Molecular design for squaraines with large positive or negative third-order optical nonlinearity

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Received 29th June 2001, Accepted 9th August 2001
First published as an Advance Article on the web 11th September 2001

The second hyperpolarizabilities $\gamma$ have been investigated for a series of centrosymmetric squaraines by using semiempirical finite-field (FF) and time-dependent Hartree–Fock (TDHF) methods. The calculation shows that the squaraines dyes may exhibit significant negative or positive $\gamma$ values, depending on their molecular structures. By choosing 2,4-diphenyl-squaraine as a prototype, the para and/or ortho substitution effect on the magnitude and sign of $\gamma$ were investigated. The dye with powerful electron-donating groups at the para positions exhibits a large negative $\gamma$ value, while the less powerful donors lead to a small $\gamma$ value. When the donors are very weak or replaced by electron-withdrawing groups, then $\gamma$ may become positive. The dye with powerful electron-withdrawing groups at the para positions may exhibit a large positive $\gamma$ value. The introduction of ortho hydroxy groups helps to polarize the carbonyl groups, making the central acceptor more powerful in its electron-withdrawing ability and enhancing greatly the negative $\gamma$ values.

1. Introduction

Organic materials have attracted much interest for nonlinear optical (NLO) applications because of their potentially large and fast second- and third-order polarizabilities, $\beta$ and $\gamma$. A large number of organic compounds have been examined experimentally and theoretically to establish the structure-property relationships of the NLO materials. Since the observation by Dirk et al., of the large negative third-order optical susceptibilities $\gamma$ in squaraines, these dyes have been considered as potential third-order nonlinear optical materials. Squaraine dyes typically contain an electron-withdrawing central four-membered ring and two electron-donating groups in the form of donor-acceptor-donor (DAD). So far, however, most efforts have focused on D–A substituted $\pi$-conjugated systems for which a carefully established structure-property relationship has been used in describing their NLO behavior or in designing new chromophores with enhanced NLO responses. For example, a large value of $\beta$ can be reached by strengthening the donor-acceptor pairs and/or lengthening the conjugation paths. Unlike the DA systems, the structure-property relationship for the DAD systems has not been well understood yet. For some compounds with DAD motifs, it has been found that their NLO properties exhibit exceptional sensitivity to subtle changes of their structures. Using a hyperpolarizability density analysis method, Nakano et al. have elucidated a structure-property relationship for the second hyperpolarizabilities of some centrosymmetric molecules. Using a valence-bond charge-transfer (VB-CT) model, Cho et al. have proposed a qualitative description for the second hyperpolarizabilities of some ‘quadrupolar’ systems. According to their conclusions, the second hyperpolarizabilities of DAD- or ADA-like molecules can be optimized by altering the electronic donating/withdrawing ability of the donor/acceptor moieties. Moreover, the sign of $\gamma$ can be controlled in the same way. In our previous study, we proposed a structure-property correlation for these types of molecules with a field simulation method. The $\gamma$ values of the prototypical molecule, 1,13-diamino-1,3,5,8,10,12-hexatriene-7-one, depend strongly on the molecular structure parameters known as bond length alternation (BLA). A large positive or negative value of $\gamma$ can be obtained by alternating the donor–acceptor pairs and/or the conjugation paths.

