Remarkable NLO Response and Infrared Absorption in Simple Twisted Molecular π-Chromophores

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Abstract: Computational modeling reveals that, by substitutional modification of interplanar dihedral angles in a series of quinopyrans, both the optical absorption cross section and the first hyperpolarizability can be widely tuned in both frequency and magnitude. This is a promising structural control scheme for modulating molecular nonlinear optical and infrared absorption properties. The maximum nonresonant $\mu\beta$ estimated for a tetraalkyl-substituted 4-quinopyran, the full AM1-optimized interplanar dihedral angle of which is 104°, is $\sim 70000 \times 10^{-48}$ esu, at an excitation energy of 0.10 eV. This is 4 orders of magnitude larger than that of the archetypical NLO chromophore, 4-*N,N*′-(dimethylamino)-4′-nitrostilbene, at the same excitation frequency. The effects of conjugation pathway, strength of the electron donor/acceptor groups, and auxiliary donor and acceptor on the molecular response properties have also been analyzed. The optical absorption at a twist angle of 90°, when the molecule can be described as two disjoint π-subfragments, exhibits characteristic absorptions from the individual subfragments and also inter-subfragment excitation; the former occur at high energies and with high oscillator strengths, while the latter occurs at low energy and with low oscillator strength.

I. Introduction

The development of all-optical and electrooptic signal transmission/processing technologies requires efficient strategies for manipulating the amplitude, phase, polarization, and frequency of optical beams. Consequently, the search for materials that can be utilized in such devices has been an area of active research in recent years.[1−8] A crucial materials requirement in fabricating such devices is that these materials exhibit large nonlinear optical response.[2] This has stimulated intense research in the area of molecular nonlinear optics, devoted to the search for efficient, robust, and simple organic molecular chromophores exhibiting large first and second hyperpolarizabilities. These studies have identified organic one-dimensional extended π-conjugated systems with appended strong electron donors and acceptors as ideal candidates.[4,7,8] While extended π-conjugated systems exhibit large NLO response properties, the increase in NLO response is usually accompanied by bathochromic shifts in the optical absorption maxima, eroding the chromophore transparency in the visible region—an unacceptable property for many photonic applications. Also, the increase in molecular conjugation length in most cases diminishes the thermal stability of such chromophores.[9,10]

These observations have stimulated the search for thermally stable, simple molecular chromophores that exhibit strong NLO response. One challenge is clear: given a molecular chromophore of fixed dimensions and donor and acceptor substituents, what parameters can be tuned to obtain stable molecular chromophores exhibiting optimal NLO response? One approach has been demonstrated by Marder et al.[11] They argued that molecular hyperpolarizability can be tuned using the bond length alterna-

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tion (BLA, the difference between the average single and double bond lengths in the conjugated pathway of a chromophore). For a wide variety of chromophores, Marder et al. argued that it is possible to tune the BLA by modifying the strength of the donor and acceptor substituents, the polarity of the solvent, or the strength of an applied electric field. In this contribution, we demonstrate an alternative approach to designing molecular chromophores that exhibit both unprecedentedly large NLO responses and strong infrared absorption cross sections. The tunable structural characteristic that promotes these optical features is a stereochemically enforced diminution in the conjugation that enforces zwitterionic behavior in the ground state and provides a strong intramolecular excitation feature of low energy and high oscillator strength.[12] In the next section, we briefly outline the theoretical basis for this approach and computational procedures used in this study, followed by a discussion of results and their ramifications in section III.

II. Approach. Dihedral Angle Tuning in Bichromophores

The simple two-level model[13] (eq 1), derived from a more general

$$\beta_{\text{two-level}} = \frac{3e^2}{2\hbar^3} \frac{\omega_{ge} f_{ge} \Delta\mu_{ge}}{[\omega_{ge}{}^2 - \omega^2][\omega_{ge}{}^2 - 4\omega^2]} \qquad (1)$$

perturbation theoretical expression for the first hyperpolarizability, shows that the response properties of any system can be tuned by varying $\hbar\omega_{ge}$, the excitation energy of the lowest charge-transfer excitation, f_{ge}, the associated oscillator strength, and $\Delta\mu_{ge}$, the difference between the dipole moments of the ground and charge transfer states. Earlier studies on organic π-conjugated systems have shown that it is possible to tune the $\hbar\omega_{ge}$ and f_{ge} parameters by varying the extent of the conjugation pathway and that $\Delta\mu_{ge}$ can be tuned by varying the donor and acceptor substituent strengths. Thus, the most commonly studied organic systems probed for NLO applications are extended π-conjugated systems functionalized with strong electron donors and acceptors. The studies of Marder et al. also showed that in many cases the above molecular properties can be modified by varying the BLA for a given chromophore system. The following paragraphs present an alternative approach to manipulating $\hbar\omega_{ge}$, f_{ge}, and $\Delta\mu_{ge}$ based on the variation of the dihedral twist angle of a simple organic π-conjugated system. Using this approach, we demonstrate that one can design simple chromophores that exhibit not only extremely large NLO response properties but also strong infrared absorption cross sections. Strong IR absorbers are of interest in filters, polarizers, optical recording,[14] photodynamic therapy, etc.[15] Most molecular infrared absorption is due to vibrational (mid- and far-infrared) or mixed-valence near-infrared transitions.[16] The oscillator strengths of such transitions are usually too small to constitute efficient absorbers. Thus, improved design principles for chromophores exhibiting tunability leading to extremely large NLO response properties and strong infrared absorption cross section would be of both scientific and technological interest.

