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(Dicyanomethylene)pyran Derivatives with C_{2v} Symmetry: An Unusual Class of Nonlinear Optical Chromophores

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Abstract: A series of symmetric derivatives of 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM laser dye) has been synthesized, and the nonlinear optical properties and thermal decomposition temperatures of each of the chromophores has been measured. The symmetric chromophores all have larger hyperpolarizabilities than one would expect based on their absorption maxima. Estimations of their oscillator strengths based upon UV/vis spectra are all well above 1.0. It is proposed that these compounds possess two excited electronic states close to each other in energy, both contributing to the hyperpolarizability in an additive fashion. Electro-optical absorption spectroscopy data and semiempirical calculations on a model compound support this hypothesis. The implications of these results with regard to the tradeoff between nonlinearity and transparency are discussed. The large dipole moments and high decomposition temperatures of these chromophores make them attractive candidates for use in electro-optic polymers.

Introduction

Design, synthesis, and characterization of organic chromophores for use in electro-optic (EO) polymers are challenging but potentially useful areas of research that are currently receiving a great deal of attention. The chromophore problem is challenging because the properties required for use in EO applications are to a large degree mutually exclusive. For example, a large dipole moment enables better alignment of the chromophore in an applied electric field (poling), but too high of a value can decrease the solubility of the chromophore in the organic host. The tradeoff that has received the most attention has been the nonlinearity−thermal stability tradeoff; aromatic groups incorporated into a chromophore's delocalized bridge generally increase the thermal stability but decrease the molecular hyperpolarizability. The decrease occurs because the intramolecular charge transfer that must occur in a useful chromophore would require the aromatic rings to adopt a quinoidal bonding pattern, which is clearly disfavored. Incorporation of one quinoidal ring into the structure for each aromatic ring, so that the net amount of aromatic stabilization energy is retained upon promotion to the first excited state, has been shown by Marder and co-workers[1] to preserve the hyperpolarizability, but the effect of this type of substitution upon the molecular decomposition temperature remains unclear. Aromatic groups may be successfully incorporated into amine donor groups (i.e., "upstream" of the donor) with beneficial effects on both the decomposition temperature and the hyperpolarizability, which defeats the tradeoff to a certain extent.[2] Combined with the enhanced hyperpolarizabilities achievable through the use of cyanovinyl acceptor groups,[3] which decrease molecular decomposition temperatures less than one would expect,[4] arylamino donor substitution has enabled the preparation of a small class of compounds that are adequate for EO applications from both a nonlinearity and a thermal stability point of view. The remaining (and more challenging) tradeoff to evade is that between molecular nonlinearity and optical transparency.

A working electro-optic device cannot afford to convert an appreciable amount of the input light to heat, and photochemistry of any kind at the operating wavelength is intolerable. Absorptive loss should be below 1 dB/cm, so that more than 90% of the light entering a 1 cm waveguide device will be transmitted. Since the chromophore concentration in a typical EO polymer is approximately 0.5 M, the extinction coefficient of the chromophore at the use wavelength must be less than about 0.2 M^{-1} cm^{-1}. The primary source of absorptive loss at the optical communication wavelengths of 1.3 and 1.55 μm is the low-energy tail of the first electronic excited state, since these wavelengths lie in the transmission windows between the C−H overtone absorptions of a typical organic material. Therefore, the absorption maximum wavelength λ_{max} is an approximate measure of the transparency achievable in a polymer containing a given chromophore. The nonlinearity achievable with the chromophore can be shown[4] to be proportional to $\mu\beta/M$, where μ is the dipole moment, β is the hyperpolarizability at the use wavelength, and M is the molecular weight of the chromophore. Unfortunately, it can also be shown that β, and therefore the nonlinearity, is a strong function of λ_{max}.