MO calculation of molecular hyperpolarizabilities and comparison of the results with the corresponding experimental results are of importance in establishing the structure-property relationship and estimating the amount of such effects on molecular optical nonlinearity. The field simulation is a helpful approach that has been widely used in investigating structure dependence of organic NLO materials. However, the large variation in NLO responses predicted by this method can hardly be observed since the molecular structure distortion is much less than that resulting from an external electric field. It also often overestimates the solvent effect of NLO properties when it is used to simulate solvent environments with various relative permittivities. A recent calculation at $ab\ initio$ level by Bishop et al. revealed that the field simulation method does not give a definite trend for NLO polarizabilities, especially for second hyperpolarizabilities, of some selected push–pull chromophores. For this reason, it is necessary to further examine the proposed structure-property relationship for DAD-like NLO organic compounds. Squaraines are typical DAD-like molecules with prominent NLO properties. We present here a theoretical study of the second hyperpolarizabilities of centrosymmetric squaraines with the aim of formulating some routes to control the signs and magnitudes of their $\gamma$ values in a molecular design procedure. The sign of $\gamma$ is important in quantum optics where a positive value causes the self-focussing effect of an incident beam, while a negative one causes self-defocussing effects. Moreover, such DAD-like compounds are expected to be candidates for ‘controllable NLO materials’ an exciting dream in nonlinear optics.

2. Computational details

We chose 2,4-diphenyl-squaraine (Fig. 1) as a parent unsubstituted molecule in which two phenyl groups tend to

DOI: 10.1039/b105717k
Phys.

groups, such as amino as well as some strong electron-(NH

and/or the

para

Various substituents are attached symmetrically to the

dividual benzene scheme of its derivatives.

Fig. 1 Molecular geometry of 2,4-diphenyl-squaraine and the num-

bering scheme of its derivatives.

Fig 1

stabilize the distorted structures caused by active substituents.

Various substituents are attached symmetrically to the para

and/or the ortho positions of the two phenyls. The substitu-

ents at para positions include some strong electron-donating

groups, such as amino (NH\textsubscript{2}), as well as some strong electron-

withdrawing groups, such as nitro (NO\textsubscript{2}). The substituents at the

ortho positions are hydroxy groups or fluorines. The hydroxys

and fluorins have different effects on the central acceptors, carboxyls. The hydrogen atoms of the hydroxys stretch towards the oxygen atoms of the carbonyls, as illustrated by crystallographic experiments.\textsuperscript{16} The molecular geometries are optimized by using AM1 parametrization\textsuperscript{17} with the ’precise’ option included in the MOPAC package.\textsuperscript{18} A single excitation configuration interaction (SCI) approach\textsuperscript{19} with AM1 parametrization involving the highest 20 occupied and the lowest 20 virtual molecular orbitals was used to calcu-

late the electronic spectra of these dyes. Then two approaches, finite-field (FF)\textsuperscript{20} and time-dependent Hartree–Fock (TDHF),\textsuperscript{21} are used to calculate the second hyperpolarizabilities. The FF procedure evaluates the second hyperpolarizabilities by numerically differentiating the energies or dipole moments with respect to the external electric fields. The strength of the applied electric field is set to 0.001 au and the SCF conver-

gence criterion is tightened to 10\textsuperscript{-12} to meet the numerical precision. The TDHF calculations were performed using the Games program.\textsuperscript{22} Since the Fock matrixes in the TDHF frame are not symmetric, the molecular symmetry was closed in the NLO calculations. A default setting of convergence tol-

erances was used to compute the first- and second-order polar-

zabilities, \(\alpha\) and \(\beta\), which are necessary for the evaluation of \(\gamma\). In the present work, in addition to the static second hyper-

polarizability \(\gamma(0,0,0,0)\), results of the calculations of the fol-

lowing frequency-dependent NLO properties at optical wavelengths \(\lambda = 710, 1064\) or 1907 nm, are reported: optical Kerr effect (OKE) \(\gamma(\omega_0,0,0,0)\), dc-electric-field-induced second-harmonic generation (dc-EFISHG) \(\gamma(2\omega,0,0,0,0)\), third-harmonic generation (THG) \(\gamma(3\omega,0,0,0,0)\). The AM1 parametrizations were used throughout our NLO properties calculation in both the FF and TDHF approaches. We have concluded previously that AM1 parametrizations and the MNDO Hamiltonian produce very similar results for the second hyperpolarizabilities of DAD systems in the FF approach.