In the next subsection, we use a simple two-site Hückel model to describe qualitatively the variation of $\hbar\omega_{ge}$, f_{ge}, and $\Delta\mu_{ge}$, and hence the first hyperpolarizability, with varying dihedral twist angle in a simple two-orbital π-conjugated system. In the following paragraphs, we then describe the geometry of the chromophores studied in this contribution. Except for the merocyanine study in section IIB, properties are computed using the reliable semiempirical INDO/S Hamiltonian[17] as implemented in the ZINDO package, and the response properties are calculated using the correction vector approach.[18]

A. Two-Site Hückel Model. Configurational modifications induced by dihedral twisting of a double bond in a π-conjugated system can lead to a variety of interesting properties. One example of such an effect, termed "sudden polarization", occurs in the visual chromophore of the vertebrate retina.[19] In this case, a photochemical *cis*−*trans* isomerization reaction induces a dihedral twist around the C11−C12 double bond of 11-*cis*-retinal that produces a charge separation and hence a large increase in the ground-state dipole moment of the molecule within a window of 5° surrounding the completely twisted geometry.[19] Qualitatively, one can understand this charge separation by considering the dihedral twist about the central double bond in ethylene.[20] In the planar configuration, ethylene belongs to the point group D_{2h}, and the π and π* orbitals are of b_{1u} and b_{2g} symmetry, respectively. As the twist angle changes, the symmetry changes to point group D_2, and the π and π* orbitals are of b_1 and b_2 symmetry, respectively. Both the b_{1u} and b_{2g} orbitals of planar ethylene, and the b_1 and b_2 orbitals of twisted ethylene, correlate to the doubly degenerate *e* orbitals of the D_{2d} point group. In the simplest one-electron picture, the degeneracy ensures that the average occupancy of each of the ethylene atomic π orbitals is 1. However, any perturbation that breaks the 2-fold symmetry will lift the degeneracy, leading to charge separation. This implies that, in the case of twisted push−pull ethylenes, the ground state is better described as a charge-separated system. Since the above charge separation produces an extremely large polarization in the system, it would be expected also to produce large response properties.

Consider a hypothetical molecule with two subunits linked by a π-bond (the simplest molecule would be an ethylene appended with a donor and an acceptor substituent at the two ends). One can then construct a simple Hückel model[21] for this system, in which the donor subunit wave function is represented by ϕ_D and the acceptor subunit wave function by ϕ_A. The two subunits are characterized by a site energy (Hückel α) ϵ and a transfer integral (Hückel β) *t*. Note that ϵ is taken to be the difference in site energies of the donor and acceptor subunits, namely $\epsilon = (\epsilon_D - \epsilon_A)$. If the dihedral twist angle about the double bond is assumed to be θ, then the transfer integral scales roughly as the cosine of the dihedral twist angle, so that it will have the largest absolute value when the two subunits are coplanar and will essentially vanish (it does not vanish completely due to σ−π mixing) when the two subunits are perpendicular. With the above assumptions and terminologies, one can write orthogonal wave functions for the ground and excited states of the system in Mulliken[21] terms as

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$$\psi_g = C_D\phi_D + C_A\phi_A \tag{2}$$

$$\psi_e = C_A\phi_D - C_D\phi_A \tag{3}$$

The above equations can be solved for the ground- and excited-state energies, which are given by

$$E_g = {}^1/_2(\epsilon - \sqrt{\epsilon^2 + 4t^2}) \tag{4}$$

$$E_e = {}^1/_2(\epsilon + \sqrt{\epsilon^2 + 4t^2}) \tag{5}$$

The Pariser approximation[22] is then used to calculate the ground- and excited-state dipole moments and the transition moment. These quantities, in terms of the Hückel parameters and the location of the donor (R_D) and acceptor (R_A) substituents, are given by

$$\mu_g/e = R_A + \frac{\epsilon}{(\epsilon^2 + 4t^2)^{1/2}}(R_A - R_D) \tag{6}$$

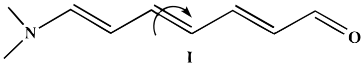
$$\mu_{ge}/e = \frac{t}{(\epsilon^2 + 4t^2)^{1/2}}(R_A - R_D) \tag{7}$$

$$\Delta\mu_{ge}/e = \frac{2\epsilon}{(\epsilon^2 + 4t^2)^{1/2}}(R_A - R_D) \tag{8}$$

$$\lambda_{\max} = \frac{hc}{\sqrt{\epsilon^2 + 4t^2}} \tag{9}$$

where μ_g is the ground-state dipole moment, μ_{ge} is the transition moment for the charge-transfer excitation, and λ_{max} is the wavelength of the excitation energy. This two-site Hückel model indicates that, while the ground-state dipole moment, the wavelength of the absorption maximum, and the difference in dipole moment between the ground and excited state maximize, the transition moment will be smallest at the configuration in which the two subunits are perpendicular. From the two-level model (eq 1), it appears that the above variation in $\Delta\mu_{ge}$ and λ_{max} should counteract the variation in μ_{ge}. In fact, one would expect a nearly vanishing first hyperpolarizability at a twist angle of 90°, since the transition moment would almost vanish, although $\Delta\mu_{ge}$ and λ_{max} would be maximum. However, at twist angles near 90°, where the transition moment is nonvanishing, large NLO responses are expected. The expected variation of μ_{ge}, $\Delta\mu_{ge}$, E_{ge}, and the dominant component of the first hyperpolarizability, β_{xxx} (from eqs 6−9), are shown in Figure 1. As expected from our picture, one observes a sharp increase in the first hyperpolarizability as the twist angle increases, with a precipitous diminution at a twist angle of 90°.

