nental regions (*24*), Greenland is influenced by a heterogenous collection of moisture sources. The ultimate signature of these moisture sources is determined by a variety of climate processes, and therefore, meaningful interpretation of the Greenland ice core record, including the implications for future climate, can only be achieved by appeal to a multidimensional perspective.

REFERENCES AND NOTES

1. S. J. Johnsen *et al.*, *Nature* **359**, 311 (1992).
2. W. Dansgaard *et al.*, *Tellus* **16**, 436 (1964).
3. W. Dansgaard *et al.*, *Nature* **339**, 532 (1989).
4. W. S. Broecker *et al.*, *ibid.* **315**, 21 (1985); S. Manabe and R. J. Stouffer, *J. Clim.* **1**, 841 (1988).
5. The magnitude of the air temperature response over Greenland to the imposition of glacial-like North Atlantic SSTs in the GISS GCM was about 2°C [D. Rind *et al.*, *Clim. Dyn.* **1**, 3 (1986)]. Central and northwest Greenland (*1*) and the Canadian Arctic ice cores [R. M. Koerner *et al.*, *Can. J. Earth Sci.* **24**, 296 (1987)] show some of the most striking isotopic changes, yet seem removed from direct North Atlantic influence in these GCM simulations.
6. R. Alley *et al.*, *Nature* **362**, 527 (1992).
7. Isotopic records from the German pine tree ring series [B. Becker *et al.*, *ibid.* **353**, 647 (1991)] and the Lake Gosciaz (Poland) varved-sediment record [K. Rosanski *et al.*, in *The Last Deglaciation: Absolute and Radiocarbon Chronologies*, E. Bard and W. S. Broecker, Eds. (Springer-Verlag, Berlin, 1992), pp. 69–80] suggest that the Younger Dryas–PreBoreal transition occurred over the course of about 100 years in Europe. This contrasts with the estimate of less than 10 years for the same event in the Summit ice cores (*6*).
8. Dates for the Younger Dryas–PreBoreal transition in the Greenland Ice-Core Project (GRIP) and Greenland Ice Sheet Project-2 (GISP2) ice cores at Summit average 11,550 years ago (*1, 7*). This age, determined by annual layer counting, is identical (within analytical uncertainties) to the age of the second pulse of ice sheet melting apparent in the Barbados sea level [11,400 years ago by U/Th dating, E. Bard *et al.*, *Nature* **345**, 405 (1990); (*25*)]. Similar correspondence (though with greater age uncertainty) exists for the "Glacial-Bolling" transition at about 14,100 years ago.
9. General considerations of $\delta^{18}O$ in water vapor and precipitation are reviewed by W. Dansgaard *et al.* (*2*), J. Gat [in *Handbook of Environmental Isotope Geochemistry*, P. Fritz and J. Ch. Fontes, Eds. (Elsevier, Amsterdam, 1980), vol. 1, pp. 21–48], and J. Jouzel (*ibid.*, vol. 2, pp. 61–112).
10. S. J. Johnsen *et al.* (*1*) and R. Alley *et al.* (*6*) argue that the modern $\delta^{18}O$-temperature relation over Greenland may be used to interpret the past ice core record. R. G. Fairbanks [*Nature* **342**, 637 (1989); (*25*)] cautions that moisture source variability and air mass mixing may have dominated certain abrupt changes in the ice cores.
11. S. Joussaume and J. Jouzel [*J. Geophys. Res.* **98**, 2807 (1993)] found that the slope of the $\delta^{18}O$-temperature relation in an ice age GCM experiment differed from the modern observed value over Greenland by about 30%.
12. A full description of the GISS II model and the basic parameterizations is provided by J. Hansen *et al.* [*Mon. Weather Rev.* **111**, 609 (1983)].