According to the two-level model of Oudar and Chemla,[5] the molecular hyperpolarizability of a chromophore can be well approximated by including only matrix elements involving the ground and first excited electronic states. This assumption is most valid for chromophores with a single, well-separated peak

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in their absorption spectra. It has been shown[2] that the zero-frequency extrapolated hyperpolarizability β_0 is proportional to the oscillator strength for the single transition multiplied by λ_{max}[3]. Therefore, for chromophores that are well described by the two-level model, loss of transparency is an unavoidable consequence of any increase in nonlinearity. In practice, the dependence is quite strong; empirical least-squares fits of log β_0 vs log λ_{max} for typical classes of chromophores where donors and/or acceptors are being varied[6] have slopes of approximately 6. If the tradeoff did not exist, and one could enhance nonlinearities dramatically without red-shifting absorbance maxima, such slopes would be infinite. Alternatively, in the less-likely situation where one has an extremely nonlinear and red-shifted chromophore and would like to move its absorption maximum toward the blue without sacrificing much nonlinearity, a slope of 0 would be optimum.

In this paper, we describe our studies on a series of five symmetrical (dicyanomethylene)pyran chromophores. Two of the compounds feature completely aliphatic amine donor groups, two others possess amines with one aliphatic group and one fused aromatic group for enhanced thermal stability, and the remaining compound features completely aromatic amine donor groups. The nonlinearities of these compounds are all substantially higher than expected, and the red shifts associated with substitutions that increase β are smaller than for most other classes of chromophores. We present evidence that the excellent nonlinear optical properties of these compounds are due to the existence of two low-lying excited states, each of which contributes to β in an additive manner.

Experimental Section

Synthesis. The target structure is a symmetric derivative of DCM laser dye, since that chromophore was used successfully in a polyimide-based electro-optic modulator.[7] Shortly before that demonstration, Yamamoto et al. had reported encouraging results in crystal studies using chromophore dimers attached at the donor end ("Λ-shaped molecules").[8] Since excellent thermal stabilities and reasonable nonlinearities had been reported for a series of triarylazole derivatives in which two donor units and one acceptor unit were attached to the azole ring,[6a] it was reasonable to attempt to prepare similar "Y-shaped" chromophores based on DCM with two donor segments and one (dicyanomethylene)pyran acceptor moiety. The six chromophores characterized in this work are shown in Figure 1. In each case, the synthesis is based on a Knoevenagel condensation of 2 moles of a desired aldehyde with 2,6-dimethyl-4-(dicyanomethylene)pyran ("(2,6-dimethyl-4*H*-pyran-4-ylidene)propanedinitrile"). The latter was prepared by the method of Woods.[9]

DCM laser dye was obtained from Exciton and used as delivered for these characterization experiments. The syntheses of DADB, DADCH, and DADIH have been previously described in detail.[10] The syntheses of the remaining two chromophores in this study are given below.

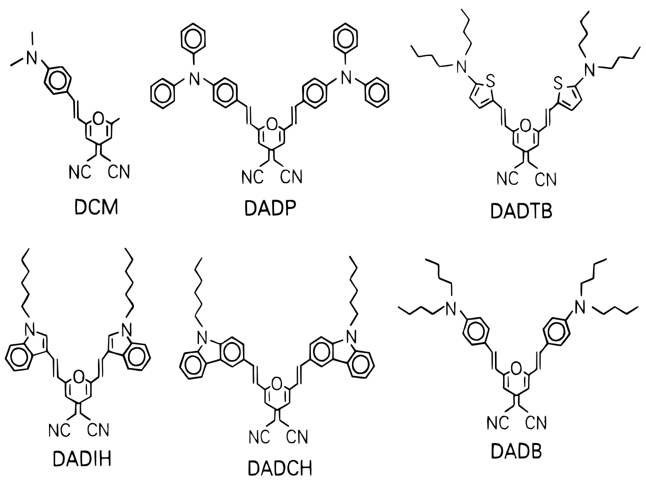

Figure 1. Chemical structures of the six chromophores investigated in this work.