B. Merocyanine Example. To explore the above scheme further, the molecular hyperpolarizability of a simple merocyanine dye (**I**, shown below) was first computed. The geometry of the merocyanine in the planar configuration was fully optimized without any symmetry restriction using the MOPAC AM1 model Hamiltonian.[23] For this geometry, the molecular hyperpolarizability was then computed at imposed twist angles ranging from 0° to 180° in steps of 15° from 0° to 75°, and in steps of 5° from 75° to 85°, followed by steps of 1° from 85° to 89°. The dihedral twist angles were varied using a similar step pattern from 91° to 180°. PPP model exact (scaled so that $H_{ij} \sim \cos\theta$ across the twist) molecular response properties were computed using the diagrammatic valence bond scheme[24] and the correction vector approach, described in detail elsewhere.[18] The variation of the linear optical and molecular first hyperpolarizability as a function of the dihedral twist angle (Figure 2) exhibits the expected trend. Thus, it is seen that the NLO response of π-conjugated systems can be incrementally varied by tuning the dihedral twist angle about a key double bond. Model exact hyperpolarizabilities of push−pull polyenes studied by Ramasesha et al.[25] also reveal maximization of the SHG coefficients at twist angles between 65° and 85°, and between 95° and 135°, and near-vanishing SHG coefficients at 90°, as predicted by the above simple theory. Note, however, that in these test calculations, or in the



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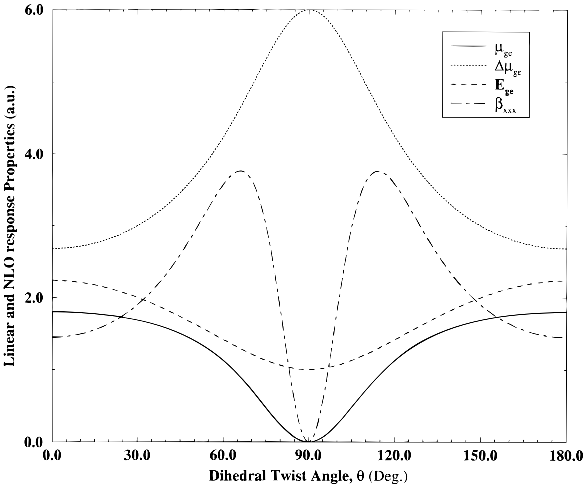

Figure 1. Variation of linear optical parameters, μ_{ge}, $\Delta\mu_{ge}$, E_{ge}, and the dominant component of the first hyperpolarizability as a function of the dihedral twist angle in a push−pull substituted ethylene as derived from a simple two-orbital Hückel model. E_{ge} is the excitation energy of the lowest optically allowed excited state, and μ_{ge} and $\Delta\mu_{ge}$ are as described in eq 1. The parameters ϵ and t are assumed to be 1.0 au, and ($R_A - R_D$) is assumed to be 3.0 au.

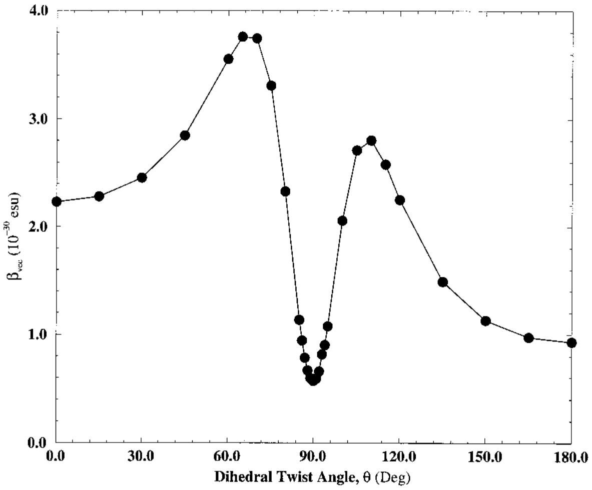

Figure 2. Variation of the PPP model exact vector component of the first hyperpolarizability of merocyanine **I** as a function of the dihedral twist angle. The calculations were performed at the indicated imposed twist angles.

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[22] (a) In a π electron approximation such as the Hückel model or the Pariser−Parr−Pople (PPP) model,[22b] the dipole moment integral can be written as

$$r^i_{\mu\nu} = \delta_{\mu\nu}R^i_\mu$$

where R^i is the geometric coordinate of the atom on which the μth atomic orbital is found. For details, see: Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. Li, D.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 1707. (b) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466; 568. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

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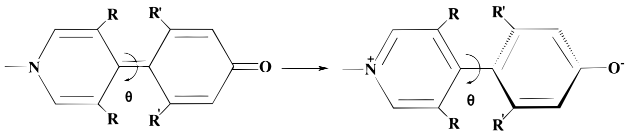
Chart 1



	R	R'
IIa	H	H
IIb	H	Me
IIc	Me	Me
IId	Me	t-Bu
IIe	t-Bu	t-Bu

work of Ramasesha et al., the molecular response properties are computed at imposed twist angles, and the geometries of the molecule are not optimized at any twist angles other than 0° and 180°. To our knowledge, no previous studies have investigated the control of linear and nonlinear optical response properties by twisting organic molecules in stable ground-state geometries. In the next section, we analyze the response properties of a series of chromophores having a stable twisted ground-state geometry (fully optimized with no symmetry constraints) and also exhibiting differing dihedral twist angles, and hence varying response properties.