13. CLIMAP Project Members, *Science* **191**, 1131 (1976); *Geol. Soc. Am. Map and Chart Ser. MC-36* (1981). Revisions to the boundary conditions used in this report may be necessary for more accurate simulations. In particular, recent evidence suggests that sea ice limits [N. Koç *et al.*, *Quat. Sci. Rev.* **12**, 115 (1993)] and tropical SSTs (T. Guilderson *et al.*, *Science*, in press) may need adjustment.
14. A description of the isotope model and the results of the modern control experiment (8° by 10° resolution) are presented in J. Jouzel *et al.*, *J. Geophys. Res.* **92**, 14739 (1987). A complete description of the relevant parameterizations, as well as the results of various sensitivity tests, can be found in J. Jouzel *et al.*, *ibid.* **96**, 7495 (1991).
15. S. Joussame *et al.*, *Ocean-Air Interactions* **1**, 43 (1986); R. D. Koster *et al.*, *Geophys. Res. Lett.* **13**, 121 (1986); R. D. Koster *et al.*, *Mass. Inst. Technol. Technol. Rep. 317* (1988).
16. S. Johnsen *et al.*, *Tellus* **41**, 452 (1989).
17. L. M. Druyan and D. Rind, *Natl. Aeronaut. Space Admin. Technol. Memo. 100722* (1989).
18. W. L. Gates, P. R. Rowntree, Q.-C. Zeng, in *Climate Change: The IPCC Scientific Assessment*, J. T. Houghton, G. J. Jenkins, J. J. Ephraums, Eds. (Cambridge Univ. Press, Cambridge, 1990), pp. 93–130. The fact that similar overestimation of Greenland precipitation appears in different models suggests that the error is not strictly the result of numerical diffusion, which is always a concern in the polar regions.
19. It is apparent that mid-latitude $\delta^{18}O$-temperature relations for the model match observations remarkably well, both over continents and over the oceans. R. Koster *et al.* [*Geophys. Res. Lett.* **20**, 2215 (1993)] have recently demonstrated that much of the scatter in the $\delta^{18}O$-temperature relation in the coarse resolution model can be explained by the degree of continental recycling of moisture.
20. N. Reeh, in *Geological History of the Polar Oceans: Arctic versus Antarctic*, U. Bleil and J. Thiede, Eds. (Kluwer, Dordrecht, Netherlands, 1990), pp. 255–272; see also (*6*).
21. S. J. Johnsen *et al.* (*1*) give a table with the average amplitude of $\delta^{18}O$ variations in the different ice cores. The issue of what sets the Camp Century core apart—including arguments for and against ice elevation changes as a significant influence—has been discussed by W. Dansgaard *et al.* [*Geophys. Monogr. Ser. 29* (American Geophysical Union, Washington, DC, 1984)] and N. Reeh *et al.* [*Palaeogeogr. Palaeoclimatol. Palaeoecol.* **90**, 373 (1991)]. R. G. Fairbanks (*25*) also discussed this subject in light of possible changes in evaporative moisture sources.
22. J. Kutzbach, in *North America and Adjacent Oceans During the Last Deglaciation.* W. F. Ruddiman and H. E. Wright Jr., Eds. (Geological Society of America, Boulder, CO, 1990).
23. K. Taylor *et al.*, *Nature* **361**, 463 (1993).
24. R. D. Koster *et al.*, *Clim. Dyn.* **7**, 195 (1992); also see (*15*).
25. R. G. Fairbanks, *Paleoceanography* **5**, 937 (1990).
26. This work was made possible by a National Research Council postdoctoral fellowship (C.D.C.). We appreciate the assistance and expertise provided by numerous collaborators at NASA/GISS, especially M. Chandler, R. Ruedy, B. Suozzo, and R. Webb. Discussions with W. Broecker, J. Cole, and D. Peteet were helpful, as were the comments made by two anonymous reviewers of a previous version of the manuscript.