The molecule lies in the \(xy\) plane with the para substituents stretching in the \(x\) direction, so that the longitudinal com-

ponent \(\gamma_{xxx,xxx}\), in most cases, dominates the averaged isotropic value \(\langle \gamma \rangle\), which is defined as

\[
\langle \gamma \rangle = \frac{1}{15} \sum_{ij} (\gamma_{ijij} + \gamma_{ijij} + \gamma_{ijij}); i, j = x, y, z
\]

For comparison, both methods were performed on the same Cartesian coordinates for each molecule.

3. Results and discussions

3.1. Molecular geometries

The two phenyls and the central squaric ring are essentially planar for all the optimized squaraines. Table 1 lists some of their structural parameters. The four CC bonds in the squaric ring have close bondlengths with an average of 1.475–1.481 Å, contrary to the squarate dyes in which distinct single and double bonds alternation exists in the squaric ring.\textsuperscript{23} The average CC length in the two phenyls is between the standard lengths of a single bonded C–C and a double bonded C=C, implying that there is extensive delocalization throughout the molecule. The phenyl groups serve as two conjugation bridges connecting the donor–acceptor–donor system. The high delocal-

ization in the conjugation paths is beneficial to the intra-

molecular charge transfer and to the stability of the molecule.

Table 1 The structural features and electronic absorption spectra of squaraines

<table>
<thead>
<tr>
<th>Squaric ring</th>
<th>Phenyls</th>
<th>Electronic absorption spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–O</td>
<td>C–C</td>
<td>(\Delta^a)</td>
</tr>
<tr>
<td>Sq1</td>
<td>1.231</td>
<td>1.475</td>
</tr>
<tr>
<td>Sq2</td>
<td>1.231</td>
<td>1.475</td>
</tr>
<tr>
<td>Sq3</td>
<td>1.231</td>
<td>1.475</td>
</tr>
<tr>
<td>Sq4</td>
<td>1.229</td>
<td>1.476</td>
</tr>
<tr>
<td>Sq5</td>
<td>1.229</td>
<td>1.476</td>
</tr>
<tr>
<td>Sq6</td>
<td>1.229</td>
<td>1.476</td>
</tr>
<tr>
<td>Sq7</td>
<td>1.227</td>
<td>1.477</td>
</tr>
<tr>
<td>Sq8</td>
<td>1.227</td>
<td>1.477</td>
</tr>
<tr>
<td>Sq9</td>
<td>1.226</td>
<td>1.477</td>
</tr>
<tr>
<td>Sq10</td>
<td>1.241</td>
<td>1.478</td>
</tr>
<tr>
<td>Sq11</td>
<td>1.226</td>
<td>1.479</td>
</tr>
<tr>
<td>Sq12</td>
<td>1.237</td>
<td>1.479</td>
</tr>
<tr>
<td>Sq13</td>
<td>1.222</td>
<td>1.481</td>
</tr>
</tbody>
</table>

\(^a\) Standard deviation of the CC bondlengths in the two phenyl groups. \(^b\) Cut-off wavelength, in nm. \(^c\) Oscillator strength of the cut-off absorption. \(^d\) Maximum absorption wavelength, in nm. \(^e\) Oscillator strength of maximum absorption. \(^f\) Measured in methylene chloride, ref. 27.
The C-O bonds in all molecules possess remarkable double-bonded character with a slight decrease in length when the two terminally strong electron-donating groups are replaced by strong electron-withdrawing groups. A similar trend is found for the average CC length in the phenyl groups. The standard deviation of the CC length in the phenyls can be used to describe their quinoid character. The standard deviation is relatively large for Sq1, Sq2 or Sq3 of which the two terminal groups are strongly electron-donating, indicating that strong donors in squaraines lead to great quinoid characters. This means that the charge-transfer resonance forms dominate the ground state, according to the viewpoint of the valence-bond charge-transfer (VB-CT) model.\textsuperscript{10,24,25} In the case of Sq7, Sq8, or Sq9, the strong electron-withdrawing groups at the two ends lead to a relatively small standard deviation. That is, the contribution from the CT forms decreases, while that from the VB form increases. Such structural features are consistent with Dirk\textsuperscript{3} and Marder\textsuperscript{26} results for some other squaraines. The variation in the molecular structures resulting from the substitution of the end groups confirms our previous description for the structural features of a DAD-like prototype molecule.