In addition to the aforementioned, twist angle-dependent variation of linear and nonlinear response properties in twisted π-conjugated systems, there are other important optical features in these structures at a twist angle of 90°. Within the Hückel picture, the transfer integral, which scales as the cosine of the twist angle, vanishes near 90° twist. This implies that the system is ideally represented by two disjoint molecular subfragments and that the linear absorption of the individual subfragments (intra-subfragment excitations) should be observable, in addition to a weak charge-transfer excitation (inter-subfragment excitation). The intra-subfragment excitations should be more intense and should occur at higher excitation energies. In contrast, for twist angles close to 90°, the charge-transfer band should have low oscillator strength and occur at much lower excitation energy. Such chromophores, which exhibit two distinct kinds of excitations, will be referred to as "bichromophores" and have potential applications in optical limiting.[26]

III. Results and Discussion

A. Simple TICTOID Structures. The general class of chromophores having stable twisted geometries, and studied in this contribution, are substituted quinopyrans and simple merocyanines. These chromophores can also be referred to as TICTOID structures, by analogy with so-called twisted intramolecular charge-transfer (TICT) chromophores.[27] To demonstrate the effect of twist angles on the linear and NLO response characteristics, we analyzed the variation of the linear and nonlinear optical responses of a simple merocyanine (chromophore **IIa** in Chart 1) at various imposed twist angles (the values of the twist angles chosen are the same as in the case of chromophore **I**). The results are shown in Figure 3. In Figure 3, we also present the computed linear and nonlinear response properties of chromophore set **II** (**IIa**−**IIe**). In these structures, the dihedral twisting is induced by steric crowding of substituents in the positions *ortho* to the double bond linking the two rings. The dihedral twisting around the central double bond leads to charge separation,[28] as discussed earlier, and this in turn leads to aromatic stabilization of the resultant pyridinium and phenolate fragments. This conformationally induced charge-transfer process is also shown in Chart 1. Thus, progression can be made from an unsubstituted quinoidal geometry (chromophore **IIa**) to a benzenoidal geometry having four bulky *tert*-butyl substituents (chromophore **IIe**). This sterically induced twisting leads to stable geometries having radically different aromaticity characteristics. The geometries of the subject merocyanines were fully optimized without symmetry restrictions using the AM1 model Hamiltonian as implemented in the Gaussian94 package.[29] The optimized geometries show that the dihedral twist angles vary from 0° in the case of unsubstituted chromophore (**IIa**) to 83° in the tetra-*tert*-butyl-substituted derivative (**IIe**), accompanied by a progression from quinoidal geometry in **IIa** to a benzenoidal skeletal geometry in **IIe**.

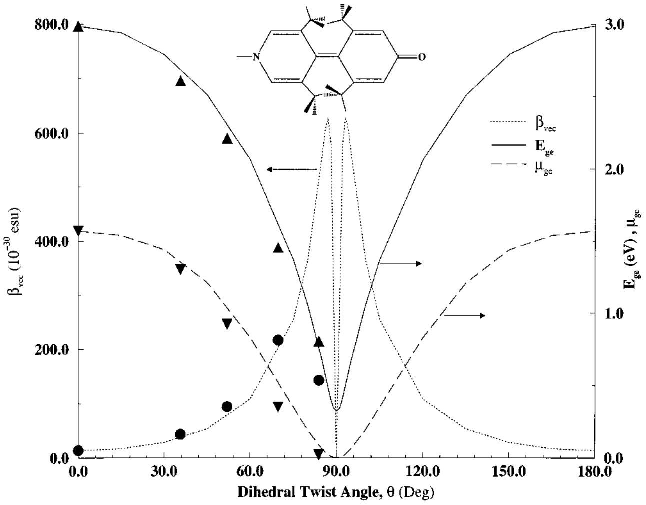


Figure 3. Variation of E_{ge} (solid line), associated transition moment μ_{ge} (dashed line), and β_{vec} (dotted line) at an excitation energy of 0.1 eV as a function of imposed twist angle for chromophore **IIa**. The parameters E_{ge} and μ_{ge} have the same significance as in Figure 1. ▲, ▼, and ● represent the corresponding values of the optimized structures of chromophore set **II** (chromophores **IIa**−**IIe**.) The arrows indicate the axis for the plots.

In Figure 3, the ZINDO-derived lowest optical transition (charge-transfer excitation) energies of chromophore **IIa** (solid line) at various imposed twist angles and those of the geometry-optimized substituted chromophores (▲) are presented. The associated transition moments (dashed line and ▼) and the molecular first hyperpolarizabilities (dotted line and ●) of these chromophores are also shown. As described in section IIA, the absorption maximum shifts to the infrared and the associated transition moment diminishes as the twist angle increases. Note that the absorption maxima of the substituted chromophores are almost identical to those of the unsubstituted ones for identical

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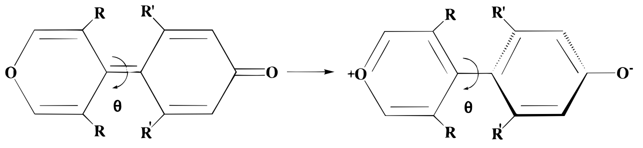
[26] Molecular systems exhibiting a much stronger excited-state than ground-state absorption frequently exhibit reverse saturable absorption (RSA). That is, intial population of the first excited state at lower incident light intensity leads to greatly enhanced total absorption as the incident light intensity is increased. For more details on RSA, see: Tutt, L. W.; Boggess, T. F. *Prog. Quantum Electron.* **1993**, *17*, 299 and references therein.

[27] (a) Sen, R.; Majumdar, D.; Battacharyya, S. P.; Battacharyya, S. N. *J. Phys. Chem.* **1993**, *97*, 7491. (b) Lippert, E.; Rettig, W.; Bonačič-Koutecký, V.; Heisel, F.; Mihe, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.

