

fluorescence measurements²⁷ on **1-5** reveals that singlet energy transfer between porphyrins is faster than or roughly comparable to the rates of the other processes which depopulate the excited singlet states. The C-¹P_A-P_B-Q singlet state also decays by other photophysical processes (step 2 in Scheme I) with $k_2 = 2.5 \times 10^8 \text{ s}^{-1}$ (based on the 4.0 ns fluorescence lifetime for **5**). C-P_A-¹P_B-Q decays by photophysical processes ($k_4 = 1.0 \times 10^8 \text{ s}^{-1}$ based on a fluorescence lifetime of 9.9 ns for **2**) and by electron transfer (step 7) to yield C-P_A-P_B^{•+}-Q^{•-}. Photoinitiated electron transfer between the porphyrins is thermodynamically unfavorable in this molecule. In the limit of rapid singlet energy transfer, the porphyrin fluorescence decay of **1** would be a single exponential with a lifetime τ , where $1/\tau = (k_2 + k_4 + k_7)/2$. On this basis, an electron transfer rate constant of $k_7 = 2.4 \times 10^8 \text{ s}^{-1}$ was calculated from the measured fluorescence lifetime of 3.4 ns and the values of k_2 and k_4 mentioned above. Given the experimental errors involved ($\pm 25\%$ for rate constants) and the use of model compounds to estimate rate constants for k_2 and k_4 , this rate constant is in good agreement with the photoinitiated electron transfer rate constant of 2.4×10^8 calculated for **4** in the manner described above from its fluorescence lifetime of 4.5 ns.

Competing with charge recombination in C-P_A-P_B^{•+}-Q^{•-} is electron transfer which ultimately yields C^{•+}-P_A-P_B-Q^{•-} with an overall quantum yield of ca. 0.25 based upon total light absorbed. In Scheme I, this is shown as a two-step process (steps 8 and 10) involving a C-P_A^{•+}-P_B-Q^{•-} intermediate. Cyclic voltammetric measurements on model compounds, which ignore coulombic stabilization, suggest that C-P_A^{•+}-P_B-Q^{•-} would be more stable than C-P_A-P_B^{•+}-Q^{•-} by roughly 0.1 eV, and this would be consistent with a discrete intermediate. On the other hand, coulombic stabilization of C-P_A-P_B^{•+}-Q^{•-} might lower the energy of this state below that of C-P_A^{•+}-P_B-Q^{•-}. In this case, conversion of C-P_A-P_B^{•+}-Q^{•-} to C^{•+}-P_A-P_B-Q^{•-} could involve a single process aided by superexchange interactions of P_A. The long²⁶ lifetime of the final state is the result of the large spatial separation of the cation and anion and the fact that endergonic electron transfers⁷ would be needed to place the charges on adjacent chromophores.

Excitation of **1-5** yields porphyrin triplet states, and in **1** and **3** both of these triplets are rapidly (≤ 20 ns) quenched by the carotenoid via triplet energy transfer; P_A is evidently serving as a triplet energy relay. In addition, the carotenoid moiety of **5** and therefore presumably that of **1** and **3** transfers singlet energy to the attached porphyrin with ca. 10% overall efficiency. Thus, tetrad **1** mimics not only multistep photoinitiated electron transfer (which is characteristic of natural photosynthesis) but also chlorophyll antenna function (singlet energy transfer between chlorophylls), carotenoid antenna function (singlet energy transfer from carotenoids to chlorophylls), and carotenoid photoprotection from singlet oxygen damage (carotenoid quenching of chlorophyll triplet states).

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(27) Several techniques were employed for these measurements. They include single photon counting with excitation at 590 or 360 nm, streak camera detection with excitation at 532 nm, and photomultiplier detection with excitation at 532 nm. We thank Professor M. A. Fox, Dr. S. Atherton, Dr. R. V. Bensasson, Dr. M. Roug e, Professor F. C. De Schryver, and Dr. M. Van der Auweraer for their help.

2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene: The First Isolation and Characterization of a Boratanorcaradiene

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The perturbation of electronic and structural properties caused by replacement of a carbon by a boron atom is a topic of expanding theoretical¹ and experimental² interest. In most of the previously examined cases, electrically neutral trivalent boron atoms are used to simulate isoelectronic and nearly isosteric carbocations. Likewise, tetravalent anionic boron groups (borates) can be thought of as negatively charged analogues of neutral carbon atoms. We report herein the first isolation and characterization of a boratanorcaradiene: 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (**1**) is a blood-red, reactive solid formed from UV irradiation of (*p*-biphenyl)triphenyl borate (**2**).