The average CO length of the carbonyls becomes longer when 4 hydroxys are attached to the ortho positions of the phenyls, induced by the hydrogen atoms of the hydroxys. The 4 hydroxys make the carbonyls stronger in their electron-withdrawing abilities. However, the fluorins do not have much effect on the carbonyls because of the long distance between the fluorine and the oxygen atom. The CC lengths in phenyls are thus affected by substitution at the ortho positions. In these cases, the relation between the standard deviation and the quinoid character of the phenyls becomes much complicated.

3.2. Electronic spectra

Experiments have revealed that squaraines exhibit sharp and intense absorption with $\lambda_{\text{max}}$ ranging from 600 to 700 nm in the visible region\textsuperscript{3,27}. The intense electronic absorption is attributed to intramolecular charge transfer from the donors to the central acceptor.\textsuperscript{27} In the DAD-like molecules, powerful donors enhance the intramolecular charge-transfer (ICT) interaction and generate an excited ICT state with lower energy. Our calculation shows that the centrosymmetric squaraines possess intense visible absorption at 630–700 nm. The calculated $\lambda_{\text{max}}$ of Sq2 is 60 nm longer than the observed value.\textsuperscript{27} The cut-off wavelengths of Sq1–3 and Sq10 are coincident with their maxima absorptions, while others possess maxima absorptions at 150–260 nm. Obviously, the introduction of strong donors into a squarine dye leads to a bathochromic shift induced by the stabilized ICT state. In this case, the introduction of ortho substituents leads to few changes in the cut-off wavelength, illustrated by comparing the UV spectra of Sq3, Sq10 and Sq11. There is no remarkable difference resulting from the substitution of weak donors or strong acceptors at both terminals of a squarine. The introduction of ortho substituents in Sq12 and Sq13, however, makes their UV cut-offs shift toward longer wavelengths with respect to Sq9.

3.3. Static second hyperpolarizabilities

Table 2 lists the calculated longitudinal components $\gamma_{\text{xxxx}}$ of the squaraines. Both FF and TDHF methods produce very similar results at the static limit. In a previous study,\textsuperscript{10,24} we predicted that the second hyperpolarizabilities of DAD-like molecules would be large and negative for those with strong acceptors at their centers and strong donors at their terminals, and become smaller in absolute values or reverse their signs for those with weaker donors and acceptors. For a typical squarine molecule, the electron-withdrawing ability of the central acceptor is fixed. It is well known that the four-membered ring with two carbonyls is quite a strong electron acceptor. Almost all the squarine molecules that have been synthesized or investigated possess strong donors at both ends, so they usually exhibit significant negative third-order NLO properties. As shown in Table 2, the calculated $\gamma_{\text{xxxx}}$ values of Sq1, Sq2 and Sq3 are large and negative. For Sq4, Sq5 and Sq6, which have weaker donors at their ends, the $\gamma_{\text{xxxx}}$ components are quite small, moreover, Sq5 and Sq6 possess positive values of $\gamma_{\text{xxxx}}$. When the donors at both terminals are substituted by strong electron-withdrawing groups, such as acyl (Sq7), cyano (Sq8) and nitro (Sq9), the $\gamma_{\text{xxxx}}$ becomes large and positive. This is an unusual result, that a squarine dye with some special structural features may possess positive third-order NLO susceptibility. All of the commonly studied squaraines, to our knowledge, are characterized by their large negative third-order NLO susceptibilities.