[28] A number of earlier studies have shown that the electronic structure of merocyanines can be described as a combination of the quinoid and benzenoid structures and that any external perturbation, such as an applied electric field or solvation, leads to stabilization of the charge-separated benzenoid structure. See, for example, ref 11 and the following: Luzhkov, V.; Warshel, A. *J. Am. Chem. Soc.* **1991**, *113*, 4800. Karelson, M. M.; Zerner, M. C. *J. Phys. Chem.* **1992**, *96*, 6949. Morley, J. O.; Morley, R. M.; Docherty, R.; Charlton, M. H. *J. Am. Chem. Soc.* **1997**, *119*, 10192.

[29] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

Chart 2



	R	R'
IIIa	**H**	**H**
IIIb	**H**	**Me**
IIIc	**Me**	**Me**
IIId	**Me**	**t-Bu**
IIIe	**t-Bu**	**t-Bu**

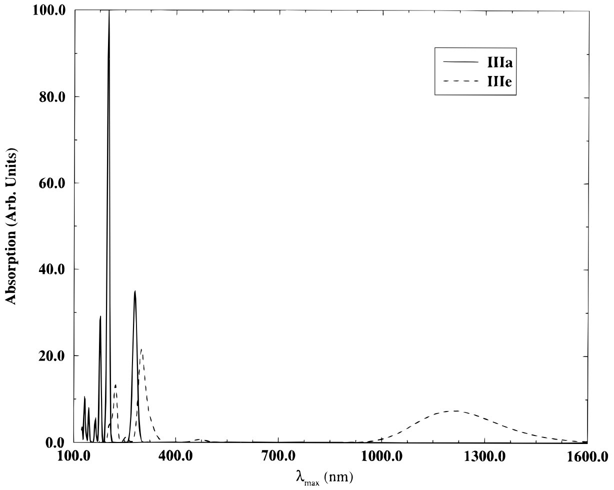
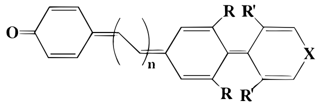
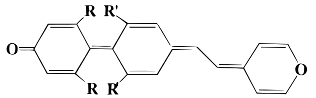


Figure 4. Optical absorption spectra[31] of chromophores **IIIa** and **IIIe** at the equilibrium geometries. The intensities are scaled with respect to the intensities of the chromophore **IIIa** absorption.

Table 1. Linear and Nonlinear Optical Properties of Extended TICTOID Structures at an Excitation Energy of 0.1 eV ($\mu\beta$ at an Excitation Energy of 0.65 eV Is Also Given for Comparison)



IV



V

molecule	n	X	R	R′	$\lambda_{max}{}^{a}$	$\beta_x(0.1)^{b}$	$\mu\beta(0.1)^{c}$	$\mu\beta(0.65)^{c}$
IIIe	0	O	*t*-Bu	*t*-Bu	1206.8	352.77	5811.4	−15727
IVa	1	O	H	H	535.60	33.95	459.16	1137.0
IVb	1	O	H	Me	579.20	1.70	35.50	679.21
IVc	1	O	Me	Me	643.40	189.80	3389.5	−6687.7
IVd	1	O	Me	*t*-Bu	805.30	391.67	17175	−78964
IVe	1	O	*t*-Bu	*t*-Bu	1204.5	2398.6	68611	−198097
IVf	2	O	*t*-Bu	*t*-Bu	1093.4	1749.0	48190	−277745
IVg	3	O	*t*-Bu	*t*-Bu	971.00	754.49	18524	−862434
IVh	1	S	*t*-Bu	*t*-Bu	988.20	1381.6	32391	−601200
V	1	O	*t*-Bu	*t*-Bu	991.60	1119.4	23471	-427375

[a] This is the lowest energy charge-transfer transition. [b] Units: 10^{-30} esu. [c] Units: 10^{-48} esu.

twist angles, indicating that any electronic/inductive effects of the bulky alkyl groups on the linear and nonlinear response properties are minimal. These substituents simply provide the steric driving force for the conformational twisting. The derived molecular hyperpolarizabilities also exhibit variations with twist angles identical to those observed in the unsubstituted merocyanine. The absorption maximum of **IId** is at ∼851 nm with an associated oscillator strength of 0.35, and the $\mu\beta$ at 0.65 eV is $\sim -30000 \times 10^{-48}$ esu, which is 2 orders of magnitude larger than that of 4,4′-*N*,*N*-(dimethylamino)nitrostilbene (DANS).[30] Thus, these chromophore calculations suggest that, by synthetically controllable variation of the twist angles in π-conjugated systems, substantial variations in both linear and nonlinear optical properties can be effected.

Variations in linear and NLO responses with dihedral twist angle were originally identified in the case of simple substituted quinopyrans.[12] The variation in linear and nonlinear responses of the smallest quinopyran homologue (chromophore set **III**, Chart 2) follows a trend similar to that of the merocyanine. As the dihedral twist angle of chromophore set **III** is varied from 0° in the case of **IIIa** to 104° in the case of **IIIe**, the associated optical transition energy and first hyperpolarizabilities exhibit substantial variations.[12] To demonstrate the presence of intra- and inter-subfragment excitations in these chromophores, as described in section IIA, the complete absorption spectra of **IIIa** and **IIIe** were computed and are shown in Figure 4. The spectra of both **IIIa** and **IIIe** exhibit three distinct maxima, corresponding to two intra-subfragment excitations and one inter-subfragment excitation.[31] While these maxima are clustered around the same region for **IIIa**, they are well separated for **IIIe**. From the Hückel analysis in section IIA, it is expected that the long-wavelength absorption corresponds to the inter-ring charge-transfer excitation, and the two high-energy transitions to intra-ring excitations. An analysis of these transitions in terms of the CI coefficients and relevant molecular orbitals indeed shows that the long-wavelength feature ($\lambda = 1200$ nm) corresponds to a HOMO → LUMO transition, a charge transfer from the phenolic ring to the pyrilium cation. The two high-energy transitions correspond to intra-ring transitions within the phenolic and pyrilium fragments. Note that **IIIe** is better described in terms of connected benzenoid structures and that the donor portion is phenolic and the acceptor portion pyrilium-like. An important conclusion is that, by simple control of the dihedral twist angle of these π-conjugated molecules, it is possible to separate the intra- and inter-subfragment excitations. This implies that these twisted chromophores would have minimal absorption in the visible region and strong absorptions in the UV and infrared. Such chromophores should be of great interest in the area of optical limiting using the reverse saturable absorption (RSA) mechanism.[26]

