

Communications to the Editor

Conformationally-Induced Geometric Electron Localization. Interrupted Conjugation, Very Large Hyperpolarizabilities, and Sizable Infrared Absorption in Simple Twisted Molecular Chromophores

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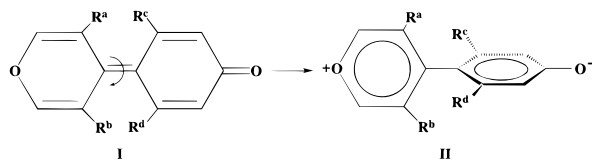
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There is intense current research activity in the area of molecular linear and nonlinear optics, devoted to the search for efficient, stable, simple organic chromophores exhibiting large first or second hyperpolarizabilities.^{1–4} Several promising structural motifs have been identified; however, the simple planar ones (strong donor or acceptor substituents linked by a polyene, heterocyclic, or aromatic π -network) are still the most common.^{1–4} Computational analysis has proven extremely valuable in suggesting new candidate species and in understanding the nature of the nonlinear response in a variety of molecular chromophores.^{4,5} Another optical property of substantial technological importance, which has been much less studied, is tunable, strong absorbance in the infrared region.⁶ Strong IR absorbers are of interest for filters, polarizers, optical recording,⁶ photodynamic therapy,⁷ etc. Most molecular infrared absorption

is due to vibrational (mid- and far-infrared) or mixed-valence near-infrared transitions.⁸ The oscillator strengths of such transitions are usually too weak to act as efficient absorbers.

We report here a simple class of donor/bridge/acceptor chromophores (3,5-dialkyl-2',6'-dialkyl-4-quinopyrans, **I**, and their zwitterionic forms, **II**)⁹ that provides both very large



Chromophore	R ^a	R ^b	R ^c	R ^d
Ia	H	H	H	H
Ib	H	H	Me	Me
Ic	Me	Me	Me	Me
Id	Me	<i>t</i> -Bu	Me	<i>t</i> -Bu
Ie	<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu

tunable first molecular hyperpolarizabilities and near-infrared cross-sections. The structural characteristic that promotes these optical features is a stereochemically enforced break 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.

Chromophore set **I** undergoes distortion from a planar quinoidal geometry to a charge-separated zwitterionic geometry (**II**) with an increase in the dihedral twist θ . While a biradical vs zwitterionic electronic ground state for twisted ethylene has been a subject of much debate,¹⁰ it is expected^{10b,g} that an unsymmetrically substituted alkene such as **I** will have a zwitterionic singlet ground state at $\theta \approx 90^\circ$. This arises principally from aromatic stabilization of the phenolate and pyrilium rings in the twisted geometry.

The geometries of the subject chromophores were fully optimized using the AM1-parametrized NDDO Hamiltonian incorporated in the MOPAC package.¹¹ The steric bulk of the R substituents was varied to enforce increasing values of θ . The linear optical and SHG coefficients of **Ia** were computed at various imposed values of θ . Note that the geometries were not optimized at these imposed twist angles. Computations of molecular linear absorption and first hyperpolarizability β were carried out using the ZINDO semiempirical electronic structure model Hamiltonian.¹² Singly excited configuration interaction was used for both properties; in molecules of this sort, ample literature precedent suggests that these calculations are reliable.^{4,13–15}

In Figure 1A, the variation of the absorption maxima of chromophore **Ia** (variable θ) and set **I** (open circles) are plotted as a function of θ . The inset shows the corresponding transition moments of the associated optical excitations. In Figure 1B are plotted the variation in β_{vec} of chromophore **Ia** as a function of θ (filled circles) and the β_{vec} values of chromophore set **I**

