in the polyene fragment for compounds **1–5** is 1.38 Å. However, the average [r(C—C) − r(C=C)] for the dicyanovinyl compounds is *less than 0.02* Å whereas for the aldehyde compounds the average [r(C—C) − r(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.

Acknowledgment. The research described in this paper was performed in part by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Center for Space Microelectronics Technology and was supported in part by the Defense Advanced Research Projects Agency (Grant No. 91-NC-146 administered by the Air Force Office of Scientific Research) and the Strategic Defense Initiative Organization, Innovative Science and Technology Office, through a contract with the National Aeronautics and Space Administration (NASA). Support from the National Science Foundation (Grant No. CHE 9106689) is also gratefully acknowledged. S.G. and G.B. thank the National Research Council and NASA for a Resident Research Associateship at JPL. C.B.G. thanks the JPL director's office for a postdoctoral fellowship. S.B. thanks JPL for a Summer Undergraduate Research Fellowship. We thank William Schaefer and Lawrence Henling for performing the crystal structure determinations of compounds **1**, **2**, **4**, and **5**.

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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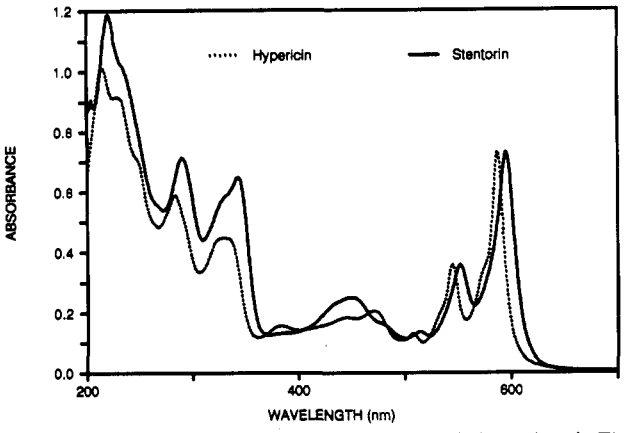


Figure 1. Absorption spectra of hypericin and stentorin in methanol. The spectra were taken on a Shimadzu UV-265 UV–visible recording spectrophotometer.

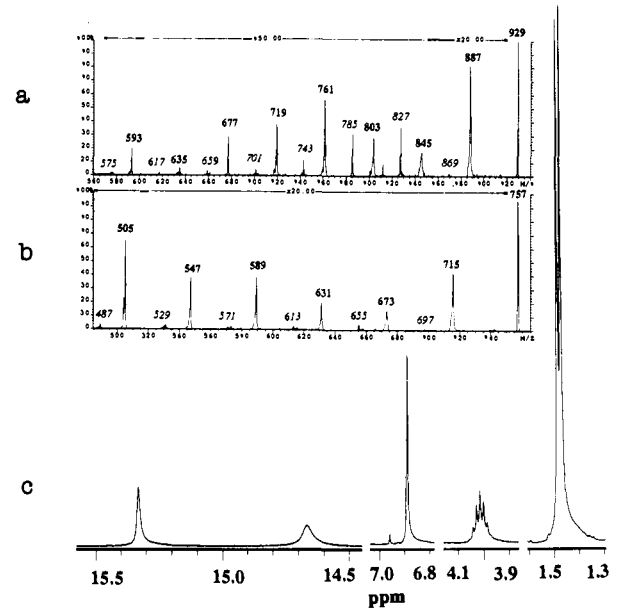


Figure 2. Collisionally activated decomposition (CAD) spectra of (a) acetylated stentorin and (b) acetylated hypericin. The precursor $(M + H)^+$ ions were desorbed by FAB, and the data were acquired on a prototype four-sector VG Analytical (Fisons) tandem mass spectrometer.[7] (c) NMR spectrum of stentorin in DMSO-d_6, acquired on a General Electric Omega-500 NMR spectrometer.

more readily from fragments formed by ketene elimination. The $(M + H)^+$ of hypericin octaacetate fragments in a similar manner.

Expulsion of ketene creates, in at least some $(M + H - 42)^+$ ions, an OH group adjoining an acetate at positions 2, 2′, 7, or 7′. The OH anchimerically assists release of acetic acid from an adjoining position to form a protonated cyclic ether. The occurrence of this loss of acetic acid is consistent with a structure having OH (OAc) groups in those positions.

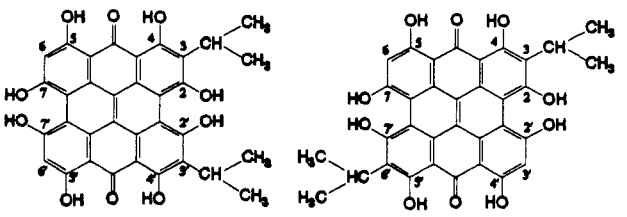
The IR spectrum of stentorin is similar to that of hypericin except for differences in the fingerprint region. Both IR spectra indicate the presence of hydrogen-bonded quinone carbonyl groups (1575 and 1590 cm^{-1}, respectively). The presence of these groups is also supported by the IR spectrum of acetylated stentorin, which absorbs at 1774 cm^{-1} (ester carbonyl) and 1676 cm^{-1} (non-hydrogen-bonded quinone carbonyl).