B. π-System Effects in TICTOID Structures. To devise chromophores with much larger NLO response properties, the above scheme was coupled with chromophore design strategies described in section II, namely extending the dimensions of the π-system, increasing substituent donor and acceptor strengths, or incorporating auxiliary donors and acceptors (section IIIC). The geometries of chromophores designed by combining the above approaches, chromophore set **IV** (Table 1), were optimized using the AM1 model Hamiltonian as implemented in the Gaussian94 package. This level of optimization was found

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(30) One of the reviewers provided a useful suggestion regarding the mixing of the HOMO and LUMO orbitals as one twists about a double bond in the π-conjugated system, and suggested doing a set of calculations using three different starting reference determinants, namely HH, HL, and LL (H and L being HOMO and LUMO orbitals), and generating all singles from these reference determinants. We performed the calculations on chromophore **II** and found that we still observed the large and sudden enhancement at twist angles close to 90°. However, there is some reduction in the extent to which the response is enhanced, and the peaking occurs at a smaller angle of 80°, as opposed to 88°.

(31) The bandwidth increase as λ_{max} shifts to the red is an artifact of the Lorentzian form with fixed broadening that we assume for the line shape.

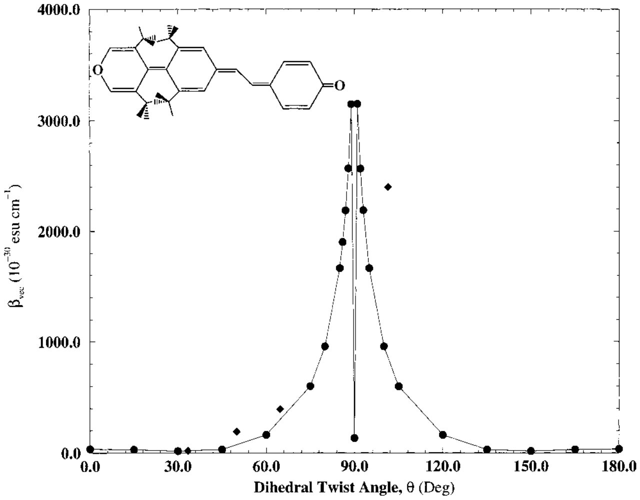


Figure 5. Variation of β_{vec} at an excitation energy of 0.1 eV as a function of imposed twist angle for chromophore **IV**. ◆ represent the corresponding values for the optimized structures of chromophores **IVa**−**IVe**.

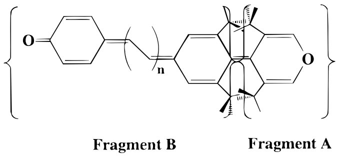
to be adequate, as judged by comparing chromophore **III** optimized geometries from the 6-31G** basis set with those derived from an AM1 level of optimization. The resulting linear and NLO response properties of chromophores **IV** are presented in Table 1.

There are a number of tactics available to increase the conjugation extent of an NLO chromophore. One common approach is to introduce conjugated ethylenic linkages between the donor and acceptor substituents. However, in the present chromophores, introduction of conjugated ethylenic linkages between the pyrilium and phenolic groups would reduce the steric crowding required to induce the dihedral twist. However, π-conjugated linkages can be appended at the phenolic fragment while retaining active steric crowding, or alternatively, additional π-conjugated links can be appended to the pyrilium fragment by inserting an additional phenylene ring, thus yielding chromophores of types **IV** and **V**, respectively (Table 1). To make a proper comparison between the two approaches, an additional phenylene moiety is also introduced in chromophores **IV** (Table 1).

The variation of the first hyperpolarizability of chromophore **IVa** as a function of dihedral twist angle is shown in Figure 5. The variation of the NLO response follows the simple Hückel picture described in section IIA, and the response properties of the substituted chromophores (**IVb**−**IVe**) are almost identical to those of the unsubstituted ones for identical twist angles. This further confirms the minimal effects of the electronic/inductive effects of the bulky groups on the linear and NLO response properties. Unlike chromophore **IIe**, the dihedral twist angle of **IVe** is close to 104°, and the molecule exhibits an unprecedentedly large first hyperpolarizability ($\mu\beta = 68611 \times 10^{-48}$ esu at 0.1 eV).