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Large First Hyperpolarizabilities in Push-Pull Polyenes by Tuning of the Bond Length Alternation and Aromaticity

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Conjugated organic compounds with 3-phenyl-5-isoxazolone or *N,N'*-diethylthiobarbituric acid acceptors have large first molecular hyperpolarizabilities (β) in comparison with compounds with 4-nitrophenyl acceptors. For example, julolidinyl–$(CH{=}CH)_3$–$CH{=}$*N,N'*-diethylthiobarbituric acid, which has 12 atoms between the donor and acceptor, has a $\beta(0)$ of 911×10^{-30} electrostatic units, whereas $(CH_3)_2NC_6H_4$–$(CH{=}CH)_4$–$C_6H_4NO_2$, with 16 atoms between its donor and acceptor, has a $\beta(0)$ of 133×10^{-30} electrostatic units. The design strategies demonstrated here have resulted in chromophores that when incorporated into poled-polymer electrooptic modulators exhibited significant enhancements in electrooptic coefficients relative to polymers containing the commonly used dye Disperse Red-1. Poled polymer devices based on these or related chromophores may ultimately lead to high-speed electrooptic switching elements with low drive-power requirements, suitable for telecommunications applications.

There is currently a concerted effort in industry, academia, and government laboratories to develop high-performance electrooptic switching elements for telecommunications, optical information processing, and sensors, based on poled polymers containing organic second-order nonlinear optical (NLO) chromophores. Substantial progress has been made in demonstrating that stable, optical quality devices can be fabricated. However, dramatic improvements in the electrooptic coefficients are required if these devices are to have wide-ranging application in photonic systems. This realization has created a pressing need for organic chromophores with an order-of-magnitude increase in the molecular first hyperpolarizability, β, over those of commonly used chromophores, such as the well-known Disperse Red-1. We synthesized chromophores with greatly enhanced β by a basic design strategy that was proposed earlier (*1*) and is outlined below.

With a two-state model (*2–4*), it was shown that there is an optimal combination of donor and acceptor strengths for a given bridge that leads to a balance of electronic asymmetry and polarizability that maximizes β (*1*). We have been exploring the hypothesis that the difference between the average lengths of carbon-carbon single and double bonds [that is, the bond length alternation ($\langle \Delta r \rangle$)] in donor-acceptor–substituted polyene and polymethine dyes is a useful structural parameter to examine when establishing generalized structure-property relations for organic materials exhibiting second-order NLO effects (*5*, *6*). Reduction of bond length alternation takes a molecule from the bond-alternate polyene limit (in which only one canonical resonance structure contributes predominantly to the ground state of the molecule) to the bond-equivalent cyanine limit (in which two canonical resonance structures contribute equally to the ground-state structure of the molecule) (*7*–*9*). Electric field–dependent calculations of molecular geometry and β indicate that for molecules with a high degree of bond length alternation, such as polyenes with weak donors and acceptors, β is initially positive; then, as a function of increasing polarization and decreasing $\langle \Delta r \rangle$, β first increases, peaks in a positive sense, decreases, crosses through zero at the cyanine limit where $\langle \Delta r \rangle = 0$ Å (Fig. 1), and becomes negative when the ground state of the molecule is zwitterionic, having both positive and negative charges (*5*, *6*). From these calculations, we estimate that the positive peak for β occurs at roughly $\langle \Delta r \rangle = 0.03$ to 0.05 Å (*5*, *6*). Most molecules that have been examined in the past, such as donor-acceptor–substituted stilbenes (*10*) or diphenyl polyenes, do not have sufficiently strong donors and acceptors to give the $\langle \Delta r \rangle$ needed to maximize β. The high degree of bond length alternation observed in the central polyene bridge of donor-acceptor–substituted stilbenes and related molecules is indicative of an insufficient contribution of the charge-separated resonance form to the ground-state configuration of the molecules and is a consequence of the loss of aromatic stabilization in the charge-separated form. We therefore designed donor-acceptor polyenes in which the loss of aromaticity in one end upon charge separation (in this case, the donor end) would be somewhat offset by a gain in aromaticity upon charge separation in the opposite end. We predicted that such molecules would have more nearly the correct contribution of the charge-separated form to the ground-state structure required to reach the bond length alternation at which β is maximized.

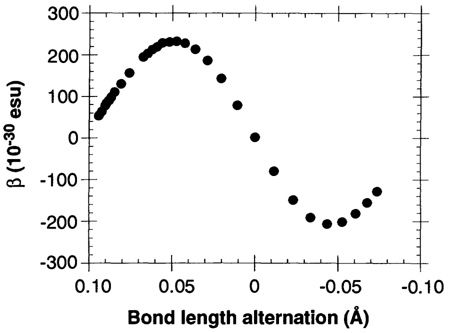

Fig. 1. Plot of β versus $\langle \Delta r \rangle$, generated with an AM1 geometry optimization (in the MOPAC package) for $(CH_3)_2N\text{–}(CH{=}CH)_4\text{–}CHO$ in the presence of a static electric field (generated with point charges) of varying strength (*5*, *6*). For each value of the static field, and thus $\langle \Delta r \rangle$, β was calculated by a finite-field procedure.