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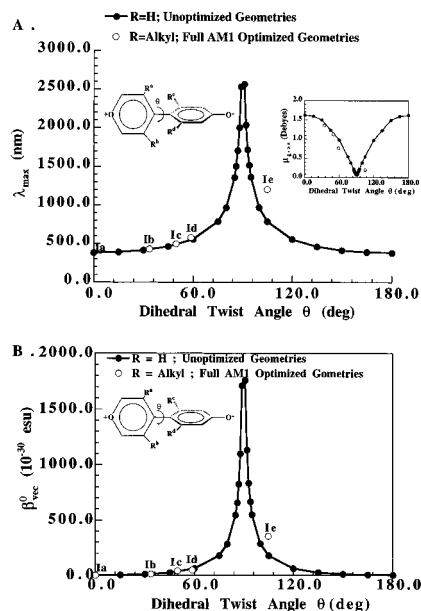


Figure 1. Variation of λ_{\max} (A) and β_{vec} (B) at an excitation energy of 0.1 eV (closed circles) as a function of the dihedral angle of chromophore **Ia**. Open circles represent the corresponding values of chromophore set **I**. The inset in (A) shows the transition moments of the first excited state.

(open circles). Note the close correspondence of the β_{vec} values at corresponding values of θ , indicating substitutional tunability of response properties. The unsubstituted planar molecule (with a fully conjugated backbone) exhibits a small first hyperpolarizability ($\mu\beta^0 = 27.9 \times 10^{-48}$ esu); however, this hyperpolarizability becomes extremely large ($\mu\beta^0(89^\circ) \approx 30\,000 \times 10^{-48}$ esu) when θ approaches $\sim 90^\circ$. While none of the fully optimized geometries of chromophore set **I** exhibit a dihedral angle of $\sim 90^\circ$, the fully optimized geometry of **Ie**, with bulky *tert*-butyl substituents, exhibits a dihedral angle of 104° and a $\mu\beta$ of $\sim 25\,000 \times 10^{-48}$ esu at an excitation energy of 0.65 eV. This response is 2 orders of magnitude larger than that of the

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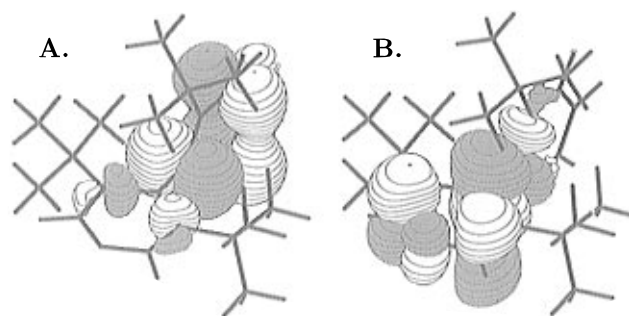


Figure 2. 3-21G orbital densities of the HOMO (A) and LUMO (B) of chromophore **Id** ($\theta = 104^\circ$). A full 3-21G-optimized geometry is used in the calculation.

archetypical NLO chromophore 4-(*N,N'*-dimethylamino)-4'-nitrostilbene (DANS), at the same frequency. The optical absorption maximum of **Ie** shifts to the infrared region, with somewhat diminished but appreciable cross-section, near 90° (Figure 1A). This transition is, in fact, analogous to the intervalence transfers of mixed valency found in binuclear metal complexes,⁸ but exhibits much greater oscillator strength because of the significant remaining orbital overlap in the two orthogonal fragments (Figure 2). This significant overlap provides the dominant contribution to the excitation and NLO response.

The present behavior of linear and NLO response properties can be understood in several ways: bond alternation in structures **I** and **II** is entirely different, and the zwitterionic structure provides alternation patterns that promote large hyperpolarizabilities.^{14,16} Perhaps more simply, both the two-level model for the hyperpolarizability¹⁷ and the very simple HOMO–LUMO picture for the optical absorption suggest that, by conformationally-induced breaking of the π -conjugation and formation of a zwitterionic structure (similar to the twisted intramolecular charge transfer (TICT) state¹⁸), the steric repulsion provides a low-energy, strongly allowed optical feature that facilitates strong linear and unprecedented NLO response. The ramifications of these observations are currently under investigation.

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