Comparison of the computed parameters for **IVe** and **V** (Table 1) shows that the response properties of chromophore **IVe** are ~2.5 times larger than those of **V**. Qualitatively, this can be understood in terms of how charge separation stabilizes the two subfragments. In **IIIe** (Table 1), while both the pyrilium and the arene ring of the resultant phenolate anion subfragment gain aromaticity on charge separation, the aromatic stabilization of the pyrilium ring occurs more directly than in the arene ring, where it arises from the stabilization of the charge by the exocyclic phenolic oxygen. This implies that appending π-conjugated groups to the phenolic ring of the chromophore skeleton (**IV**) should enhance the response properties more effectively than when a π-conjugated group is appended to the pyrilium end (**V**), because direct aromatic stabilization of the pyrilium ring is retained. This is confirmed by comparing the response properties of **IVa** and **V**. The effect of the conjugation length in a given skeletal series can be discerned by analyzing the response properties of chromophores **IIIe**, **IVe**, **IVf**, and **IVg**. Interestingly, it can be seen in Table 1 that increases in conjugation length do not guarantee enhanced response properties. An initial increase in the first hyperpolarizability is observed on proceeding from **IIIe** to **IVe**, followed by a decline from **IVe** to **IVg**. This can explained on the basis of the aromatic stabilization arguments. While aromatic stabilization of the pyrilium ring is still favored in all the chromophores, the aromatic stabilization of the phenolate ring is reduced by increasing the conjugation length, as the proximity of the =O group to the central double about which the twisting occurs, which eventually becomes an O^- group on charge separation, decreases. Note that the initial charge separation occurs as a result of a heterolytic cleavage of the central double bond (about which the twisting occurs), and this charge is stabilized by the aromatic stabilization of the pyrilium and phenolate rings. In chromophores **IV**, as the molecular length increases, the proximity of the phenolate group to the central double bond decreases. This reduces the charge separation and hence reduces the response.

Table 2. Intra- and Inter-Subfragment Optical Excitation Energies (in nm) of Extended TICTOID Structures



molecule	n	X	λ_{max} (fragment A)[a]	λ_{max} (fragment B)[a]	λ_{max} (CT)
IIIe	0	O	225.0 (181.9)	297.1 (268.8)	1206.8
IVe	1	O	224.2 (181.9)	465.4 (440.3)	1204.5
IVf	2	O	226.8 (181.9)	484.1 (489.9)	1093.4
IVg	3	O	226.9 (181.9)	574.8 (532.9)	971.0

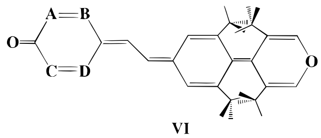
[a] The values in the parentheses are the absorption maxima of the respective isolated fragments.

To further test the arguments regarding intra- and inter-subfragment excitations in these extended TICTOID chromophores, the three dominant excitations in chromophores **IIIe**, **IVe**, **IVf**, and **IVg** are compared in Table 2. As described above, all the chromophores exhibit three characteristic excitations: (1) an excitation within the pyrilium subfragment (A), the energy of which is nearly invariant with increase in conjugation length, (2) an excitation within the α,ω-diphenyl polyene fragment functionalized at one end with an O^- group, the energy of which decreases with increasing conjugation length, as expected from particle-in-box notions, (3) an inter-subfragment excitation, the energy of which increases with increasing conjugation length, owing to initial state stabilization. The properties of these characteristic absorptions not only reflect three optically distinct subfragments but also confirm the hypothesis concerning reduction in efficiency of charge separation with increasing conjugation length. While an increase in conjugation length leads to an *increase* in NLO response in smaller systems, it can lead to a *decrease* in extended conjugated TICTOID structures. The electronic structure of the long-chain TICTOID structures can be described in terms of the electronic structure of the subfragments, as substantiated by the presence of the intra- and inter-subfragment optical excitations.

The effect of increasing the strength of TICTOID donor and acceptor substituents can be appreciated by comparing the responses of chromophores **IVe** and **IVh** (Table 1). In chromophore **IVh**, the acceptor strength of the chromophore is increased by replacing the O atom of the pyrilium ring with an S atom. Curiously, the probable increased acceptor strength of the thiopyrilium moiety[32] does not effect an increase in β. Rather, the response of **IVh** is only about half that of **IVe**. A possible source of reduced response properties of **IVh** is reduced aromatic stabilization of the thiopyrilium ring. Nevertheless, intra-fragment excitations are also observed in the case **IVh**. The $\mu\beta$ response of these chromophores (**IVe**−**IVh** and **V**) at an excitation energy of 0.65 eV (Table 1) ranges from 200000 $\times 10^{-48}$ to $\sim 860000 \times 10^{-48}$ esu. To our knowledge, these are the largest NLO responses ever obtained for organic molecular chromophores either from theoretical calculations or from experimental measurements. Note also the change in sign of $\mu\beta$ at an excitation energy of 0.65 eV. This is because the two-photon resonance for most of these chromophores is at energies less than 1.3 eV. Thus, the real part of the response changes sign.

C. Auxiliary Donor−Acceptor Effects. An alternative approach to enhancing the NLO response of organic molecules was originally proposed by Reinhardt et al.,[33] who pointed out that aromatic heterocycle rings can serve as additional donors or acceptors, owing to the electron excessivity or deficiency[34] of the heterocycle, which depends on the number of π orbitals, π electrons, and heteroatoms in the ring. A recent detailed theoretical analysis[35] of the response properties of simple heterocycle-containing stilbene-based chromophores showed that electron excessive/deficient heterocycles effectively screen ground-state polarization and hence amplify substituent donor/acceptor effects. This increased donor/acceptor capability leads to enhanced NLO response properties.[36] In an attempt to incorporate the above electron excessivity/deficiency effects in the present TICTOID structures, chromophores **VIa**−**VIf** (Table 3) were designed. In these chromophores, the phenolate portion of the chromophore is replaced with five- and six-membered heterocycles functionalized with a ═O/O$^-$ group. The electron excessivity of the heterocycles increases from thiophene to furan to pyrrole, and the electron deficiency increases from diazene to tetrazene.[35]

