. The E_{ge} for X/Y (×) is compared to the calculated values in the two parent molecules, X/X (▵) and Y/Y (○), as well as to the average of these two values (+).

The vertical excitation energies, E_{ge}, calculated at the INDO/SCI level are reported in Figure 6. In symmetrical squaraines, the gap is calculated to shift to the red as the donor substituents become stronger. We note, however, that this red-shift is rather small, when compared to that of a series of donor–acceptor *para*-substituted benzene compounds. From our calculations on isolated ("gas-phase") molecules, the shift observed between NMe_2/NMe_2 and H/H is about 0.27 eV; experimental data on donor–phenylene–CH=CH–NO_2 compounds show a shift of up to 1 eV on going from NMe_2 to a simple H as the end-group.[32, 33]

In unsymmetrical squaraines, the E_{ge} value is always estimated to be between the values calculated for the parent symmetrical squaraines, and again very close to the average value calculated for the parent molecules (see Figure 6). Brooker has made similar comparisons of the experimental data for merocyanines and related cyanine and oxonol molecules, and for unsymmetrical cyanines and the related symmetrical cyanines; his goal was to determine the relative donor and acceptor strengths of the end groups in merocyanines and cyanines. The way Brooker proceeded was to compare the λ_{max} value of a merocyanine (or unsymmetrical cyanine) compound with the average value calculated on the basis of the measured λ_{max} of the parent compounds. The difference between these two values is now known as the *Brooker deviation* and constitutes a measure of the effective degree of electronic asymmetry.[34, 35] Within the series of unsymmetrical squaraines investigated in this work, the deviation (which we prefer to evaluate in eV) is always rather small; this suggests that even though the geometric structure is somewhat unsymmetrical, the electronic structure can effectively be considered as nearly symmetrical. Indeed, in some of his examples, Brooker obtained deviations on the order of several tenths of an eV (which is considered to be large), whereas we only obtain deviations of a few hundredths of an eV. This very weak deviation is in agreement with the experimental data gathered for the squaraine derivatives that we are interested in: in chloroform, NMe_2/NMe_2 has a λ_{max} of 624 nm (1.99 eV), and OMe/OMe a λ_{max} of 536 nm (2.31 eV).[36, 37] The average of these values is about 2.16 eV; this is identical to the experimental λ_{max} measured in chloroform for NMe_2/OMe, namely, 2.14 eV (λ_{max} of 579 nm).

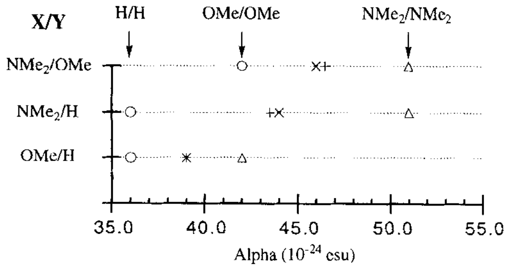


Figure 7. The average first-order polarizability, $\langle\alpha\rangle$, for the squaraine compounds. See caption of Figure 6 for the description of symbols.

Molecular polarizabilities: The first-order polarizability, α, was calculated within the INDO–SCI–SOS formalism, including the lowest 50 states. The results are illustrated in Figure 7. The average first-order polarizabilities of the symmetrical squaraines increase with increasing donor strength. This trend is suggested by the trend in E_{ge} values; in fact, the simplest formulation of α, within a two-state model, indicates that the first-order polarizability is inversely proportional to E_{ge}^2. Since the NMe_2/NMe_2 absorption is the one that is most red-shifted, this compound is expected to have the largest polarizability.

The results obtained for the unsymmetrical squaraines are comparable to those obtained for the symmetrical compounds. α is calculated to be very close to the average of the values obtained for the parent (symmetrical) molecules. This trend is consistent with that observed for the E_{ge} values.

We now turn to the second-order polarizabilities. For reasons of symmetry we are now restricted to the unsymmetrical systems. As in the case of the first-order polarizability, we calculated β within an SOS formalism including up to 50 states. First, it is useful to compare the 50-state converged value with that obtained with the simple two-state model, where the only excited state included in Equation (2) is S1. This comparison allows us to point out the *failure of the simple two-state model to accurately describe the second-order polarizability for such D–A–D compounds*. The failure of this simple model is certainly not unprecedented.[29, 38, 39] In Figure 8, we present the convergence of the SOS approach as a function of the number of states

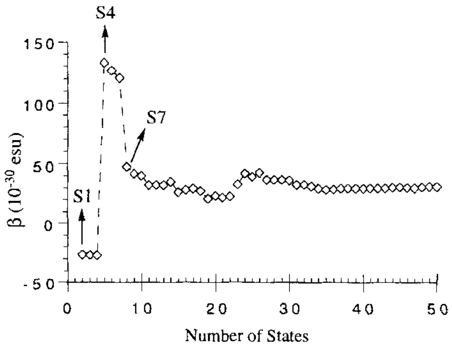


Figure 8. Plot of β of NMe_2/OMe as a function of the number of states; the two-state value, implying the contribution of only S0 (the ground state) and S1 (the first excited state) is marked as S1 [1 β (10^{-30} esu) = 3.71×10^{-51} $C^3m^3J^{-2}$].

