a large fractional loss of this interaction on moving to the carbocation-like transition state for the hydrolysis reactions.[8,9,12] The difference in the geminal stabilization energy of HOCH$_2$F compared with HOCH$_2$Cl obtained from ab initio calculations, 10.4 kcal/mol,[2a] is significantly larger than the 6.4 kcal/mol geminal stabilization of MeOCH$_2$F toward hydrolysis. This difference may reflect only a partial loss of stabilizing geminal interactions at the transition state for the hydrolysis reaction and/or a failure of the assumption that geminal interactions in 4-MeOC$_6$H$_4$CH$_2$X are negligible.

Data for the acid-catalyzed hydrolysis reactions of MeOCH$_2$OMe and 4-MeOC$_6$H$_4$CH$_2$OMe yield similar conclusions. The 35 000-fold difference between the rate constant ratios $k_{\mathrm{Cl}}/k_{\mathrm{MeOH}} = 3.8 \times 10^9$ M for the reaction of MeOCH$_2$X and $k_{\mathrm{Cl}}/k_{\mathrm{MeOH}} = 1.1 \times 10^5$ M for the reaction of 4-MeOC$_6$H$_4$CH$_2$X is consistent with a ≥6.1 kcal/mol larger geminal ground-state stabilization of MeOCH$_2$OMe than of MeOCH$_2$Cl.[13] By comparison, the difference in the geminal stabilization energies of HOCH$_2$OMe and HOCH$_2$Cl obtained from ab initio calculations is 11.6 kcal/mol.[2a]

The 10^4-fold greater reactivity of MeOCH$_2$Cl than of 4-MeOC$_6$H$_4$CH$_2$Cl toward hydrolysis (Table I) shows that MeOCH$_2^+$ is at least 5.5 kcal/mol more stable than 4-MeOC$_6$H$_4$CH$_2^+$ relative to the neutral chloride ion adducts. However, the relative rate constants for hydrolysis of MeOCH$_2$F and 4-MeOC$_6$H$_4$CH$_2$F or the corresponding methyl ethers show that 4-MeOC$_6$H$_4$CH$_2^+$ is slightly more stable than MeOCH$_2^+$ relative to the neutral fluoride or methoxide ion adducts. These data show that it is difficult to infer the relative stability of MeOCH$_2^+$ and 4-MeOC$_6$H$_4$CH$_2^+$ directly from the relative rate constants for solvolyses of neutral derivatives, because these depend upon the relative stabilities of the ground states and the carbocation-like transition states, both of which may differ. Similar difficulties have been encountered in the determination of the relative stabilities of α-cyano- and β-cyano-substituted carbocations[6a,b] and of α-methyl- and α-silyl-substituted carbocations[15,16] from relative rate constants for solvolysis reactions of neutral precursors.

We conclude that care must be exercised in the choice of a neutral ground state when evaluating substituent effects on carbocation stability. The use of leaving groups from the second and lower rows on the periodic table (e.g., I$^-$, Cl$^-$), which show relatively weak electronic geminal interactions,[2a] is to be preferred over the use of oxygen leaving groups for the estimation of carbocation stabilities from the relative rate constants for solvolyses reactions. Electronic geminal interactions with hydrogen are particularly weak and are used as the 0 reference point in determination of geminal interactions between other groups. Therefore, substituent effects on *carbocation stability* are best determined from experimental or computational data for the formation of carbocations from neutral alkanes.

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Direct Observation of Reduced Bond Length Alternation in Donor/Acceptor Polyenes

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There has been tremendous interest in asymmetric cyanine and merocyanine compounds because of their applications as photographic sensitizers,[1,2] membrane potential probes,[3,4] and photochromic dyes for all-optical memory.[5] On the basis of UV–visible spectroscopic data, Brooker suggested that merocyanine molecules could be described by a superposition of neutral and charge-separated canonical resonance forms and that, by changing the basicity of the endgroups and/or the solvent polarity, one could tune the molecular structure from neutral and polyene-like through polar and cyanine-like (with equal contributions from neutral and charge-separated resonance forms) to highly polar, charge-separated polyene-like.[1,6-10] Since the neutral and charge-separated resonance structures have different equilibrium geometries, the degree of bond length alternation in merocyanines can be tuned from close to that found in a polyene [i.e., the difference between the average length of the carbon–carbon single and double bonds $[r(\mathrm{C{-}C}) - r(\mathrm{C{=}C})]$ equals 0.11 Å (for diphenyloctatetraene[11] and for octatetraene[12])] to essentially none, as found in cyanines.[13,14]