Table 3. Linear and First Hyperpolarizabilities of Extended TICTOID Structures Incorporating Auxiliary Donor and Acceptor Fragments (Heterocyclic Rings) at an Excitation Energy of 0.1 ev



VI

molecule	A	B	C	D	λ_{max}	$\beta_x(0.1)$	$\mu\beta(0.1)$	$\mu\beta(0.65)$
VIa	CH	CH	S		974.4	818.32	17181	−526150
VIb	CH	CH	O		921.1	476.06	11501	239245
VIc	CH	CH	NH		857.9	428.61	8077.8	58852
VId	N	N	CH	CH	458.6	103.68	4193.8	6061.4
VIe	N	N	N	N	437.6	71.30	3031.6	4008.8
VIf	CH	N	CH	N	601.6	752.41	27112	50242

The calculated responses of chromophores **VIa**−**VIf** are presented in Table 3. Interestingly, and unlike simple stilbene-like or porphyrinic chromophores, the SHG coefficients of the TICTOID structures *decrease* with increased donor fragment electron excessivity. Thus, the response of chromophore **VIc** at 0.65 eV is an order of magnitude smaller than that of **VIa**. This can be attributed to two effects. First, an electron excessive heterocycle hinders efficient charge separation[37] at twist angles close to 90°, hence opposing the formation of an O$^-$ group that acts as the dominant donor in these chromophores. This is supported by the fact that the response decreases with increasing electron excessivity (**VIa** → **VIb** → **VIc**). Second, the presence of electron-deficient heterocycles also fails to increase the response, because the electron-deficient heterocycles both hinder charge separation[38] and diminish the donor ability of the O$^-$ group. Thus, replacing a phenylene fragment with an electron excessive or deficient ring actually leads to a reduction in the NLO response of these TICTOID chromophores.

IV. Conclusions

Analysis of the linear and NLO response characteristics of simple and extended TICTOID structures demonstrates the attractive, substitutionally tunable features of these simple twisted π-conjugated systems. Such chromophores exhibit not only some of the largest nonlinear responses ever identified but also very large, tunable infrared absorption cross sections and the possibility of optical limiting behavior. Even though the responses of these relatively simple chromophores are far larger than those of conventional organic π-conjugated chromophores, tactics to enhance these large responses additionally by conventional approaches, such as increasing the conjugation length, increasing the donor/acceptor substituent strength, or employing auxiliary donor and acceptor groups, are suprisingly ineffective. While an increase in the conjugation length increases the response in smaller TICTOID systems, the response drops off for larger conjugation lengths. For the chromophores studied in this contribution, increased donor/acceptor strength does not lead to increased response properties. This is true even in the case of auxiliary donor and acceptor groups, where increasing strength also leads to a decrease in the response properties. The principal factor that affects the linear and NLO response in TICTOID chromophores is the ease with which charge separation can be effected and how the charge separation is stabilized (by aromaticity in the present chromophores).

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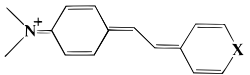
(32) The first hyperpolarizabilities of chromophore set **VII** were calculated using the methods described herein.



IV

At a nonresonant excitation energy of 0.1 eV, the β responses of chromophores **VIIa** (X = N−CH$_3$), **VIIb** (X = O), and **VIIc** (X = S) are 100.50×10^{-30}, 91.81×10^{-30}, and 96.13×10^{-30} esu, respectively. The response properties indicate acceptor strength increases from O+ to S+ to N+. However, it must be noted that variations of the acceptor strengths are modest.

(33) (a) Reinhardt, B. A.; Kannan. R.; Bhatt, J. C. *Proc. SPIE-Int. Soc. Opt. Eng.* **1994**, *2229*, 24. (b) Reinhardt, B. A. *Proc. SPIE-Int. Soc. Opt. Eng.* **1993**, *1853*, 50. (c) Karna, S. P.; Zhang, Y.; Samoc, M.; Prasad, P. N. Reinhardt, B. A.; Dillard, A. G. *J. Chem. Phys.* **1993**, *99*, 9984.

(34) Electron excessivity and deficiency are defined as the actual electron density on the carbon atoms of the heterocycle minus the number of π electrons donated by the carbon atoms to the π framework.[35]

(35) (a) Varanasi, P. R.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *188*, 12443. (b) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575.

(36) Albert, I. D. L.; Marks, T. J.; Ratner, M. A.; *Chem. Mater.* **1998**, *10*, 753.

(37) The aromaticity of the heterocycles decreases on going from thiophene to pyrrole, hence the aromatic stabilization on charge separation decreases in that order, and hence the presence of electron excessive rings does not facilitate efficient charge separation.

(38) The aromaticity of the six-membered rings decreases from benzene to tetrazine, and hence a reduction in the aromatic stabilization of the resultant anion occurs on replacing a phenyl ring by an electron deficient heterocycle (aromatic stabilization decreases on going from benzene to tetrazine[35b]). Thus, efficient charge separation is observed.

In all the TICTOID chromophores examined, the optical spectrum exhibits three characteristic absorption bands. Two occur at high energies and with large oscillator strengths, while the redmost is at lower energy with oscillator strength decreasing with extent of twist. Analysis of these bands using the CI wave functions and relevant molecular orbitals shows that the two intense absorptions originate in the two disjoint chromophore subfragments, while the third, weaker absorption is an inter-subfragment transition involving charge transfer from the donor to the acceptor. While these transitions lie close in energy when the chromophore rings are coplanar, they are well-separated in twisted TICTOID structures and exhibit minimal absorption in the visible region. Such chromophores (that exhibit two distinct absorptions) are of obvious interest in optical limiting, as well as for tunable refractive index and very large tunable hyperpolarizability.

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