To a great extent, the nature of the terminal groups of the squaraines affects the magnitudes and signs of their second hyperpolarizabilities. However, modifying the property of the central squaric ring in a squarine molecule may also lead to significant change in its NLO properties. With hydroxys at the ortho positions, Sq10 has an extremely large negative value of $\gamma_{\text{xxxx}}$, 4 times greater in absolute value than that of Sq3 without any hydroxys. Obviously, the electron-withdrawing ability of the carbonyls is strengthened by the introduction of hydroxys. The hydroxys groups help to polarize the carbonyls since the hydrogen atoms of the hydroxys

### Table 2  Calculated longitudinal components $\gamma_{\text{xxxx}}$ of squaraines (in $10^4$ au)

<table>
<thead>
<tr>
<th></th>
<th>FF static $\gamma(0,0,0,0)$</th>
<th>TDHF static $\gamma(0,0,0,0)$</th>
<th>1907 nm $\gamma(-2\omega,0,0,\omega)$</th>
<th>1064 nm $\gamma(-2\omega,0,\omega,\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sq1</td>
<td>$-362$</td>
<td>$-359$</td>
<td>$-5144$</td>
<td>$-718$</td>
</tr>
<tr>
<td>Sq2</td>
<td>$-202$</td>
<td>$-199$</td>
<td>$-2713$</td>
<td>$-412$</td>
</tr>
<tr>
<td>Sq3</td>
<td>$-190$</td>
<td>$-189$</td>
<td>$-1606$</td>
<td>$-336$</td>
</tr>
<tr>
<td>Sq4</td>
<td>$-29$</td>
<td>$-28$</td>
<td>$-494$</td>
<td>$-82$</td>
</tr>
<tr>
<td>Sq5</td>
<td>$5$</td>
<td>$5$</td>
<td>$-185$</td>
<td>$29$</td>
</tr>
<tr>
<td>Sq6</td>
<td>$5$</td>
<td>$6$</td>
<td>$-166$</td>
<td>$16$</td>
</tr>
<tr>
<td>Sq7</td>
<td>$166$</td>
<td>$167$</td>
<td>$131$</td>
<td>$173$</td>
</tr>
<tr>
<td>Sq8</td>
<td>$175$</td>
<td>$176$</td>
<td>$112$</td>
<td>$180$</td>
</tr>
<tr>
<td>Sq9</td>
<td>$202$</td>
<td>$202$</td>
<td>$258$</td>
<td>$221$</td>
</tr>
<tr>
<td>Sq10</td>
<td>$-895$</td>
<td>$-910$</td>
<td>$-5938$</td>
<td>$-1389$</td>
</tr>
<tr>
<td>Sq11</td>
<td>$-191$</td>
<td>$-189$</td>
<td>$-2773$</td>
<td>$-368$</td>
</tr>
<tr>
<td>Sq12</td>
<td>$-314$</td>
<td>$-318$</td>
<td>$-2314$</td>
<td>$-511$</td>
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<tr>
<td>Sq13</td>
<td>$197$</td>
<td>$198$</td>
<td>$87$</td>
<td>$209$</td>
</tr>
</tbody>
</table>
are close to the oxygen atoms of the carbonyls (about 1.84 Å). Therefore, Squ10 has strong donors at both ends and a much stronger acceptor at its center. This is the reason why it has an extremely large second hyperpolarizability.

Another striking change caused by hydroxyls at ortho positions occurs for Squ12, which has strong electron-withdrawing groups at its center and both terminals. The $\gamma_{xxxx}$ value is large and negative for Squ12, but large and positive for its parent molecule Squ9. The ortho hydroxyls not only change the magnitude of $\gamma$ of a squaraine, but also reverse its sign in some cases.

In contrast to hydroxyls, ortho fluorions lead to little change in $\gamma_{xxxx}$ values. Squ3 and Squ11, Squ9 and Squ13 have similar values both in magnitude and sign. The distances between the fluorions and the oxygen atoms of the carbonyls are about 2.55 Å in Squ11 and Squ13, much longer than that between the hydroxy-H and carbonyl-O in Squ10 and Squ12. Thus, the substitution of ortho fluorions does not change the properties of the central acceptor, and consequently the NLO properties.