The degree of bond length alternation has been used as a structural parameter in interpreting electronic spectra of poly-

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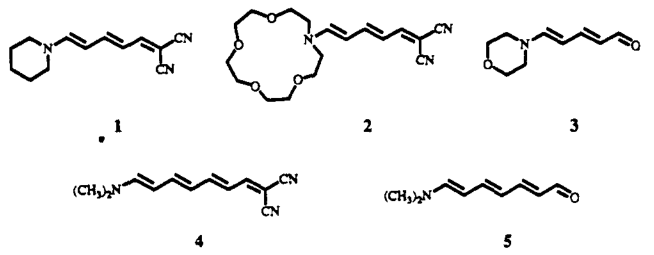

Figure 1. Chemical structures of donor/acceptor polyenes discussed in this study.

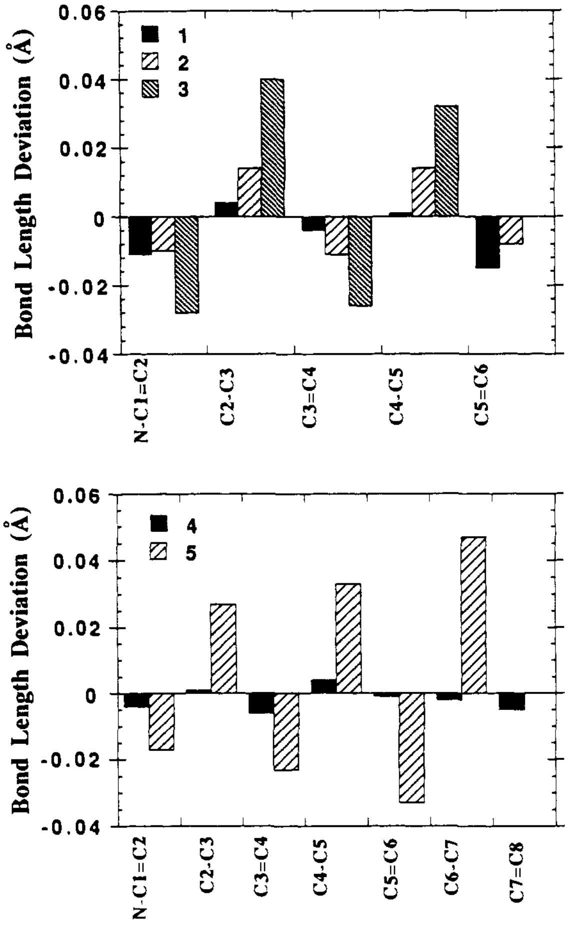

Figure 2. Top: Histogram of bond length alternation for compounds **1**-**3**. Bottom: Histogram of bond length alternation for compounds **4** and **5**. Carbon 1 is the carbon directly attached to the amine donor, and the carbon number increases along the chain through the acceptor.

methine dyes.[15] We are investigating the hypothesis that bond length alternation is a useful parameter to examine in developing structure-property relationships for nonlinear optical chromophores, and preliminary evidence suggests that both second-order[16,17] and third-order hyperpolarizabilities are correlated to changes in this parameter.[18] In addition, diminished bond length alternation has been noted upon doping conjugated polymers, and it has been suggested as a means to engineer new polymers with low band gaps.[19] Surprisingly, although bond length alternation plays a key role in determining the electronic and optical properties of conjugated organic molecules and polymers, very little structural data has been reported that documents the transition from bond alternate, polyene-like materials to bond equivalent, cyanine-like materials.[13,14] Indirect evidence for variation of bond length alternation in simple donor/acceptor polyene dyes has been obtained from nuclear magnetic resonance spectroscopic studies on proton-proton coupling constants.[15,20] These studies demonstrated that the difference in the three bond coupling constants for compounds of the form $R_2N-(CH=CH)_n-CHO$, where n = 2 or 3, decreases as a function of increasing solvent polarity, suggesting a shift from a polyene to a cyanine structure. However, the correlation of solvent-induced changes in spectroscopic properties of merocyanines with changes in bond length alternation has been called into question by other groups.[21,22] In this communication, we provide direct structural evidence of diminished bond length alternation for simple donor/acceptor polyenes both in the solid state and in solution.

