Nonlinear Optical Chromophores with Large Hyperpolarizabilities and Enhanced Thermal Stabilities

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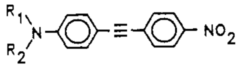
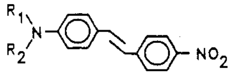
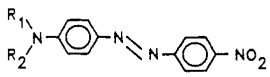
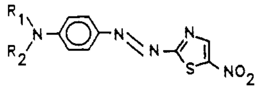
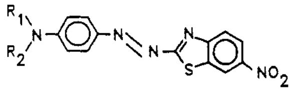
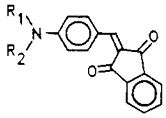
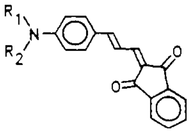
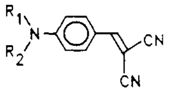
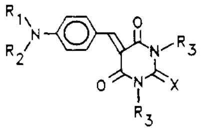
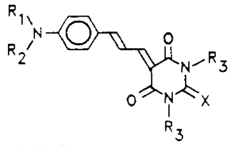
Among the many experimentally observed tradeoffs between molecular hyperpolarizabilities and other useful properties is that between nonlinearity and thermal stability. Compounds with appreciable values of the first hyperpolarizability β will be required if organic nonlinear optical materials are to find practical application in electrooptic devices or frequency doublers.[1] Such chromophores must also be sufficiently thermally robust to survive the fabrication steps for those devices. Additional thermal stability can be added to a nonlinear chromophore by substitution of aromatic moieties for aliphatic ones along the delocalized path between an electron donor and an acceptor; but since the hyperpolarizability is a measure of the ease of excitation to a state in which substantial intramolecular electron transfer has taken place, additional aromatic rings disfavor that electron transfer (since it would require them to adopt quinodal bonding patterns) and β is reduced.[2]

We report here the surprising but apparently general observation that replacement of aliphatic dialkylamino donor groups with diarylamino groups in nonlinear optical chromophores results not only in the anticipated increase in thermal stabilities but also in ample nonlinearities, sometimes larger than those of the aliphatic compounds.

Dialkylamino and diarylamino versions of 10 different delocalized chromophore structures, bearing a variety of acceptor groups, have been synthesized and characterized. Thermal stabilities were estimated by differential scanning calorimetry (DSC, 20 deg/min); the intercept of the leading edge of the decomposition exotherm with the base line of each DSC scan was

Table I. Molecular Parameters of Amino Donor Chromophores[a]

structure	R_1	R_2	R_3	X	μ	β_0	λ_{max}	$\mu\beta_{1300}$	T_d
(1) 	Me	Me			6.58	32.8	416	497	290
	Ph	Ph			4.84	28.2	418	315	336
(2) 	Me	Me			6.69	42.1	438	662	290
	Ph	Ph			4.75	37.3	436	416	358
(3) 	Me	Me			7.66	39.9	480	751	307
	Et	Et			8.04	49.6	494	996	322
	Ph	Ph			5.87	54.3	486	788	393
(4) 	Et	$HO(CH_2)_6$			8.96	52.2	582	1310	213
	Ph	Ph			6.89	68.2	582	1320	295
(5) 	Et	$HO(CH_2)_6$			9.47	60.1	548	1520	259
	Ph	Ph			7.21	71.8	550	1390	356
(6) 	Et	Et			3.74	37.9	490	352	286
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$			2.02	63.7	498	323	396
(7) 	Et	Et			4.35	91.8	552	1070	270
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$			2.02	93.0	544	499	328
(8) 	$-(CH_2)_5-$				8.45	16.6	440	332	315
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$			7.60	25.2	452	460	>380
(9) 	Et	Et	Me	O	6.21	19.8	470	299	226
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	Me	O	4.47	40.2	486	445	370
	Me	Me	Et	S	6.40	19.9	494	318	215*
	Et	Et	Et	S	7.10	20.3	500	362	218
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	Et	S	5.18	45.0	518	599	352
	Et	Et	Ph	S	7.59	25.6	502	490	263*
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	Ph	S	5.66	56.9	520	830	330*
(10) 	Et	Et	Ph	O	7.06	91.1	558	1740	268*
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	Ph	O	4.00	97.1	560	1050	301*
	Et	Et	Ph	S	8.29	93.7	588	2200	263*
	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	Ph	S	6.48	119	594	2200	333*

