J. Am. Chem. Soc. 1993, 115, 3006-3007

Stronger Acceptors Can Diminish Nonlinear Optical Response in Simple Donor-Acceptor Polyenes

Seth R. Marder,[*,†,‡] Christopher B. Gorman,[†]
Bruce G. Tiemann,[†,‡] and Lap-Tak Cheng[*,§]

Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive, Pasadena, California 91109
Molecular Materials Resource Center
The Beckman Institute, California Institute of
Technology, Pasadena, California 91125
Central Research and Development Department
E. I. Du Pont de Nemours & Co. (Inc.)
Experimental Station, P.O. Box 80356
Wilmington, Delaware 19880-0356

Received November 9, 1992

There has been much recent effort in the design of optimal chromophores for second-order nonlinear optical (NLO) applications.[1,2] Most studies of organic molecules have focused on donor-acceptor π-conjugated molecules containing aromatic groups.[3-9] We will show that the NLO response of aromatic donor-acceptor chromophores is dramatically different than their simple polyene analogs. Although there have been several computational studies of the first hyperpolarizability (β) of the simple organic donor-acceptor chromophores, the polyenes,[10] few molecules in this class have been studied experimentally.[4] These molecules are the prototypical conjugated donor-acceptor chromophores and as such can serve as a base line reference for both experimental and theoretical NLO structure/property relationships. Accordingly, we report the results of electric-field-induced second-harmonic generation (EFISH) studies of simple donor-acceptor polyenes as a function of donor and acceptor strengths and of molecular length.

Donor-acceptor polyenes containing between 3 and 11 conjugated atoms have been purchased or synthesized as described in the literature,[11-13] and their dipole moment (μ) and β have been measured by EFISH with 1.907-μm fundamental radiation in $CHCl_3$.[8,9] Values of β and μ are presented in Table I, as are the optical absorption maximum (λ_{max}), $\beta(0)$ corrected for dispersion within a two-state model, and the dot product of μ with β, ($\mu\cdot\beta$), a quantity of interest in poled polymers applications. These chromophores possess large dipole moments (8-10 D for the dicyanovinyl acceptor) and large $\mu\cdot\beta$ values. Computations were performed using the AM1 parameterization available in MOPAC,[14,15] and molecular hyperpolarizabilities were computed using the finite-field method.[16]

It has been recently suggested that there is an optimal degree of bond length alternation that maximizes β (Figure 1).[17,18] Reduction of bond length alternation takes a molecule from the bond-alternate polyene limit (in which one canonical resonance structure contributes mainly to the ground-state of the molecule, Figure 2, top) to the bond-equivalent cyanine limit (in which two canonical resonance structures contribute equally to the ground-state structure of the molecule, Figure 2, bottom).[19-21] Molecules with too much bond length alternation (e.g., unsubstituted polyenes,[22] donor-acceptor substituted stilbenes,[23] or diphenyl polyenes) do not have sufficiently strong donors and acceptors to give the correct balance of electronic asymmetry and polarizability needed to maximize β within the context of a two-state model.[24-26] In the zero bond length alternation (cyanine) limit, linear polarizability is expected to be maximized.[27] However, a two-state model predicts β to be roughly 0, since roughly half the charge is transferred from the donor to the acceptor[21,28] in *both* the ground and excited states, resulting in *no change in dipole moment between these states*.[17] This point is easily illustrated in the particular case of a cyanine (Figure 2, bottom), which can be viewed as donor-acceptor polyene with a strong (dimethylamine) donor and a strong (dimethyliminium) acceptor. Despite the stronger acceptor, charge is symmetrically distributed on the nitrogens in both the ground and excited states, resulting in a negligible β.[21,28]

Values of $\beta(0)$ for the simple polyene series are greater than those for polyenes containing an α-phenyl ring.[8] It can be rationalized that the former set of molecules has the more optimal degree of bond length alternation to maximize β. One can rationalize the ground-state geometry of these two classes of molecules in terms of a linear combination of neutral and charge separated resonance forms (Figure 2, top and middle). For the α-phenyl polyene series, aromaticity is lost upon charge separation, diminishing the contribution of the charge-separated resonance form to the ground-state wave function. Thus, the α-phenyl polyene series may have too much bond length alternation to maximize β. In contrast, the simple donor-acceptor polyenes, unhampered by aromaticity, will exhibit greatly reduced bond length alternation. The crystal structures of $Me_2N(CH{=}CH)_3CHO$[29] (average $r(C{=}C) = 1.356$ Å, $r(C{-}C) = 1.416$ Å, $\Delta = 0.06$ Å) and $Me_2N(CH{=}CH)_3CHC(CN)_2$[29] (average $r(C{=}C) = 1.376$ Å, $r(C{-}C) = 1.381$ Å, $\Delta < 0.01$ Å) provide direct evidence for decreased bond length alternation in simple donor-acceptor polyenes relative to unsubstituted polyenes (average $r(C{=}C) = 1.340$ Å, $r(C{-}C) = 1.445$ Å, $\Delta = 0.11$ Å from the crystal structure of 1,3,5,7-octatetraene[22] and diphenyl-1,3,5,7-octatetraene[30]). Raman spectra of $Me_2N(CH{=}CH)_3CHO$ and

---

[†] Jet Propulsion Laboratory.
[‡] Molecular Materials Resource Center.
[§] Central Research and Development Department.