Compounds with acceptors that can gain aromaticity in their charge-separated resonance forms, such as $(CH_3)_2NC_6H_4\text{–}(CH{=}CH)_n\text{–}A$ and julolidinyl–$(CH{=}CH)_n$–A, where A is *N*,*N*′-diethylthiobarbituric acid (series **1**[*n*] or **2**[*n*], respectively) or 3-phenyl-5-isoxazolone (series **3**[*n*] or **4**[*n*], respectively) for $n = 0$ to 3 (Fig. 2), have large β values and reduced $\langle \Delta r \rangle$ in comparison with compounds for which A = C_6H_4-NO_2. We synthesized the molecules in Fig. 2 by reaction of 3-phenyl-5-isoxazolone or *N*,*N*′-diethylthiobarbituric acid with (*N*,*N*-dimethylamino)phenyl–$(CH{=}CH)_n$-CHO, julolindinyl–$(CH{=}CH)_n$CHO (where *n* is as defined in Fig. 2), or julolidinyl–$(CH{=}CH)_2$–$C(CH_3){=}CH\text{-}CH{=}CH\text{-}CH{=}C(CH_3)$–$CH{=}CH\text{–}CHO$ (*11*) under standard Knoevenagel conditions (*12*). We characterized the compounds by ^{1}H nuclear magnetic resonance and ultraviolet-visible spectroscopy as well as elemental analysis and mass spectroscopy. We expected that the potential gain in aromaticity upon charge separation (Fig. 3) would lead to a substantial charge transfer and reduced bond length alternation in the ground state. Thus, molecules containing acceptors whose topology dictates that aromaticity is gained upon charge separation (such as 3-phenyl-5-isoxazolone or *N*,*N*′-diethylthiobarbituric acid) would have more nearly the correct degree of bond length alternation needed to optimize β and could thus give rise to extremely large optical nonlinearities compared to conventional molecules of similar length.

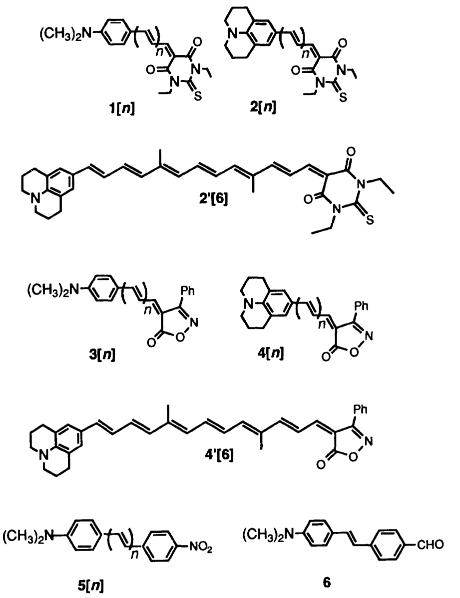

Fig. 2. Structure and labeling scheme for compounds investigated in this study. In all cases, $n = 0$ to 3, except for **5**[*n*], where $n = 1$ to 4.

We measured the hyperpolarizabilities by electric field–induced second harmonic generation (EFISH) (*13*–*16*) in chloroform, with 1.907-μm fundamental radiation. The values of β we obtained support the hypothesis that molecules of only moderate lengths containing the 3-phenyl-5-isoxazolone or *N*,*N*′-diethylthiobarbituric acid acceptor can have unprecedented β values (Table 1). The dispersion-corrected (*2*–*4*) $\beta(0)$ and $\mu\beta(0)$ values of the $n = 0$ and 1 compounds, which are analogous to ones previously reported (*17*–*19*), are not exceptional in comparison to other molecules in the literature. However, the longer $n = 2$ and 3 compounds exhibit strikingly large $\beta(0)$ and $\mu\beta(0)$ values (Table 1) for their lengths. The importance of the topology of the π system is clearly illustrated if one considers that both $(CH_3)_2NC_6H_4\text{–}CH{=}CH\text{–}C_6H_4CHO$ (**6**) and julolidinyl–$(CH{=}CH)_2$–$CH{=}$*N*,*N*′–diethylthiobarbituric acid (**2**[**2**]) have 10 conjugated atoms between the amine donor and the carbonyl acceptor, yet the former has a $\beta(0)$ of 20×10^{-30} electrostatic units (esu), whereas the latter compound has a $\beta(0)$ of 490×10^{-30} esu.