[a] Dipole moments given in debyes, wavelengths in nanometers, β values in 10^{-30} esu, and temperatures in degrees Celsius. Decomposition temperatures marked with an asterisk are assumed to be upper limits; the compounds decomposed immediately upon melting. β_0 values were determined from EFISH data on chloroform solutions in the tradiational manner;[9] 1300-nm nonlinearities include a conventions adjustment[10] and are referenced to the most recent value for d_{11} of quartz.[11,12]

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assigned as the decomposition temperature (T_d). Nonlinear susceptibilities of the chromophores were determined in chloroform solution at 1907 nm by electric-field-induced second harmonic generation (EFISH) as previously described.[3] For comparison purposes, $\mu\beta(-\omega;\omega,0)$ at 1300 nm (where μ is the dipole moment), the key molecular parameter for electrooptical applications at that wavelength,[4] was calculated.

In every case, the diarylamino compound exhibited a lower dipole moment and a significantly higher decomposition temperature. In almost every case, the extrapolated zero-frequency hyperpolarizability β_0 (determined using the two-level model dispersion expression[5]) was larger for the diarylamino analogue, and for five of those compounds the difference was enough to compensate for the decreased dipole moment so that the net $\mu\beta$ product was greater. The results are shown in Table I.

Under the assumptions of the two-level model,[5] β_0 can be expressed as follows,[6]

$$\beta_0 = \frac{3{\mu_{ge}}^2\Delta\mu}{\hbar^2{\omega_{max}}^2} = \frac{3{\mu_{ge}}^2\Delta\mu{\lambda_{max}}^2}{h^2c^2} \qquad (1)$$

where ω_{max} is the circular frequency of the transition to the first excited state, μ_{ge} is the transition dipole moment, and $\Delta\mu$ is the difference in dipole moment between ground and excited states. The oscillator strength f, which can be determined from the absorption spectrum, may be expressed[7] in terms of the transition dipole moment and the mass of the electron:

$$f = \frac{8\pi^2 m_e c {\mu_{ge}}^2}{3he^2\lambda_{max}} \qquad (2)$$

so that

$$\beta_0 = 1.617 f \Delta\mu{\lambda_{max}}^3 \qquad (3)$$

where β_0 is expressed in units of 10^{-30} esu, $\Delta\mu$ is in debyes, and ${\lambda_{max}}^3$ is in 10^7 nm^3. For each compound listed in Table I, values of β_0, f, $\Delta\mu$, and λ_{max} were extracted from the EFISH measurements and spectral data. The major difference between the aliphatic and aromatic amine donor chromophores was that the latter almost always exhibited larger values of $\Delta\mu$. Since their measured ground state dipole moments are uniformly lower, their excited state dipole moments are comparable to those of the aliphatic derivatives. The oscillator strengths are not dramatically reduced in the aryl derivatives because no loss in aromatic stabilization energy occurs upon intramolecular charge transfer.

Recent calculations[8] have indicated that substitution of an amine hydrogen by an unsaturated moiety decreases the energy gap between the ground and first excited states (creating a slight red shift), and also decreases the energies of higher excited states, so that several states may contribute to the hyperpolarizability rather than just the lowest one. If so, then nonlinear optical chromophores with arylamino donor groups are not accurately described by the two-level model. Note that all but two of our chromophore structures show either a red shift or no change in λ_{max} (within the 2-nm experimental uncertainty) upon aryl substitution, and in both of those cases (**3** and **7**) the aliphatic derivative has a higher net nonlinearity $\mu\beta_{1300}$ (although a slightly lower β_0). The origins and generality of the observed benefits of aryl donor substitution are being pursued, and the chromophores are being incorporated in electrooptical polymer systems.

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