DADP. In a 200 mL round-bottomed flask equipped with stirbar, reflux condenser, and nitrogen bubbler were placed (2,6-dimethyl-4*H*-pyran-4-ylidene)propanedinitrile (0.861 g, 5.0 mmol), 4-(*N*,*N*-diphenylamino)benzaldehyde (3.01 g, 11 mmol), 1-propanol (25 mL), and piperidine (0.425 g, 5.0 mmol). The resulting mixture was refluxed for 8 h and cooled, and the solid product was isolated by suction filtration, washed well with 1-propanol, and air dried. The crude product was filtered hot and recrystallized twice from *n*-butyl acetate. Because the product tends to retain solvent, it was heated under house vacuum (80 mmHg) for an hour at 175 °C prior to characterization, yield 2.64 g (77%): mp (DSC 1°/min) 285−291 °C; ^1H NMR ($CDCl_3$) δ 6.58 (d, $J = 16$ Hz, 2H), 6.61 (s, 2H), 7.00−7.46 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 58.16, 106.345, 115.681, 115.737, 121.544, 124.315, 125.582, 127.439, 129.056, 129.589, 137.505, 146.723, 150.038, 155.888, 158.767; UV/vis λ_{max} ($CHCl_3$) 486 nm ($\epsilon = 7.37 \times 10^4$). Anal. Calcd for $C_{48}H_{34}N_4O$: C, 84.43; H, 5.02; N, 8.21. Found: C, 84.32; H, 5.16; N, 8.15.

DADTB. A solution of 5-(dibutylamino)-2-thiophenecarboxaldehyde (1.38 g, 5.76 mmol, prepared in very low yield from 5-bromo-2-thiophenecarboxaldehyde, dibutylamine, anhydrous potassium carbonate, and Aliquat 336 in DMSO at 110 °C for 3 days), (2,6-dimethyl-4*H*-pyran-4-ylidene)propanedinitrile (0.4976 g, 2.89 mmol), piperidine (2 mL), and glacial acetic acid (1 mL) in benzene (100 mL) was refluxed for 22 h using a Dean−Stark trap. The reaction solution was cooled to room temperature and rotary evaporated. Hexane was added to the solid, which was filtered and redissolved in dichloromethane. The organic solution was washed with water and brine, dried with anhydrous magnesium sulfate, filtered through a short bed of flash silica, and rotary evaporated. The crude solid was recrystallized from ethyl acetate/hexane to give the product as green crystals, 1.12 g (63%): mp 209−210 °C; ^1H NMR (DMF-d_7) δ 0.96 (t, $J = 7.1$ Hz, 12H, four CH_3), 1.31−1.45 and 1.61−1.72 (two m, 8H each, eight aliphatic CH_2), 3.42 (t, $J = 7.3$ Hz, 8H, four NCH_2), 6.06 and 7.28 (two d, $J = 4.2$ Hz, 2H each, four thiophene ring CH), 6.58 (s, 2H, two pyran ring CH), 6.41 and 7.89 (two d, $J = 15.4$ Hz, 2H each, four *trans* double bond CH); FTIR (KBr) 2192, 2177 cm^{-1} (CN stretch); UV/vis λ_{max} ($CHCl_3$) 526, 586 nm (($\epsilon = 7.16$ and 5.68×10^4, respectively). Anal. Calcd for $C_{36}H_{46}N_4OS_2$: C, 70.32; H, 7.54; N, 9.11; S, 10.43. Found: C, 70.21; H, 7.57; N, 9.03; S, 10.50.

Characterization. All six chromophores were characterized by electric field-induced second harmonic generation (EFISH) in chloroform solution as previously described.[6a] The susceptibilities of the chromophore solutions were referenced to a crystalline quartz wedge during each experiment. The second harmonic generation coefficient of the quartz (d_{11}) was determined using the most recent literature value for the absolute nonlinearity of potassium dihydrogen phosphate (KDP) at 1064 nm and the well-established ratio[11] between KDP and quartz at that wavelength, as recommended by Roberts.[12] Extrapolation to 1907 nm was performed using the scaling factor determined by

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Table 1. Experimental Data for (Dicyanomethylene)pyran Chromophores[a]

compound	λ_{max}	f	μ	β	β_0	$\mu\beta^{1.3}/M$	T_d
DCM	468	0.7	10.2 ± 0.1	88.8 ± 6.6	63.3 ± 4.6	2.69	332
	(480)		(8.6)	(82)	(58)		
DADIH	456	1.2	11.9 ± 0.1	70.8 ± 3.3	51.5 ± 2.5	1.29	392
DADCH	458	1.6	10.7 ± 0.1	106 ± 3	77.0 ± 2.1	1.48	412
DADP	486	1.3	9.9 ± 0.2	175 ± 3	121 ± 2	2.28	404
DADB	496	1.4	12.6 ± 0.1	197 ± 2	134 ± 1	3.65	348
	(500)		(9.7)	(160)	(108)		
DADTB	526, 586	1.4	13.1 ± 0.1	215 ± 11	130 ± 9	3.90	300