(1) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: San Diego, 1987; Vols. 1 and 2.

(2) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives*; American Chemical Society Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(3) Huijts, R. A.; Hesselink, G. L. J. *Chem. Phys. Lett.* **1989**, *156*, 209-212.

(4) Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Zyss, J. *Chem. Phys.* **1989**, *133*, 323-329.

(5) Ikeda, H.; Kawabe, Y.; Sakai, T.; Kawasaki, K. **1989**, *157*, 576-578.

(6) Zyss, J. *J. Chem. Phys.* **1979**, *71*, 909-916.

(7) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339-1350.

(8) Cheng, L.-T.; Tam, W.; Marder, S. R.; Steigman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643-10652.

(9) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631-10643.

(10) Morley, J. O.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans. II* **1987**, 1351-1355.

(11) Scheibe, P.; Schneider, S.; Dörr, F.; Daltrozzo, E. *Ber. Bunsen Ges. Phys. Chem.* **1976**, *80*, 630-638.

(12) Malhotra, S. S.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3812-3822.

(13) Becher, J. *Synthesis* **1980**, *8*, 589-612.

(14) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209-220.

(15) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221-264.

(16) Kurtz, H. A.; Stewart, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82-87.

(17) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103-106.

(18) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L.-T. *Proc. SPIE* **1993**, *1775*, 19-31.

(19) Dähne, S. *Science* **1978**, *199*, 1163-1167.

(20) Dähne, S.; Hoffman, K. *J. Mol. Struct.* **1990**, *219*, 403-409.

(21) Dähne, S. *Chimia* **1991**, *45*, 288-296.

(22) Baughman, R. H.; Kohler, B. E.; Levy, I. J.; Spangler, C. *Synth. Met.* **1985**, *11*, 37-52.

(23) Grubbs, R. B.; Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Chem. Mater.* **1991**, *3*, 3-4.

(24) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664-2668.

(25) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1977**, *66*, 1070.

(26) Lalama, S. J.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.

(27) Dähne, S.; Nolte, K. D. *J. Chem. Soc., Chem. Commun.* **1972**, 1056-1057.

(28) Dähne, S.; Nolte, K.-D. *Acta Chim. Acad. Sci. Hung.* **1978**, *97*, 147-157.

(29) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Biddle, S.; Gilmour, S.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524-2526.

0002-7863/93/1515-3006$04.00/0

Table I. Linear and Nonlinear Optical Properties of Donor–Acceptor Polyenes of the form $D(CH{=}CH)_nA^a$

D	A	n	no. conjd atoms	λ_{max} (nm)	$\mu \times 10^{18}$ (esu)	$\beta \times 10^{30}$ (esu)	$\beta(0) \times 10^{30}$ (esu)	$\mu\beta \times 10^{48}$ (esu)	$\beta_u \times 10^{30}$ (esu, calcd)^b
Me_2N	CHO	0	3	<240	3.5	0.5	0.5	1.8	0.1
Me_2N	CHO	1	5	284	6.3	3.3	2.9	21	3.9
Et_2N	CHO	2	7	363	6.5	20	16.5	130	13.7
Me_2N	CHO	3	9	422	6.9	53	41	366	30.2
Me_2N	$CH{=}C(CN)_2$	0	5	352	7.6	1.0	0.9	7.6	1.7
Me_2N	$CH{=}C(CN)_2$	1	7	374	8.9	6.1	5.0	54	15.0
Et_2N	$CH{=}C(CN)_2$	2	9	476	10.7	45	32	482	42.9
Me_2N	$CH{=}C(CN)_2$	3	11	550	9.9	211	129	2089	76.9
$Me_2NC_6H_4$	CHO	0	7	326	5.1	6.3[8,9]	5.4	32	7.7
$Me_2NC_6H_4$	CHO	1	9	384	5.6	30[8,9]	24	168	17.7
$Me_2NC_6H_4$	$CH{=}C(CN)_2$	0	9	420	7.8	32[8,9]	25	250	23.1
$Me_2NC_6H_4$	$CH{=}C(CN)_2$	1	11	486	8.4	82[8,9]	57	689	45.8

[a] Experimental measurements were obtained in $CHCl_3$. Values for β were determined by EFISH using 1.907 μm fundamental radiation. [b] For all computations, D was Me_2N or $Me_2NC_6H_4$ as was appropriate for comparison to experimental results. The values for β_μ are defined as $\beta_\mu = (^3/_5)(\beta\mu/|\mu|)$ where $\beta\cdot\mu = \beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z$ and $\beta_i = \{\beta_{iii} + \beta_{ijj} + \beta_{ikk}\}$.