taken into account; it illustrates that for NMe_2/OMe, the contribution of higher excited states is significant. Within the SOS formalism, terms proportional to $\mu_{ge}\mu_{ee'}\mu_{e'g}/E_{ge}E_{ge'}$ can provide either a positive or negative contribution to the second-order polarizability. For example, in the case of NMe_2/OMe, the analysis of the SOS terms reveals three major contributions: one involving S1 (-29×10^{-30} esu), one involving excited state S4 (with a contribution of about $+160 \times 10^{-30}$ esu), and one involving S7 (with a contribution of about -70×10^{-30} esu).

The discrepancy between the two-state model value and the 50-state converged value precludes any simple analysis to correlate β with the transition energy, the transition dipole moment, and the difference between the dipole moments in the first excited state and the ground state. Nevertheless, in an attempt to establish structure–property relationships, we investigated the possibility of relating β to a structural parameter that could translate the degree of ground-state polarization. A total of ten asymmetrical squaraines were analyzed, namely, all the possible combinations of NMe_2, NH_2, OMe, OH, and H as donor groups. Three different structural parameters were analyzed:

1) ΔR_1, the average value of the Δr parameters for the two benzene rings in X/Y.
2) ΔR_2, the deviation relative to the related symmetrical squaraine, defined as $(\Delta r - \Delta r(\text{sym}))_X + (\Delta r - \Delta r(\text{sym}))_Y$. Thus, if Δr of X in X/Y is less (i.e., more aromatic) than that of X/X [i.e., $(\Delta r - \Delta r(\text{sym}))_X$ is negative] and Δr of Y in X/Y is greater (i.e., more quinoidal) than that of Y/Y [i.e., $(\Delta r - \Delta r(\text{sym}))_Y$ is positive], the sign of ΔR_2 then reflects the dominant trend (i.e., more aromatic if negative, or more quinoidal if positive).
3) ΔR_3, the difference in bond length within the squaraine ring, defined as $[f - f']$ (see formula, Table 1).

The results of these three analyses are reported in Figure 9; unfortunately, they do not provide any straightforward conclusions, as the correlation between β and ΔR_i is in each case very poor.

At this point, we can certainly question the soundness of such analyses. In fact, even though the ground-state polarization and the second-order polarizability are both dependent on the molecular structure, this does not imply that the hyperpolarizability only depends on the ground-state polarization. In others words, the fact that no clear trends are observed between structure (as reflected in ΔR_1, ΔR_2, or ΔR_3) and property (β) for a series of unsymmetrical squaraines (Figure 9) might be related to a basic assumption of our approach, which supposes that it is only through its influence on the molecular structure that the end group is important in determining the magnitude of β. We are currently developing a novel approach that goes beyond such limitations.[40]

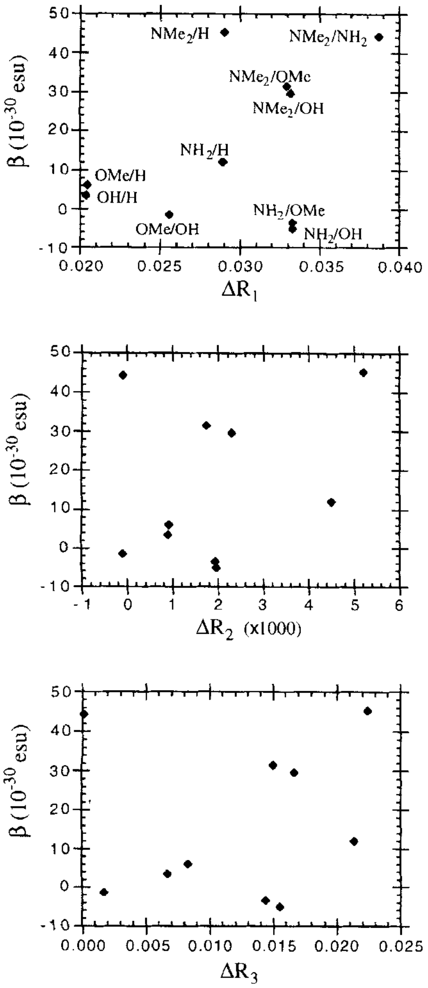
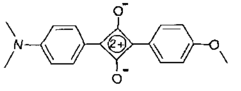
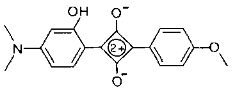
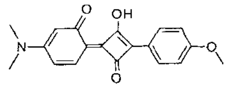
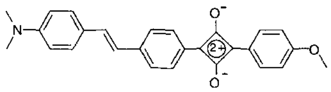
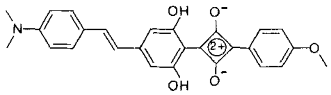
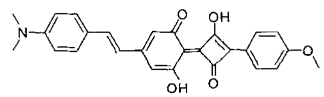


Figure 9. Plot of β as a function of three different structural parameters, calculated on the basis of the optimized AM1 bond lengths (see text for details).