Furthermore, the ^1H NMR spectrum (Figure 2c) of stentorin has two singlets at δ 15.3 and 14.7, confirming the hydrogen-bonded hydroxyl groups. These two low-field peaks are comparable to those of hypericin (δ 14.8 and 14.3),[8] pointing to a naphthodianthrone skeleton with four peri-hydroxyl groups for stentorin.

The NMR spectra of stentorin and hypericin indicate that the molecules are symmetrical. There is a very broad peak for stentorin at approximately δ 5.4, which is attributable to the hydroxyl groups at positions 2,2′ and 7,7′ by comparison to similar broad peaks in the NMR spectra of hypericin, 3,4,8-trihydroxy-1-methylanthra-9,10-quinone-2-carboxylic acid methyl ester,[9] 2,2′-dihydroxybiphenyl, and 2,2′,4,4′-tetrahydroxybiphenyl.[10] The integration of this peak gives an area that is too large, possibly owing to the presence of water, even though the sample was dried extensively. The peak broadening may be due to intra- or intermolecular hydrogen bonding and/or to the proton exchange of those hydroxyl groups and water molecules.

The NMR spectrum of stentorin reveals the presence of isopropyl groups, which are characterized by a septet signal centered at δ 4.0 (J = 7 Hz, 1 H) and a doublet at δ 1.5 (J = 7 Hz, 6 H). This is confirmed by a 2D NMR spectrum, which shows a strong coupling between those protons.

Unlike hypericin, which has two aromatic proton signals at δ 7.4 (H-3, H-3′, which are adjoining the methyl groups) and δ 6.6 (H-6, H-6′, which are adjoining the OH groups) in its NMR spectrum, stentorin has only a single peak at δ 6.9, suggesting that only two out of four positions at 3, 3′, 6, or 6′ are occupied by protons. The other two positions are occupied by isopropyl groups. Thus, the structure of stentorin involves one of three possible symmetrical arrangements of those protons and isopropyl groups, namely, 2,2′,4,4′,5,5′,7,7′-octahydroxy-3,3′-diisopropylnaphthodianthrone (**1**), 2,2′,4,4′,5,5′,7,7′-octahydroxy-3,6′-diisopropylnaphthodianthrone (**2**), or 2,2′,4,4′,5,5′,7,7′-octahydroxy-3,6-diisopropylnaphthodianthrone (**3**).



1 **2**

The last choice (**3**) may be ruled out by considering the usual routes of biosynthesis, since hypericin is produced in vivo through the polyketide pathway.[11] The choice between **1** and **2** must await the crystallographic determination.[12] Interestingly, 2,2′,4,4′,5,5′,7,7′-octahydroxymesonaphthodianthrone, a fossil pigment called fringelite D,[13,14] was found in a fossil sea lily of Jurassic age. The structure of this pigment resembles more closely that of stentorin than that of hypericin. Stentorin may be synthesized via a pathway similar to that for fringelite. That polyketide pathway is similar to that for hypericin, although we are not sure how the isopropyl group is introduced. One possibility is via an isoprenoid.

The nature of the primary photoprocess mediated by the native stentorin (λ_{max} 610–620 nm[15,16]) is not known. Proton dissociation

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of the excited chromophore was suggested to initiate the sensory signal transduction in *Stentor*.[17] It was recently reported that 2- or 2'-hydroxyl is the preferred site of deprotonation of hypericin.[18] It is reasonable to speculate that similar deprotonation of stentorin could serve as the initial photosensory transduction step. Photoinduced electron transfer, however, is also possible. A complete understanding of the photosensory transduction mechanism of *Stentor* awaits further characterization of the native stentorin.

Acknowledgment. This work was supported by grants from the National Institutes of Health (RO1-NS15426), the U.S. Army Research Office (28748-LS-SM and 29597-LS-EPS), and the National Science Foundation (DIR-9017262). We thank Dr. Rich Shoemaker for his assistance with NMR, Dr. J. S. Rhee for preliminary mass spectrometric measurements, and Dr. David Berkowitz and Dr. Desmond Wheeler for helpful discussions.

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α- versus β-Elimination of (*Z*)-(β-Halovinyl)iodonium Salts: Generation of (α-Haloalkylidene)carbenes and Their Facile Intramolecular 1,2-Migration

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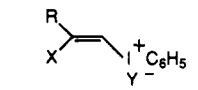
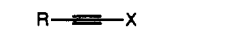
Base-induced dehydrohalogenation of vinyl halides leading to the formation of alkynes can take place through either α- or β-elimination.[1,2] The kinetic results for E2-type dehydrohalogenation of vinyl halides show that the relative rates of elimination decrease in the order anti β- > syn β- ≫ α-elimination.[3] We report herein competition between the base-induced α- and β-eliminations of (*Z*)-(β-halovinyl)phenyliodonium salts, which make possible the generation of (α-haloalkylidene)carbenes (Scheme I).