[a] Wavelengths given in nm, dipole moments in D, hyperpolarizabilities in units of 10^{-30} esu, and temperatures in °C. All spectral and EFISH data were taken in chloroform solution. Values in parentheses were recently reported by Cheng and co-workers;[17] spectra in that work were taken in *N*-methylpyrrolidinone (NMP) rather than in chloroform.

Meredith.[13] The hyperpolarizability β was defined using the B convention of Willetts et al.[14] UV/vis spectra were recorded in the same solvent, and the λ_{max} values obtained from the spectra were used to extrapolate the β values measured at 1907 nm to zero frequency by means of the two-level model.

Oscillator strengths for all of the chromophores except DADTB were determined first by calculating the area of a triangle defined by the absorption maximum, the two half-maximum points, and the base line for each spectrum plotted as extinction coefficient vs reciprocal wavelength. For DADIH, DADCH, and DADTB, a second procedure was used to determine the area of the absorption bands. Five points (the two local maxima, the minimum between them, and the two half-maximum points) were used to define a quartic function whose coefficients were determined by solution of the system of five equations in the five unknowns. Ten significant figures had to be retained in the coefficients for the quartic function to include the five points accurately. Integration of the quartic function between its two x-intercepts provided the area. For the two compounds whose oscillator strengths were determined by both methods, the area under the triangle was equal to the area under the quartic curve within experimental error (a difference of 0.02 in oscillator strength in each case).

Dipole moments were determined by measurements of the dielectric constants of chromophore solutions, also in chloroform, as previously described.[6a] Solution capacitances were measured at 50 kHz, because the primary peaks in the Fourier transform of the "DC" pulse applied across the cell during the EFISH experiments appear at 25 and 75 kHz.

Thermal decomposition temperatures were determined by differential scanning calorimetry (DSC) as follows. Each sample was placed in a covered aluminum pan in air, and the temperature was increased at 20 °C/min until the decomposition exotherm had been traversed. A tangent to the exotherm onset was extrapolated back to the base line, with the intersection assigned as the decomposition temperature T_d. The fairly rapid scan rate causes the exotherm to appear at a temperature between 50° and 80° higher than it would in a quasi-equilibrium scan (which would be prohibitively slow). Therefore, a conservative estimate of the maximum processing temperature for any given chromophore would be $T_d - 80°$.

Electroabsorption (EOA) spectroscopy experiments were performed as previously described.[15] The EOA spectrum is related to the imaginary part of the susceptibility $\chi^{(3)}(-\omega; \omega,0,0)$ and is given by

$$L(\phi,\nu)\kappa(\nu)/\nu = [\kappa^{E}(\phi,\nu)/\nu - \kappa(\nu)/\nu]/E_0^{\,2} \quad (1)$$

The terms κ and κ^E denote the molar decadic absorption coefficients in the absence and presence of the externally applied electric field E_0, respectively, and ν is the wavenumber. Usually, the quantity $L\kappa/\nu$ is measured for several wavenumbers within the absorption band for both parallel ($\phi = 0°$) and perpendicular ($\phi = 90°$) polarizations of the incident light relative to the applied field. The band shape analysis of EOA spectra yields, among other information, the ground- and excited-state dipole moments as well as the direction of the transition dipole in the molecule-fixed frame.[15,16]

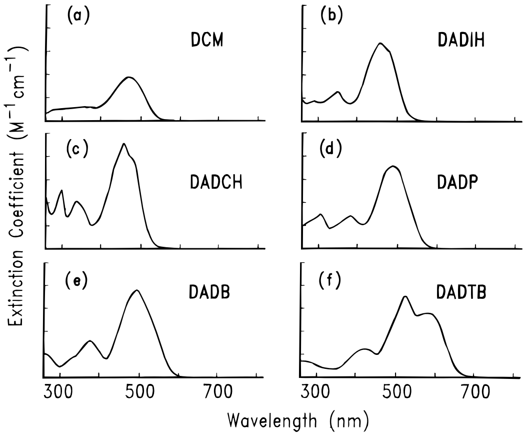

Figure 2. UV/vis spectra of the six chromophores in chloroform solution. Each hash mark on the vertical axes corresponds to 20 000 M^{-1} cm^{-1}.