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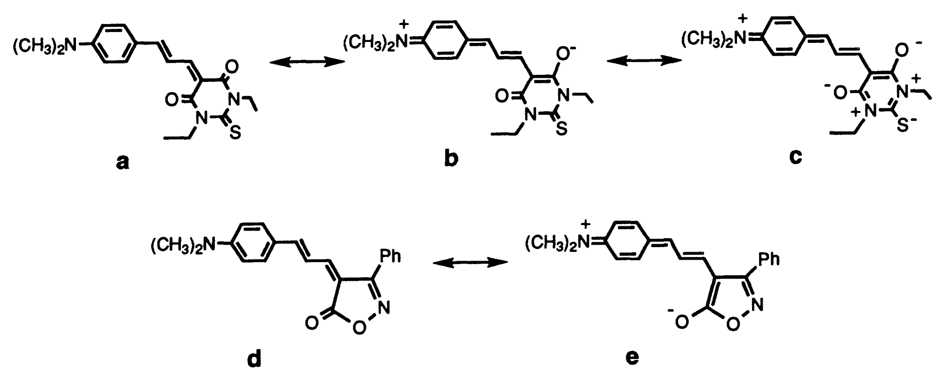

Fig. 3. For compound **1[1]**: a, neutral resonance form; b, one of the charge-separated resonance forms; and c, a charge-separated resonance form in which the acceptor ring has aromatic character. For compound **3[1]**: d, neutral resonance form; and e, a charge-separated resonance form in which the acceptor ring has aromatic character.

Table 1. Selected linear (absorption maximum, λ_{max}) and nonlinear optical data for compounds of the form in Fig. 2.

Compound	λ_{max} (nm)	μ (10^{-18} esu)*	β (10^{-30} esu)*	$\beta(0)$ (10^{-30} esu)*	$\mu\beta$ (10^{-48} esu)*	$\mu\beta(0)$ (10^{-48} esu)*
1[0]†	484	5.4	68	48	370	259
1[1]†	572	5.7	256	150	1,457	855
1[2]	604	6.2	636	347	3,945	2,151
1[3]	624	6.6	1490	772	9,831	5,095
2[0]	522	7.0	87	56	609	394
2[1]	614	6.6	355	186	2,210	1,159
2[2]	680	6.3	1141	490	7,152	3,069
2[3]	686	8.8	2169	911	19,086	8,019
2′[6]	680	—	—	—	34,770	14,920
3[0]	478	8.3	37	27	312	221
3[1]	530	8.6	140	90	1,202	771
3[2]	562	8.7	362	218	3,156	1,895
3[3]	582	8.9	918	528	8,171	4,696
4[0]	504	9.5	51	34	488	328
4[1]	586	9.1	180	100	1,638	919
4[2]	620	9.0	656	339	5,812	3,000
4[3]	640	9.8	995	485	9,750	4,753
4′[6]	647	16	1781	849	28,500	13,600
5[1]	430	6.6	73	55	482	363
5[2]	442	7.6	107	80	813	608
5[3]	458	8.2	131	95	1,074	779
5[4]	464	9	190	133	1,700	1,197
6	360	3.5	24	20	84	70

*The error in the measurements is estimated to be ±20%. The β values have not been corrected for the electronic deformation contribution to the EFISH signal. †$\mu\beta$ values of the *N,N′*-dimethylthiobarbituric acid analogs of the $n = 0$ and 1 compounds, measured at 1.34 and 1.064 μm, have been reported previously (*17–19*).

To our knowledge, no compounds with values of $\mu\beta$ greater than 10,000 × 10^{-48} esu have been reported, but we found the dispersion-corrected $\mu\beta(0)$ of julolidinyl–$(CH=CH)_2$–$C(CH_3)$=CH–CH=CH–CH=C(CH_3)–CH=CH–CH=*N,N′*–diethylthiobarbituric acid (**2′[6]**) to be ~15,000 × 10^{-48} esu, more than 40 times $\mu\beta(0)$ = 363 × 10^{-48} esu for $(CH_3)_2NC_6H_4$-CH=CH-$C_6H_4NO_2$ (**5[1]**), esu, which is commonly used in poled-polymer applications. This exceptionally high value is not surprising because it has been demonstrated that donor-acceptor–substituted carotenoids can display large quadratic nonlinearities (*20, 21*).