3.4. Dispersion effect

The current TDHF calculation is invalid near to the resonant frequency of a molecule. Since the squaraine dyes under study have intense absorption bands around 500 nm, our calculations were carried out at 1907 and 1064 nm. At both wavelengths, the THG coefficients are unavailable, since the tripled frequencies are covered in or near to the absorption bands, as are the EFSHG coefficients at 1064 nm. The OKE coefficients involve only the frequency ($\omega$) of the optical field, 5244 cm$^{-1}$ (1907 nm) or 9398 cm$^{-1}$ (1064 nm), which is far from the resonant absorption bands of squaraines. Table 2 lists the calculated frequency-dependent $\gamma_{xxxx}$ values of the EFSHG process at 1907 nm and the OKE process at 1907 and 1064 nm.

A significant dispersion effect is found for the longitudinal components $\gamma_{xxxx}$ of centrosymmetric squaraines. The EFSHG coefficients, $\gamma(-2\omega, \omega, \omega, \omega)$, are much lower than their static counterparts except for Squ9. For those with negative static $\gamma_{xxxx}$, the changes are more significant. The $\gamma(-2\omega, \omega, \omega, \omega)$ of Squ1 is 14 times larger in absolute value than its static $\gamma(0,0,0,0)$. However, for those with positive static $\gamma_{xxxx}$, the changes are relatively modest. A similar dispersion effect is found for the OKE coefficients, $\gamma(\omega, \omega, \omega, \omega, \omega)$, of the dyes with negative $\gamma(0,0,0,0)$. For those with positive $\gamma(0,0,0,0)$, their $\gamma(-\omega, \omega, \omega, \omega)$ values at 1907 nm change by a very small amount. When the wavelength of the optical field moves to the shorter wavelength 1064 nm, the OKE coefficients increase dramatically (in negative magnitude) except for Squ9. Similarly the changes for those with negative $\gamma(0,0,0,0)$ values are more significant.

The dispersion effect of the second hyperpolarizability for DAD systems is significant but has not yet been systematically addressed. Based on our calculations, some trends for the frequency-dependent second hyperpolarizabilities of centro-

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**Table 3** Averaged second hyperpolarizabilities $\langle \gamma \rangle$ of some centrosymmetric squaraines

<table>
<thead>
<tr>
<th>Squaraine</th>
<th>TDHF calculation</th>
<th>Previous results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma(0,0,0,0)$</td>
<td>$\gamma(-2\omega, \omega, \omega, \omega)^a$</td>
</tr>
<tr>
<td>Squ14</td>
<td>-205</td>
<td>-2121</td>
</tr>
<tr>
<td>Squ15</td>
<td>-317</td>
<td>-3131</td>
</tr>
<tr>
<td>Squ16</td>
<td>-350</td>
<td>-6463</td>
</tr>
<tr>
<td>Squ7</td>
<td>-46</td>
<td>-560</td>
</tr>
<tr>
<td>Squ17</td>
<td>-166</td>
<td>-1480</td>
</tr>
<tr>
<td>Squ18</td>
<td>-108</td>
<td>-592</td>
</tr>
<tr>
<td>Squ19</td>
<td>-482</td>
<td>-51186</td>
</tr>
</tbody>
</table>