Results

Data from spectral, dielectric, differential scanning calorimetry, and EFISH experiments for all six chromophores are included in Table 1. EFISH data from another laboratory for DCM and DADB have previously been reported,[17] and those values are included in the table for comparison.

The β_0 values were determined as if each chromophore followed the two-level model, namely by using the absorption maximum as a measure of the energy difference between the ground and excited states. For DADTB, where two maxima clearly appear, the extrapolation was performed using each one and then the average value was included in the table. The β_0 values were extrapolated to 1.3 μm using the two-level model dispersion expression for the electro-optic effect[18] in order to determine the molecular nonlinearity $\mu\beta^{1.3}/M$, the chromophore figure of merit for device applications at that wavelength.

Figure 2 shows the UV/vis spectra of each of the chromophores in chloroform solution. The spectra have been scaled so that the top mark on each y-axis corresponds to an extinction coefficient of 100 000 M^{-1} cm^{-1}.

EOA spectroscopy was performed on DADB in dioxane solution. The experimental data are shown in Figure 3. Parameters determined from these data are presented in Table 2.

Discussion

Several aspects of the data in Table 1 are quite striking. First, it is clear that the symmetrical DCM derivatives are substantially more nonlinear than one would expect from the data on DCM,

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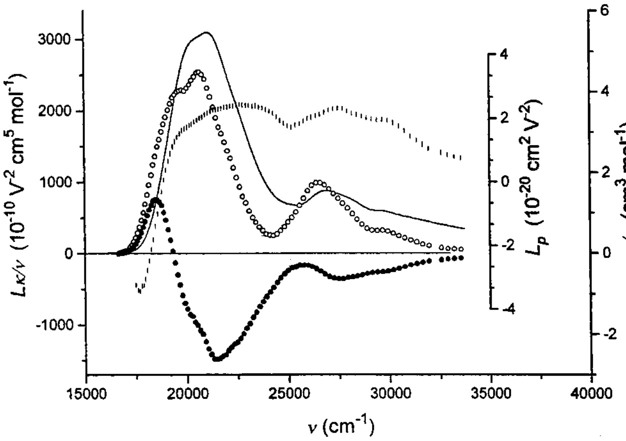

Figure 3. Optical (solid line) and electro-optical (circles) absorption spectra of DADB in dioxane. The figure shows EOA data points for parallel (○) and perpendicular (●) polarization of the incident light relative to the externally applied field. L_p (vertical lines) is the electro-optical anisotropy function.

Table 2. Electro-optical Absorption Data for DADB

parameter	peak 1	peak 2
λ_{max} (nm)	473	371
ϵ_{max} (M^{-1} cm^{-1})	65300	23700
μ_{ge} (D)	10.8	5.4
μ_g (D)	9.6 ± 0.6	9.3 ± 0.6
$\Delta\mu$ (D)	13.5 ± 2.1	13.2 ± 4.2
β_0 (10^{-30} esu)	275 ± 47	41 ± 27

which is itself an excellent chromophore. For example, the absorption maximum of DADCH is 466 cm^{-1} to the blue of DCM, but β_0 is 22% larger rather than being smaller. Second, the absorption peaks of all of the symmetrical chromophores correspond to oscillator strengths greater than unity. Third, the dipole moments of all six compounds are quite high—10 D or greater. Only the large molecular weights, particularly for DADP, prevent the molecular nonlinearities ($\mu\beta/M$) from being extremely large. Fourth, the experimental decomposition temperatures are all above 300 °C, with two of them surpassing 400 °C. Despite the lack of complete aryl substitution at the amine donor (except for DADP), these compounds exhibit excellent thermal stability.