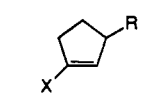
Exposure of (*Z*)-(β-bromovinyl)iodonium bromide **1a** (Y = Br) to $NaHCO_3$ in CH_2Cl_2–MeOH–H_2O at 0 °C for 4 h afforded the rearranged 1-bromoalkyne **4a** in high yield (Table I). Similarly, **2a** (Y = Br) and **3a** (Y = Br) produced exclusively **5a** and **6a**, respectively. These experiments were the first to show that (α-bromoalkylidene)carbenes could be generated and undergo 1,2-migration of α-bromine to terminal carbons more rapidly than the intramolecular 1,5-carbon–hydrogen insertion yielding 1-bromocyclopentenes.[4,5] The relative rates of 1,2-migration and



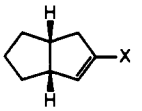
1a: R = n-C_8H_{17}, X = Br
1b: R = n-C_8H_{17}, X = Cl
1c: R = n-$C_{14}H_{29}$, X = F
2a: R = c-$C_5H_9CH_2$, X = Br
2b: R = c-$C_5H_9CH_2$, X = Cl
3a: R = t-Bu, X = Br
3b: R = t-Bu, X = Cl



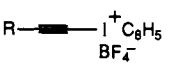
4a: R = n-C_8H_{17}, X = Br
4b: R = n-C_8H_{17}, X = Cl
5a: R = c-$C_5H_9CH_2$, X = Br
5b: R = c-$C_5H_9CH_2$, X = Cl
6a: R = t-Bu, X = Br
6b: R = t-Bu, X = Cl
7a: R = C_6H_5, X = I
7b: R = C_6H_5, X = Br
7c: R = C_6H_5, X = Cl



8a: R = n-C_5H_{11}, X = Br
8b: R = n-C_5H_{11}, X = Cl
8c: R = n-$C_{11}H_{23}$, X = F



9a: X = Br
9b: X = Cl



10: R = n-C_8H_{17}
11: R = c-$C_5H_9CH_2$
12: R = C_6H_5

1,5-C–H insertion depend on the α-halogen atoms of alkylidenecarbenes. Thus, in the case of (α-chloroalkylidene)carbenes, 1,2-chlorine shift competes with 1,5-C–H insertion yielding 1-chlorocyclopentenes: treatment of **1b** (Y = Cl) with $NaHCO_3$ or *n*-Bu_4NF gave a 59:41 mixture of the 1-chloroalkyne **4b** and the 1-chlorocyclopentene **8b** in high yields. Similar ratios of 1,2-shift to 1,5-C–H insertion were obtained in the reaction of **2b** (Y = Cl). Most importantly, the level of selectivity does not depend on the base used. This strongly suggests that the same intermediates are involved in the reactions. On the other hand, 1-fluorocyclopentene **8c** was obtained selectively in the reaction of **1c** (Y = Cl), albeit in low yield.[6]

Base-induced α-elimination of the phenyliodonio group with super nucleofugalities from (*Z*)-(β-halovinyl)phenyliodonium salts would directly generate (α-haloalkylidene)carbenes.[4] However, the following mechanistic alternative should be considered for the generation of (α-haloalkylidene)carbenes: (1) stereoelectronically preferable anti β-elimination of hydrogen halides by base yielding alkynyliodonium salts, (2) Michael type addition of the halide ions, and (3) reductive elimination of the phenyliodonio group (Scheme I). It appears that the intermolecular crossover experiments shown in Scheme II could distinguish between these two reaction pathways. Both the vinyliodonium-derived product **4a** and the alkynyliodonium-derived product **5a** were obtained in a ratio of 70:30 from the reaction of a 1:1 mixture of **1a** (Y = BF_4) and **11** with $NaHCO_3$. With a 1:1 mixture of **1b** (Y = BF_4) and **11**, the ratio of the alkynyliodonium-derived products (**5b** and **9b**) decreased to the extent of one-third. The same holds true for a combination of **2a,b** (Y = BF_4) and **10**. These results clearly demonstrate that the generation of (α-haloalkylidene)carbenes involves not only α-elimination of phenyliodonio groups but also anti β-elimination of hydrogen halides. Furthermore, (β-bromovinyl)iodonium salts show a greater tendency toward anti β-elimination of hydorgen halides than (β-chlorovinyl)iodonium salts. These were further supported by the intramolecular version of the crossover experiments using **1a** (Y = Cl) and **1b** (Y = Br), as shown in Scheme II.[7]

The earlier reports that 1,5-C–H insertion of alkylidenecarbenes cannot compete with 1,2-aryl migration,[8,9] combined with the

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