Unsymmetrical squaraines with OH substitution: We finally focus on NMe_2/OMe molecules substituted with an OH group on the aniline ring or having a longer conjugation pathway between the amino substituent and the squaraine unit (replacing the aniline ring by an aminostilbene unit, see Table 3), since these can be related to molecules that have been investigated experimentally. In these longer systems, the molecular structure has a more "asymmetrical" character and therefore stronger similarities with dipolar systems might be expected. We also examine the effect of a possible enol–ketone isomerization, shown in Table 3.

The OH substitution in the aniline ring and even more so the ketone isomeric form induce a stronger aromatic character in the phenylene ring located to the right of the squaraine moiety (the corresponding Δr values are reported in Table 3). Accordingly, the overall character on the left-hand side becomes more quinoidic. We observe a concomitant increase in total π charge

Table 3. Structure and properties (Δr in the benzene ring on the right-hand side, total π charges on the squaraine unit, and second-order polarizability β) for the OH-substituted series.

	Δr (in Å)	π charges (in lel)	β (10^{-30}esu)
NMe2/OMe and OH-substituted analogues			
	0.024	6.37	32
	0.021	6.41	-86
	0.017	6.82	-97
"Stilbene analogues"			
	0.026	6.34	370
	0.022	6.42	178
	0.017	6.82	66

on the squaraine ring itself (Table 3) upon OH substitution and isomerization, which thus acts as a stronger acceptor. OH substitution *ortho* to the squaraine ring and ketone isomerization thus both appear to increase the ground-state polarization in the left-hand D–A segment.

The calculated hyperpolarizabilities β are reported in Table 3, and a rough attempt at interpreting the data is given in Figure 10. Qualitatively, the shape of the β curve appropriate for a dipolar compound, provides a zero value for a "symmetrical" ground-state polarization (central portion of the curve); in other words, in the context of the present study, this would correspond to the case of a symmetrical squaraine. The NMe_2/OMe and OH analogues with phenylene rings between the donors and the squaraine unit are only slightly asymmetrical; they would therefore belong to the central part of the curve and might go from positive to negative β values when the ground-state polarization is increased (e.g., by going from the NMe_2/OMe compound to the OH-substituted analogue and then to the ketone isomer). The molecules containing a stilbene unit are less centrosymmetric to begin with and are therefore found to the left of the zero-point of the curve; increasing the ground-state polarization (by OH substitution and isomerization) then results into a gradual decrease in β (i.e., towards the zero point). This interpretation is of course oversimplified, since we are effectively reducing the complexity of a quadrupolar system to a dipolar one. Nevertheless, we gain some confidence in its validity by looking at the experimental behavior observed for the squaraines studied. First, the OH analogue of NMe_2/OMe, for which a negative β is calculated, has a negative hyperpolarizability as measured by EFISH, and exhibits a slight negative solvatochromism.[18] Also, the positive β values calculated for the stilbene analogues are in agreement with the experimental observations, including the results of EFISH measurements and the positive solvatochromism reported by Chen et al.[18]

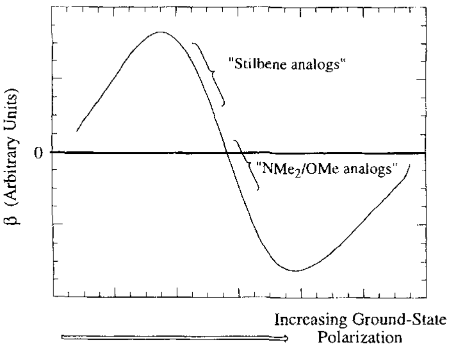


Figure 10. Sketch of β as a function of the ground-state polarization for the NMe_2/OMe and OH-substituted compounds, and for the stilbene analogues.

Conclusion

We have presented a theoretical study of a series of symmetrical and unsymmetrical squaraines. These molecules are best described by a *quadrupolar* charge distribution, in contrast to the more traditional organic *dipolar* compounds studied for their large second-order polarizabilities. Our calculations have addressed the trends in molecular and electronic structures, charge distributions, and first- and second-order polarizabilities. The results emphasize the unusual behavior of squaraine-type molecules and the failure of a two-state model to describe the second-order polarizability β. The magnitude of β cannot be related in a straightforward manner to a structural parameter that reflects the degree of ground-state polarization. Such a concept has been previously applied with much success to dipolar systems, but appears not to be appropriate for the type of quadrupolar system examined here.

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