The unusually large nonlinearities and oscillator strengths suggest that the symmetric DCM derivatives have two charge-transfer excited states lying close to each other in energy, each providing a contribution to β with the same sign. Accordingly, we performed a semiempirical calculation on the simple diamino analogue of DADB (DADH) using the DZDO program. By examining the coefficients of the p_z orbitals in the various molecular orbitals, one can determine the change in electron density on all of the sp^2- and sp-hybridized atoms in the molecule induced by excitation from the ground state to a given excited state. The calculation indicates that DADH has its lowest transition at 391 nm, with a second excited state absorption appearing at 380 nm. The peak separation of approximately 740 cm^{-1} is rather small, so we infer that the spectrum of DADH would resemble that of the *n*-butylamino analogue DADB, with the less-intense peak appearing as a shoulder.

The electron density change upon promotion to each of the first two excited states calculated for DADH is shown in Figure 4. Interestingly, the $C(CN)_2$ moiety is not calculated to be the principal electron acceptor in this compound. Indeed, in the first excited state, it acts as a net electron donor, while in the second excited state it is merely a weak acceptor. It is the 2-, 4-, and 6-positions on the pyran ring that develop the largest amount of negative charge in both excited states. In addition, most of the atoms in the delocalized bridge between the donor and acceptor display appreciable changes in electron density; mere loss of electron density at the donor and gain at the acceptor is obviously an excessively simplistic picture. The pattern in the first excited state is particularly interesting. Charge is transferred from the nitrogen donors to their adjacent carbons, then from the next adjoining set of carbons in the phenyl rings to the following ones, and so on. There is a node between every two adjacent atoms except those in the C—O bonds. Charge ultimately ends up moving from the dicyanomethylene group into the ring as well.

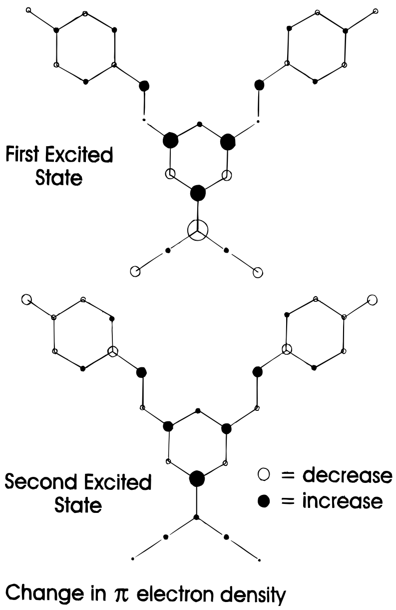

Figure 4. Occupancy changes in p_z orbitals upon promotion to the two low-lying excited states of DADH, the simple amino analogue of DADB (NH_2 donor groups instead of NBu_2 groups).

DADH has C_{2v} symmetry in its lowest-energy conformation. It is important to note that the appearance of two low-lying excited states close in energy is not a consequence of this C_{2v} symmetry, at least not in the obvious way. Compounds of sufficiently high symmetry can have degenerate excited states, which might be expected to interact and split to a small amount. But C_{2v} is too low of a symmetry group to induce this effect; it has no degenerate irreducible representations. If the symmetry is increased to 3-fold, such as C_{3v}, degenerate representations appear, but it is difficult to imagine a delocalized organic donor—acceptor compound with C_{3v} symmetry.

A simple valence-bond picture provides an indication of how to proceed if more compounds of this type are desired. In a molecule with two donors and one acceptor, the ground state can be described as D_1D_2A. If the donor groups do not interact, then there will be two degenerate excited states: $D_1^+D_2A^-$ and $D_1D_2^+A^-$. If the two donors interact, the two excited states will be linear combinations of the form $[D_1^+D_2A^- + D_1D_2^+A^-]$ and $[D_1^+D_2A^- - D_1D_2^+A^-]$, and their energies will be split by an amount proportional to the strength of the interaction. The bigger the splitting, the smaller the contribution made by the second excited state to the molecular hyperpolarizability. Therefore, if one desires a chromophore with quasi-degenerate excited states, one needs to design a compound whose multiple donors (or, equivalently, multiple acceptors) interact as little as possible.