Preliminary experiments indicate that poled polymers containing the chromophores in Table 1 exhibit large electrooptic coefficients (r_{33}). For example, poly(methyl methacrylate) (PMMA) guest-host films containing **3[1]**, **3[2]**, **3[3]**, and **1[3]**, as well as Disperse Red-1 (a chromophore whose $\mu\beta$ is comparable to that of **5[1]**), at 2% by mole loading, poled at 10^6 V cm^{-1}, gave $|r_{33}|$ values at 820 nm of 5, 10, 24, 52, and 1 pm V^{-1}, respectively. Although the absorption maximum in the visible for **3[1]** is at lower energy than that for Disperse Red-1, the band for the latter is much broader, resulting in a lower energy cutoff. Therefore, even though **3[1]** has a greater transparency range than Disperse Red-1, its nonlinearity at the same loading is roughly a factor of 5 greater.

The measurements for **3[1]**, **3[2]**, and Disperse Red-1 showed no significant imaginary component of the electrooptic coefficient; however, the values for **1[3]** and **3[3]** did exhibit imaginary components because of absorption at 820 nm. Many telecommunications applications will use modulators operating at ~1300 and 1500 nm; thus, although dyes such as **3[3]** and **1[3]** have low-energy absorption bands in the visible, they may nonetheless be useful at these technologically important wavelengths. Measurements at 1300 nm for both **3[3]** and **1[3]** gave a nonresonant value of 5 pm V^{-1}, suggesting that systems with larger loadings of chromophores similar to **3[3]** and **1[3]** covalently attached to the polymer could have unprecedented nonresonant nonlinearities (at this wavelength, the Disperse Red-1 sample gave a value of 0.8 pm V^{-1}).

We performed single-crystal x-ray determinations on julolidinyl–$(CH=CH)_2$–CH=3-phenyl-5-isoxazolone (**4[2]**) and julolidinyl–$(CH=CH)_3$–CH=3-phenyl-5-isoxazolone (**4[3]**) (*22*) to provide experimental evidence for the decrease in bond length alternation in these highly optically nonlinear compounds. Several points about their molecular structures are worth noting. First, the julolidinyl rings exhibit significant quinoidal character, as evidenced by the unequal C–C bond lengths in the rings (Fig. 4).

Second, the difference in length between adjacent C–C bonds increases upon going from the acceptor (3-phenyl-5-isoxazolone) end to the donor (julolidinyl) end of the molecule. Perhaps this can be viewed as a result of the acceptor "pulling" on the π electrons more than the donor is "pushing" on them. Whatever the case, the observation that bond length alternation is not constant across the length of the polymethine chain is general to the eight donor-acceptor polyene compounds we have crystallographically characterized and may ultimately limit the utility of using a single parameter, $\langle\Delta r\rangle$, to describe the degree of ground-state polarization in a molecule.

Third, **4[2]** and **4[3]** have $\langle\Delta r\rangle$ = 0.05 and 0.03 Å, respectively. For comparison, $\langle\Delta r\rangle$ in simple polyenes is 0.11 Å, from the crystal structure of 1,3,5,7-octatetraene (*23*) and diphenyl-1,3,5,7-octatetraene (*24*), and $\langle\Delta r\rangle$ for the nonring C–C bonds in a donor-acceptor–substituted stilbene is 0.14 Å, from the crystal structure of 2-methoxy-4′-nitro stilbene (*10*). Thus, the values for the 3-phenyl-5-isoxazolone acceptor–substituted compounds are sig-