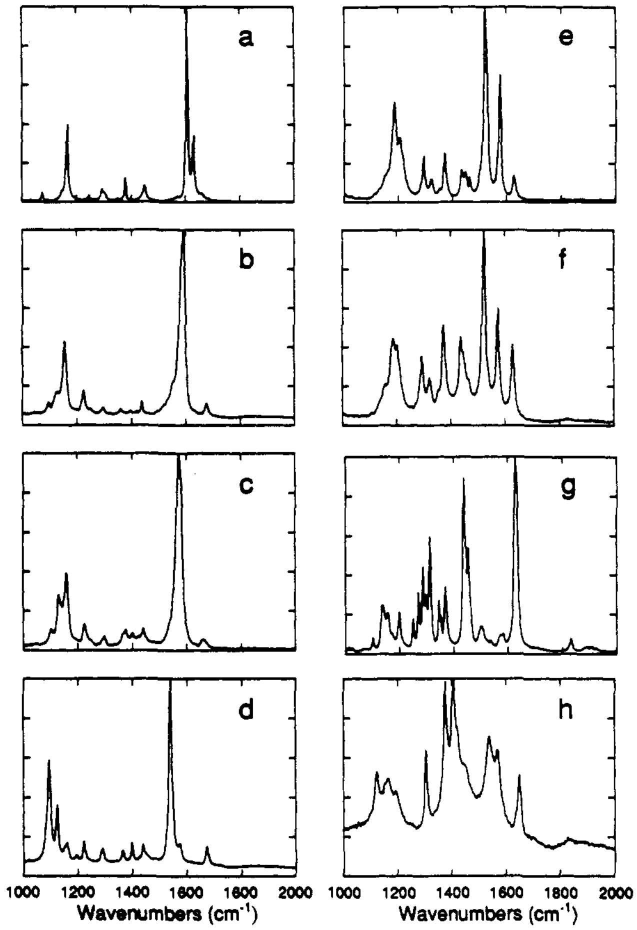

Figure 3. Raman spectra of (a) decatetraene in the solid state; (b) **5** in CCl_4; (c) **5** in CH_3CN; (d) **5** in the solid state; (e) **1** in $CHCl_3$; (f) **1** in CH_3CN; (g) **1** in the solid state; (h) $[(CH_3)_2N(CH=CH)_3CH=N(CH_3)_2]^+ClO_4^-$ in CH_3CN.

The crystal structures of four simple donor/acceptor polyenes of the general form $R_2N-(CH=CH)_n-A$, where R is an alkyl group, n is 2 or 3, and A is either formyl (CHO), a moderately strong acceptor, or dicyanovinyl $[CH=C(CN)_2]$, a strong acceptor, have been determined. The chemical structures of these four compounds and that of the previously determined 5-morpholinopenta-2,4-dien-1-al (n = 2, A = CHO)[23] are shown in Figure 1. In each compound the sum of the angles around the amine nitrogen atom is 360° ± 1°. This implies that the nitrogen is sp^2 hybridized and is therefore acting as an effective donor to the π-system. The average carbon-carbon bond length

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in the polyene fragment for compounds **1–5** is 1.38 Å. However, the average $[r(\mathrm{C-C}) - r(\mathrm{C=C})]$ for the dicyanovinyl compounds is *less than 0.02* Å whereas for the aldehyde compounds the average $[r(\mathrm{C-C}) - r(\mathrm{C=C})]$ is *0.05* Å (*Figure* 2), compared to 0.11 Å cited above for polyenes. Although compounds **1** and **2** have very different substituents on the amine nitrogen and therefore different packing arrangements in the crystal, both have similar degrees of bond length alternation. This suggests that the diminished bond length alternation in the dicyanovinyl compounds is intrinsic and not the result of crystal packing distortions.