EOA results, in combination with the other results described above, can shed some light on the nature of the two excited states in DADB. For example, a combination of polarization-dependent EOA and EFISH measurements was used to investigate β in 3,5-dinitroaniline (3,5-DNA).[19] 3,5-DNA exhibits a low-lying charge transfer (CT) absorption band with a transition dipole perpendicular to the C_2 axis of this C_{2v} chromophore. At higher energy, a more intense absorption band with a parallel transition dipole is observed. These two CT bands are responsible for the two-dimensional character of β in this chromophore and cause interesting phenomena such as deviations from Kleinman symmetry.

DADB has two donors and one acceptor, and thus shows a multiple donor–acceptor substitution pattern similar to that of 3,5-DNA. Two absorption maxima, the first at 473 nm and the second at 371 nm were observed in dioxane solution. The band shape analysis of the EOA spectrum yields values for the ground-state dipole moment and the dipole moment change upon excitation, given in Table 2. Lorentz-type local field corrections were applied.[20] Integration of the bands yields the magnitude of the transition dipoles for the two excited states. The observed magnitudes of all of these dipoles were large and comparable to those found in a recent study of donor–acceptor conjugated polyenes of comparable conjugation length.[21]

Remarkably, both transitions are polarized parallel to the C_2 axis and contribute additively to the hyperpolarizability with dipolar two-level terms of the form

$$\beta_0 = 3\Delta\mu(\mu_{\mathrm{ge}})^2/(hc\nu_{\mathrm{ge}})^2 \qquad (2)$$

The results show that the intense low-lying CT transition accounts for most of the experimental hyperpolarizability.

In order to identify a possible low-lying perpendicular transition in DADB as observed previously in 3,5-DNA, we calculated the electro-optical anisotropy function

$$L_p(\nu) = 6[L(\phi = 0, \nu) - 3L(\phi = 90, \nu)] \approx 2\mu_{\mathrm{g}}^2/(kT)^2 \qquad (3)$$

This function is expected to be positive and constant for a purely parallel transition, as is indeed observed for the 473 and 371 nm bands. But at the red edge of the 473 nm transition, the function drops dramatically, even to negative values. This is a clear indication of a transition with a nonparallel transition dipole. The transition could not be identified as being perfectly perpendicular because of overlap with the more intense parallel band and/or varying transition dipole directions caused by conformational fluctuations. The intensity of this band is weak, its oscillator strength being only 5–10% of the parallel transition.

The semiempirical calculations for DADH predicted a very intense low-lying parallel transition to an A_1 excited state, followed by a weaker perpendicular transition to a B_2 excited state, in reasonable agreement with the EOA results for DADB. These two excited states correspond to the symmetric (A_1) and antisymmetric (B_2) valence bond combinations described above. Interestingly, both results suggest that the first of the two excited states (A_1) is responsible for the vast majority of the experimentally observed hyperpolarizability. The calculations also indicate that the dipole moment of the second excited state of DADH is greater than that of the first. The sign of β is determined by that of the excited state dipole moment minus the ground state dipole moment, and we know from the slopes of second harmonic intensity vs concentration in EFISH experiments for all of the chromophores that this quantity is positive. If the relative magnitudes of the dipole moments of the first two excited states follow the same trend that we calculate for the analogous structure with simple NH_2 donor groups, then the contribution to β from the second excited state must also be positive.

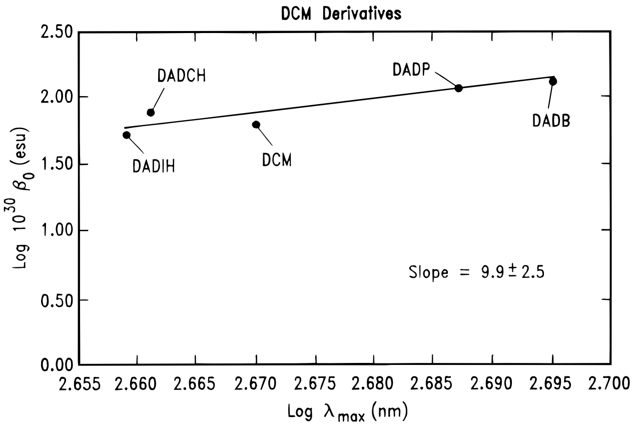

Figure 5. Nonlinearity–transparency plot for the chromophores that do not exhibit two discrete absorption maxima in Figure 2. The DCM data were not used to calculate the least-squares line shown in the figure.