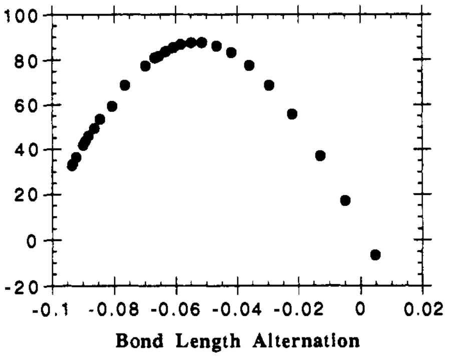

Figure 1. Plot of β versus bond length alternation (Å) from electric-field-dependent AM1 geometry optimizations and finite field calculations[18] on $(CH_3)_2N(CH{=}CH)_3CHO$.

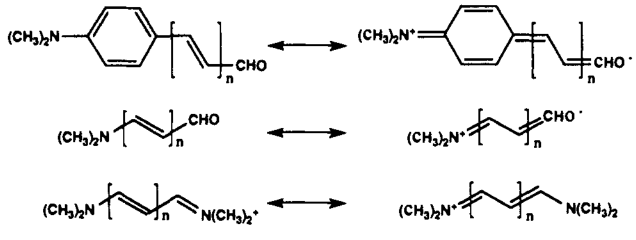

Figure 2. Canonical charge-transfer resonance structures for a series of (top) α-phenyl polyenes, (middle) donor–acceptor polyenes, and (bottom) cyanines.

$Me_2N(CH{=}CH)_3CHC(CN)_2$ in polar solvents and in the solid state are qualitatively similar, suggesting that the compounds exhibit significantly reduced bond length alternation in polar solvents as well.[29]

Although a dicyanovinyl group is generally considered to be a better acceptor than an aldehyde group, the $\beta(0)$ values of the polyene aldehyde chromophores are greater than those for the dicyanovinyl chromophores with the same number of conjugated atoms. In contrast, gas-phase calculations on both the polyene and α-phenyl polyene series indicate that the dicyanovinyl-substituted compounds have larger β values and less bond length alternation than the aldehyde-substituted compounds. It is possible that these results are due to ineffective electron delocalization into the cyano groups (evidenced by the typically short C≡N bond), thereby reducing the effective conjugation length of the molecule. However, the experimental results for the α-phenyl polyene molecules and the computations indicate that ineffective delocalization into the cyano group is not limiting the β values of the dicyanovinyl polyenes relative to the analogous aldehydes. More importantly, in a nonpolar environment (the gas phase), the computations predict stronger acceptors to decrease bond length alternation and to increase β.[31] These results contradict the experimental results for the dicyanovinyl polyenes. They are, however, consistent with the hypothesis that, in the relatively polar solvent in which the EFISH experiment was performed ($CHCl_3$), charge separation is stabilized and the dicyanovinyl acceptor on the polyene decreases the magnitude of bond length alternation past that which is optimal to maximize β (Figure 1, right). These results suggest a limit to the applicability of gas-phase calculations on molecules whose structures are highly sensitive to the polarity of their environment.

The data in Table I can be fit to the function $\beta(0) \propto N^m$, where N is the number of conjugated multiple bonds in the molecule (including the carbon–heteroatom bond as one and the phenyl group as two). The exponent m lends insight into the chain length dependence of $\beta(0)$. The values of m for the simple polyene aldehydes and dicyanovinyl series are 3.2 and 5.4, respectively. For comparison, the α-phenyl polyene aldehyde and dicyanovinyl series[8] gives $m = 3.5$ and 3.6, respectively. The exponent observed for the dicyanovinyl polyene series is larger than those previously reported in either experimental[3,4,8] or computational[10] studies.

In conclusion, the nonlinear optical behavior of simple donor–acceptor polyenes, in particular the dicyanovinyl series, is both qualitatively and quantitatively different from that of diphenyl and α-phenyl polyenes which have been previously studied. In particular we have observed that, in contrast to all previous computational and experimental studies, the strongest acceptor does not necessarily lead to the largest nonlinearity.

Acknowledgment. The work in this paper was performed, in part, at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA). The work was sponsored by the Defense Advanced Research Projects Agency and the Strategic Defense Initiative Organization Inovative Science and Technology Office. Support from the National Science Foundation (Grant CHE-9106689) is also gratefully acknowledged. C.B.G. thanks JPL for a postdoctoral fellowship.

Supplementary Material Available: ^1H nuclear magnetic resonance spectroscopic and elemental analytical data for $Et_2N(CH{=}CH)_2\text{-}CH{=}C(CN)_2$ (1 page). Ordering information is given on any current masthead page.

---

(30) Drenth, W.; Wiebenga, E. H. *Acta Crystallogr.* **1955**, *8*, 755–760.

(31) The stronger nitro acceptor leads to larger nonlinearities than the weaker aldehyde acceptor for analogous donor–acceptor polyenes. See ref 15.