All of these compounds exhibit positive solvatochromic behavior, which has been attributed both to stabilization of dipolar excited states *and to a reduction in bond length alternation*, by polar solvents.[24,25] We have examined the Raman spectra of compounds **1–5** in the solid state and in a variety of solvents ranging in polarity from CCl_4 to CH_3OH; selected spectra for compounds **1** and **5** are shown in Figure 3. For comparison we also examined decatetraene (Figure 3a) and $[(CH_3)_2N(CH{=}CH)_3CH{=}N(CH_3)_2]^+ClO_4^-$ (Figure 3h). The polyene spectrum is characterized[26] by two bands at roughly 1150 and 1600 cm^{-1}, whereas in the cyanine spectra these bands have greatly diminished intensity and several bands of intermediate energy are apparent. Qualitatively, the spectra of the compounds in polar solvents are quite similar to those in the solid state. This is shown for compounds **1** and **5** in Figure 3. In all cases, upon increasing the solvent polarity, the spectra became increasingly cyanine-like. The spectra of the aldehyde compounds are intrinsically more polyene-like[26] than those of the dicyanovinyl[27] compounds, consistent with the structural determinations. Overall, the aldehyde compounds in the *most* polar solvents have spectra similar to those of the dicyanovinyl compounds in the *least* polar solvent.

In conclusion, we have demonstrated that simple donor/acceptor polyenes span the gap, structurally, between polyenes and cyanines. Furthermore, our Raman data suggests that the compounds in this study, in polar solvents, have structures similar to those found in the solid state and that solvent can be used to tune the geometries of these important compounds. Therefore, these data taken in combination provide strong support for the previous assertions[24,25] that bond length alternation in donor/acceptor polyenes can be tuned with solvent from a polyene to a cyanine limit.

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Supplementary Material Available: Details of the crystal structure determinations and bond lengths and angles for compounds **1**, **2**, **4**, and **5** (42 pages); listing of observed and calculated structure factors for compounds **1**, **2**, **4**, and **5** (43 pages). Ordering information is given on any current masthead page.

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A New Photoreceptor Molecule from *Stentor coeruleus*[†]

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Stentor coeruleus, a heterotrich protozoan, is a unicellular and blue-green colored ciliate that exhibits a step-up photophobic response and a negative phototactic response.[1,2] Stentorin is the photoreceptor, and its chromophore structure is significantly different from those of rhodopsin, bacteriorhodopsin, carotenoids, chlorophylls, phytochrome, phycocyanins, and flavins. Although stentorin has been proposed to contain a hypericin-like chromophore,[3,4] its exact structure is not known. This report describes the structure. The structure of stentorin is not only photobiologically significant but also phototherapeutically relevant because it is related to hypericin, which has highly specific anti-HIV viral activity.[5]

Stentorin, which was isolated by sonicating *Stentor* cells in acetone and purified by reverse-phase HPLC, shows an absorption spectrum very similar to that of hypericin with λ_{max} at 595 nm (588 nm for hypericin; Figure 1). Under acidic conditions, the two absorption spectra match more closely, with 587 and 588 nm for stentorin and hypericin, respectively, suggesting that stentorin has a naphthodianthrone skeleton.[3,4] When acidified, stentorin exhibits a weak hyperchromic effect whereas hypericin shows hypochromism, indicating that stentorin is not structurally identical to hypericin.

Stentorin in negative ion fast atom bombardment mass spectrometry showed a molecular ion at 591.1304, which is in accord with the molecular formula $C_{34}H_{23}O_{10}$ (calculated molecular weight 591.1291).

Acetylated stentorin, when FAB-desorbed as $(M + H)^+$, shows a series of ions at *m/z* 593, 635, 677, 719, 761, 803, 845, 887, and 929, with the most abundant ion at 929, whereas acetylated hypericin shows an ion series at *m/z* 505, 547, 589, 631, 673, 715, and 757, with the most abundant ion at 757. A similar series of ions occurs upon EI of hypericin hexaacetate.[6] The ion series for stentorin establishes that there are eight hydroxyl groups.

Additional confirmation is provided by a collisionally activated decomposition (CAD) spectrum of the $(M + H)^+$ of the octaacetate[7] (see Figure 2a). As expected, the parent ion undergoes eight consecutive losses of 42 u (apparently ketene), one for each acetate. More surprising, however, is the loss of 60 u (acetic acid), which is not expected for acetylated phenol-like functionalities. Although this latter loss is not facile from $(M + H)^+$, it does occur

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[†] This paper is dedicated to Professor W. Rüdiger on the occasion of his 60th birthday.

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