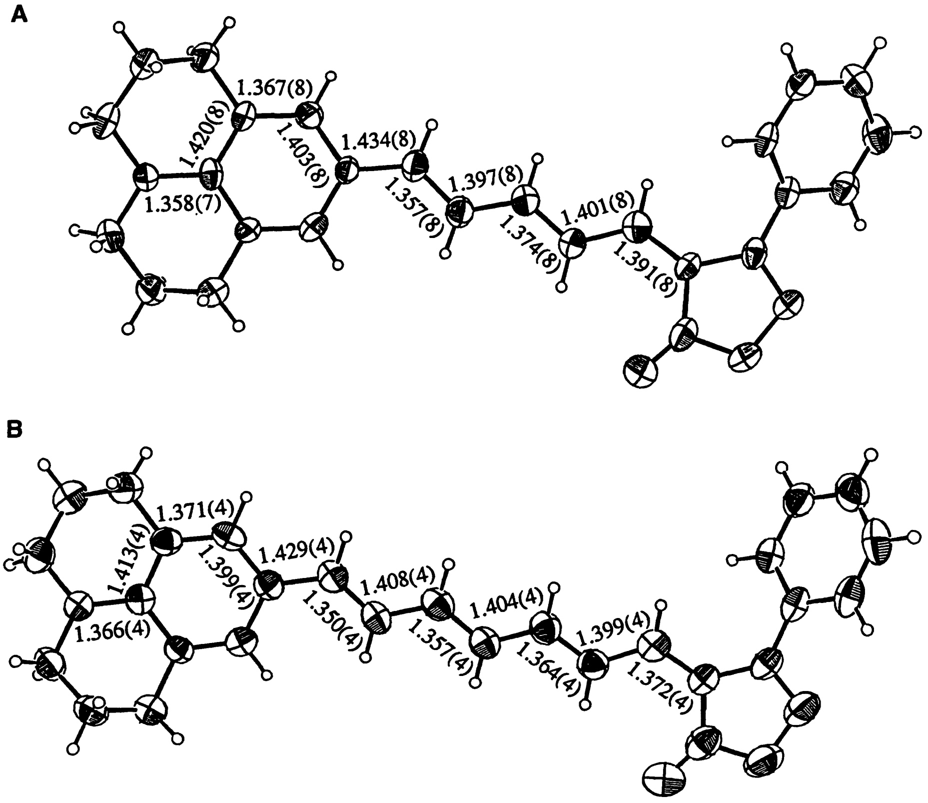

Fig. 4. Drawings (made with ORTEP) of (**A**) **4[2]** and (**B**) **4[3]** with 50% probability ellipsoids showing the bond lengths for the conjugated pathway between the donor and the acceptor. Hydrogen atoms in both structures are shown with thermal parameters one-tenth those assigned.

nificantly lower than those found in the polyene and stilbene compounds mentioned above and are close to the values we predict are needed to optimize β. However, as noted earlier (*25*), care must be taken in the use of solid-state structural data to gain insight about molecular structure in solution.

In general, the solid state behaves like an especially polar environment, which tends to result in a relatively high degree of charge separation and, in this case, a somewhat low $\langle \Delta r \rangle$ relative to what might be found for the molecule in a moderately polar solvent such as chloroform. On the basis of previous studies, we estimate that the difference between $\langle \Delta r \rangle$ in the solid state and in chloroform is less than ~0.03 Å, and thus, the structural data reported here provide strong evidence for reduced $\langle \Delta r \rangle$ in 3-phenyl-5-isoxazolone–substituted compounds.

In conclusion, we have demonstrated that derivatives containing 3-phenyl-5-isoxazolone and *N*,*N'*-diethylthiobarbituric acid can exhibit very large nonlinearities in comparison to compounds with nitro or simple carbonyl acceptors but with bridges that are strongly aromatic. Thus, the greater than 25-fold enhancement of $\beta(0)$ for **2[2]** as compared with **6** illustrates that judicious manipulation of the π-electron system is a key to the optimization of hyperpolarizability. Our crystallographic structural data demonstrate that molecules that have acceptors that can gain aromaticity upon charge separation have $\langle \Delta r \rangle$ values significantly lower than those found in polyenes or stilbenes, where $\langle \Delta r \rangle$ is greater than 0.12 Å. Thus, our strategy of reducing bond length alternation by tuning the relative contributions of neutral and charge-separated resonance to the ground-state structure has led to molecules with large nonlinearities and may result in promising materials for electrooptic modulator applications.