*a In 10$^14$ au. *b At 1907 nm. c AM1-FF calculation, ref. 2, 16. For reducing computational costs, the longer alkyl chains in Squ14 and Squ15 were shortened to methyl groups. Therefore, our calculated results are larger in absolute value than those in the literature. d EFSHG measurements at 1907 nm in methylene chloride. e THG measurements at 1390 nm in chloroform. f DFWM measurements at 696 nm in CH$_2$Cl$_2$. g DFWM measurements at 710 nm in polystyrene.
symmetric squaraines can be summarized as follows: (1) Both the static and dynamic second hyperpolarizabilities have the same order of magnitude for most dyes under study, even though their great dispersion effect generates large differences between static and dynamic values or between dynamic values at different wavelengths. (2) The dispersion effect is greater at shorter wavelength. This is true for most organic molecules. (3) The dispersion effect is greater for squaraines with negative static $\gamma$ values, and their dynamic $\gamma$ values are much greater in negative magnitude than their static counterparts. For the dyes with large positive $\gamma$ values, however, the dispersion effect is relatively less significant.

4. Comparison with experiments and other calculations for some centrosymmetric squaraines

To examine the validity of our calculation, we calculated the averaged second hyperpolarizabilities $\langle \gamma \rangle$ of some squaraines and compared our results with other theoretical results and available experimental data. With the aim of investigating the structure dependence for the third-order NLO properties of squaraines, we were concerned mostly with the trend in the changes of $\langle \gamma \rangle$ due to the changes in their structures rather than the absolute magnitudes of $\langle \gamma \rangle$. A reliable trend is most important during the design process of new molecules for NLO applications. All the squaraines listed in Table 3 have strong electron-donating groups at both ends of the molecule. As expected, the experimental results for $\langle \gamma \rangle$ in EFSHG, SHG and DFWM processes are negative. The TDHF calculation for $\gamma(\pi-\sigma,0,0,0)$ at $1907 \text{ nm}$ greatly overestimates the observed EFSHG coefficients for all dyes. The calculated values of $\gamma(0,0,0)$, $\gamma(\pi-\sigma,0,0,0)$ and $\gamma(0,0,0,0)$ for Sq14-16 have the same trend in magnitude as the AM1-FF results of Dirk et al. Polarized by two ortho hydroxys, the central carbonyl is more powerful in electron-withdrawing ability than that in Sq14. Therefore, Sq15 has larger $\langle \gamma \rangle$ (negative) than Sq14. The EFSHG and THG measurements for Sq14 and Sq15 support the calculated results, but the EFSHG result for Sq16 is not so large as the theoretical prediction. This contradiction arises from the nonsymmetric isomer of Sq16, which exists in the samples and contributes positively to $\langle \gamma \rangle$. For the same reason, the observed $\langle \gamma \rangle$ of Sq18 is smaller than that of Sq2, in contrast to the calculated trend. Both the DFWM measurements and our TDHF calculations gave the same order of magnitude of the $\langle \gamma \rangle$ values except for Sq18. Squares possesses very large static and dynamic $\langle \gamma \rangle$ values because it has the longest conjugation path in both its branches. In our previous study, we predicted the conjugation length to be another important factor that influences greatly both the magnitude and sign of the $\gamma$ values of DAD systems.

5. Conclusion

By using FF and TDHF methods, the second hyperpolarizabilities $\gamma$ have been investigated for a class of typical DAD-like compounds, centrosymmetric squaraines. Both the magnitudes and signs of the $\gamma$ values of the prototype molecule, 2,4-diphenyl-cyclobutane-1,3-dione, and its derivatives are closely related to the nature of the para or ortho substituents. The dye with powerful electron-donating groups at the para positions exhibits a large negative $\gamma$ value, but the substitution of less powerful donors makes $\gamma$ smaller in absolute value. When the donors are weak or replaced by electron-withdrawing groups, $\gamma$ may become positive. A dye with powerful electron-withdrawing groups at the para positions may have a large positive $\gamma$ value. The introduction of ortho hydroxys enhances greatly the negative $\gamma$ values because of the more powerful central acceptors, carbonyls, induced by the hydroxys.

Acknowledgement

This work was supported by the National Natural Science Foundation of China. MY thanks W. Zhu, Z. Chen, S. Li, J. Ma and G. Zhang for very helpful discussions.

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