EOA data also indicate that the two contributions to β, while different in magnitude, have the same sign and are therefore additive. If so, one would expect that a nonlinearity–transparency plot would exhibit a greater than normal slope. This plot is shown in Figure 5. DADTB is not included on the plot since its two excited states are sufficiently separated (1950 cm^{-1}) to produce two distinct maxima (as opposed to a shoulder) and therefore a larger uncertainty in β_0 (as indicated in Table 1). DCM is shown for reference purposes, but was not included in the least-squares calculation because it is not a simple modification of the other four chromophores and should therefore not necessarily be expected to fall along the same rough line. The slope of that line is approximately 10, a substantial increase over the typical value of 6. Therefore, for a given amount of red shift induced by substitution of a different donor group in the DAD structure, an unusually large increase in nonlinearity is obtained. This result supports the conclusion that both excited states contribute to the hyperpolarizabilities, and thus the usefulness, of these chromophores.

What are the disadvantages of this class of chromophores? So far, only two have surfaced. The first is their large size, which restricts the concentration that one can obtain in an electro-optic polymer. Because the electro-optic coefficient is proportional to chromophore concentration, the molecular weight ends up in the denominator of the figure of merit.[4] It might therefore be of interest to determine whether similar compounds lacking the two double bonds next to the pyran ring can be synthesized. Such compounds would be physically smaller and probably more thermally stable, but their donor–donor interactions would probably be stronger, increasing the energy gap between the two useful excited states, and their hyperpolarizabilities would probably be lower. Another obvious modification is to decrease the size of the amine donor alkyl groups (hexyl in DADIH and DADCH, butyl in DADB and DADTB). But that modification leads to the other limitation of the (dicyanomethylene)pyrans: limited solubility. Polyaromatic compounds often display limited solubility, and these are no exception. The earlier EFISH work on these compounds included primarily compounds with dimethylamino donor groups (DAD, DADC, DADI).[17] DADI was insufficiently

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soluble to yield reliable results, and so were the other two in our hands. But the DADCH results reported here and the DADC results reported in ref 17 are in good agreement, therefore perhaps these long alkyl chains are not always needed.

Large alkyl groups added for solubility reasons might also cause difficulties with regard to poling. If the chromophores become entangled with the polymer chains, orientation in an electric field at temperatures higher than the glass transition temperature T_g could be sterically hindered enough so that prohibitively long times would be required to achieve the maximum degree of orientation possible in a given applied field. For these chromophores, however, complete orientation is not required in order for a given molecule to make an appreciable contribution to the nonlinearity of the material. It has been shown[22] that the β_{zxx} tensor component can be enhanced in C_{2v} molecules by using two donor groups. The off-diagonal contribution ensures that much less orientation is required before the hyperpolarizability of each molecule contributes to the electro-optic coefficient of the polymer. An extension of this concept is the work of Zyss and co-workers on octupolar chromophores with D_{3h} symmetry, such as triaminotrinitrobenzene,[23] which have no dipole moment and cannot be oriented, but which nevertheless have nonlinearities due to off-diagonal components of β.

Conclusions

Symmetric (C_{2v}) derivatives of DCM laser dye have two low-lying electronic excited states that contribute to the molecular hyperpolarizability β in an additive manner, making these compounds potentially very useful for second-order nonlinear applications such as electro-optic modulators and frequency doublers. The molecular nonlinearities are comparable to those of chromophores from other classes that exhibit absorption maxima well to the red[2] (and are therefore much less transparent in the near-IR where they would be used). The enhanced nonlinear response of these compounds has been achieved with little sacrifice in thermal stability; all of the chromophores decompose above 300 °C. The (dicyanomethylene)pyrans therefore represent the best progress to date in simultaneously achieving the three criteria required for usefulness: nonlinearity, transparency, and thermal stability.

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