REFERENCES AND NOTES

1. S. R. Marder, D. N. Beratan, L.-T. Cheng, *Science* **252**, 103 (1991).
2. S. J. Lalama and A. F. Garito, *Phys. Rev. A* **20**, 1179 (1979).
3. J. L. Oudar and D. S. Chemla, *J. Chem. Phys.* **66**, 2664 (1977).
4. B. F. Levine and C. G. Bethea, *ibid.*, p. 1070.
5. S. R. Marder, C. B. Gorman, L. Cheng, B. G. Tiemann, *Proc. SPIE* **1775**, 19 (1993).
6. C. B. Gorman and S. R. Marder, *Proc. Natl. Acad. Sci. U.S.A.* **90**, 11297 (1993).
7. S. Dähne, *Science* **199**, 1163 (1978).
8. ______ and K. Hoffman, *J. Mol. Struct.* **219**, 403 (1990).
9. S. Dähne, *Chimia* **45**, 288 (1991).
10. R. B. Grubbs, S. R. Marder, J. W. Perry, W. P. Schaefer, *Chem. Mater.* **3**, 3 (1991).
11. M. Barzoukas, M. Blanchard-Desce, D. Josse, J.-M. Lehn, J. Zyss, in *Materials for Nonlinear and Electro-Optics*, M. H. Lyons, Eds. (Institute of Physics Conf. Ser., IOP Publishing, Bristol, United Kingdom, 1989), vol. 103, p. 239.
12. J. March, *Advanced Organic Chemistry: Reaction Mechanisms and Structure* (Wiley-Interscience, New York, 1985).
13. B. F. Levine and C. G. Bethea, *Appl. Phys. Lett.* **24**, 445 (1974).
14. J. L. Oudar and H. L. Person, *Opt. Commun.* **15**, 258 (1975).
15. K. D. Singer and A. F. Garito, *J. Chem. Phys.* **75**, 3572 (1981).
16. L.-T. Cheng *et al.*, *J. Phys. Chem.* **95**, 10631 (1991).
17. H. Ikeda, Y. Kawabe, T. Sakai, K. Kawasaki, *Chem. Lett.* **1989**, 1803 (1989).
18. P. A. Cahill and K. D. Singer, *Proc. SPIE* **1560**, 130 (1991).
19. ______, in *Materials for Nonlinear Optics: Chemical Perspectives*, S. R. Marder, J. E. Sohn, G. D. Stucky, Eds. (American Chemical Society, Washington, DC, 1991), vol. 455, pp. 200–213.
20. M. Barzoukas, M. Blanchard-Desce, D. Josse, J.-M. Lehn, J. Zyss, *Chem. Phys.* **133**, 323 (1989).
21. J.-M. Lehn, in (*19*), pp. 436–445.
22. For **4[2]**: $C_{26}H_{24}N_2O_2$; molecular weight, 396.49. Monoclinic, $P2_1/n$ (#14), a = 9.372(3) Å, b = 21.457(7) Å, c = 10.828(3) Å, β = 111.67(2)°, V = 2023.6(12) Å^3, Z = 4 (numbers in parentheses are the estimated standard deviations in the last digit or digits); MoKα radiation, 4267 reflections collected, 1879 independent reflections used in refinement, full-matrix least squares, $R = 0.092$ ($= \Sigma |F_o - |F_c|| / \Sigma F_o$, where F_o and F_c are the observed and the calculated structure factors) for 1632 reflections with $F_o > 0$, goodness of fit is 1.16 $\{[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where w is the weight of the reflection, n is the number of data, and p is the number of parameters refined$\}$. All non-hydrogens refined anisotropically. Hydrogen atom parameters were assigned from difference maps or by calculation with C–H = 0.95 Å. For **4[3]**: $C_{28}H_{26}N_2O_2$; molecular weight 422.53. Monoclinic, $P2_1/n$ (#14), a = 9.551(2) Å, b = 22.787(6) Å, c = 10.688(2) Å, β = 109.61(2)°, V = 2191.2(9) Å^3, Z = 4. MoKα radiation, 7047 reflections collected, 2669 independent reflections used in refinement, full-matrix least squares, R = 0.065 for 1632 reflections with $F_o > 0$, goodness of fit equals 1.41. All nonhydrogens refined anisotropically. Hydrogen atom parameters placed by calculation with C–H = 0.95 Å and repositioned once before final least squares cycle.
23. R. H. Baughman, B. E. Kohler, I. J. Levy, C. Spangler, *Synth. Met.* **11**, 37 (1985).
24. W. Drenth and E. H. Wiebenga, *Acta Crystallogr.* **8**, 755 (1955).
25. S. R. Marder *et al.*, *J. Am. Chem. Soc.* **115**, 2524 (1993).

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