Borate **2** (Me₄N⁺ salt, ¹¹B NMR: $\delta -6.76$, BF₃·OEt₂ = 0.00) is easily prepared by reaction of biphenyllithium with triphenylborane.³ Its absorption spectrum in acetonitrile solution shows a band at 272 nm ($\epsilon_{\text{max}} = 22600 \text{ M}^{-1} \text{ cm}^{-1}$) characteristic of biphenyl derivatives. Irradiation of **2** in a degassed acetonitrile solution at 254 nm ($1.2 \times 10^{-2} \text{ M}$, Rayonet Reactor, 0 °C, 2 h) leads to formation of a deeply red reaction mixture and appearance of new ¹¹B NMR resonances at $\delta -26.6$ and -27.2 . Integration of the product peaks immediately after irradiation shows them to be present in a ratio of 1:1; after 2 h at 30 °C this ratio becomes 5:1. Additional heating causes no further change.

The major product from photolysis of **2** can be isolated in 30% yield by repeated fractional crystallization from CH₃CN/ether. The air and water sensitive red solid has an ¹¹B NMR absorption at $\delta -26.6$. Its elemental analysis gives the formula C₃₄H₃₆BN.³ The same as that of starting borate. The product's UV-vis spectrum in CH₃CN shows two bands: 294 nm ($\epsilon_{\text{max}} = 19000 \text{ M}^{-1} \text{ cm}^{-1}$) and 510 nm ($\epsilon_{\text{max}} = 2700 \text{ M}^{-1} \text{ cm}^{-1}$).⁴

The ¹H and ¹³C NMR spectra of the photoproduct are particularly revealing. Its 500 MHz ¹H NMR spectrum in THF-*d*₈ at room temperature is shown in Figure 1. The two singlets (δ 1.39, 5.55), the triplets at δ 7.17 and 7.02, and the doublet at 7.69 are unaffected when the solution is cooled to -10 °C, but the triplets at δ 6.81 and 6.68 and the doublet at δ 7.10 begin to broaden. Further cooling results in additional broadening until at -80 °C the broadened peaks split into sharpened multiplets. The ¹³C NMR spectrum of the photoproduct shows detectable peaks for only nine carbons, two (δ 37.1 and 135.5) broadened

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(3) Anal. Calcd for C₃₄H₃₆BN: C, 86.98; H, 7.73; N, 2.98; B, 2.30. Found (**1**): C, 86.50; H, 7.62; N, 3.10; B, 2.05. Found (**2**): C, 86.68; H, 7.75; N, 2.97; B, 2.07.

(4) The red color of **1** persists, apparently undiminished, even at liquid N₂ temperature. This observation rules out the possibility that it is due to the presence of a minor isomer in equilibrium with **1**.

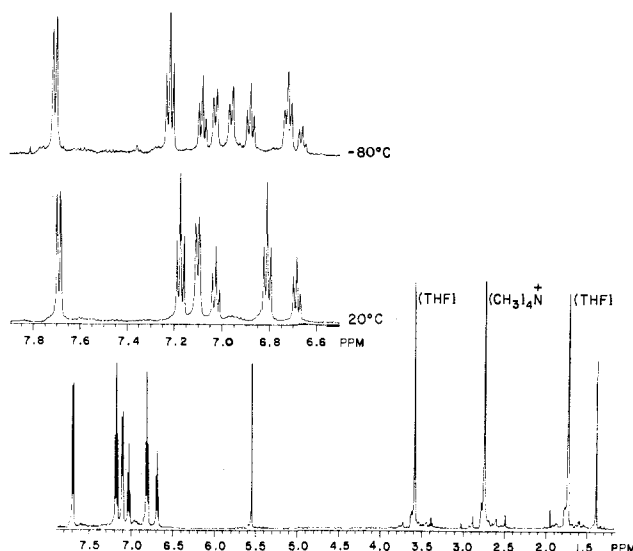
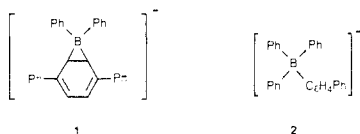


Figure 1. The 500 MHz ^1H NMR spectrum of boratanocaradiene **1** in THF-d_8 solution recorded at ambient temperature. The expanded insets of the aromatic region were recorded at 20 $^\circ\text{C}$ (lower) and -80 $^\circ\text{C}$ (upper). The resonances that broaden and then split as the temperature is lowered have chemical shifts $\{\delta, 20\text{ }^\circ\text{C} [-80\text{ }^\circ\text{C}]\}$ 7.10 [7.03, 6.96]; 6.81 [6.88, 6.72]; 6.68 [6.72, 6.66].

Chart I



by coupling to boron.⁵ A proton-carbon HETCOR experiment⁶ reveals that carbons with resonances at δ 135.5, 125.5, and 122.0 are bound to the protons whose absorptions are temperature dependent. These data support the boratanocaradiene structure for **1**, an assignment confirmed by X-ray crystallography, Figure 2.⁷

The X-ray data show that within experimental error, the boron-containing ring of **1** is an equilateral triangle inclined at an angle of 104 $^\circ$ with respect to the four nearly coplanar diene carbon atoms. The six-membered ring is twisted; C₂ (Figure 2) is 24 (5) $^\circ$ above the diene plane. In many respects, the structure of **1** resembles that of the norcaradienes,⁸ its related all-carbon analogues.

With the structure of the major product defined, the photochemical and spectroscopic results may be interpreted. The ^1H

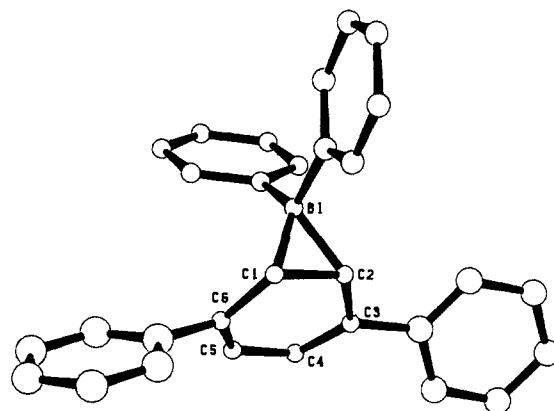
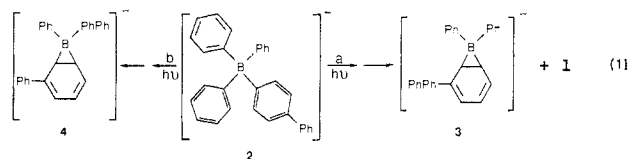


Figure 2. Structure of boratanocaradiene **2** determined by X-ray crystallography of its tetramethylammonium (not shown) salt. Key bond lengths and angles: B₁-C₁, 1.60 (5); C₁-C₂, 1.58 (5); C₂-C₃, 1.45 (5); C₃-C₄, 1.40 (5); C₄-C₅, 1.46 (5) Å. $\angle\text{C}_1\text{B}_1\text{C}_2$, 60(2) $^\circ$; $\angle\text{B}_1\text{C}_1\text{C}_2$, 59(2) $^\circ$.

NMR spectrum of the reaction mixture immediately after irradiation⁹ is consistent with the formation of three di- π -borate¹⁰ rearrangement products, two (**1** and **3**) formed by coupling of the biphenyl and phenyl groups (eq 1, path a), the other (**4**) from



the coupling of two phenyl groups (path b). Both **3** and **4** seem to have ^{11}B chemical shift of -27.2. A series of thermal sigma-tropic rearrangements apparently converts **3** to **1** ($k = 1.0 \times 10^{-4} \text{ s}^{-1}$, 30 $^\circ\text{C}$). These findings are entirely consistent with our previous analyses of the photochemistry of tetraphenylborate¹¹ and styryltriphenylborate¹² and with the related work of Grisdale and co-workers,¹³ but they abrogate the claim¹⁴ that irradiation of tetrylborates leads to hypovalent borenes.

The temperature dependence of the ^1H NMR spectrum of **1** is specially revealing when considered in relation to similar studies of the conversion of norcaradienes to cycloheptatrienes.¹⁵ Analysis of these spectra shows that at room temperature a rearrangement exchanges the two phenyl groups bound to boron without the concomitant exchange of the bridgehead or vinyl protons. These observations probably signal ring opening of **1** to 1,1,3,6-tetraphenylboratepine (**5**), "boat-boat" interconversion, and reclosure to **1**, eq 2. Calculations from the observed coalescence temperature

(5) The ipso carbon of the phenyl group bound to boron is not observed presumably because of broadening by boron. The carbon resonance at δ 135.5 is assigned to the ortho carbons of the phenyl groups bound to boron.

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(7) Crystal data for $[(\text{CH}_3)_4\text{N}][\text{C}_{30}\text{H}_{24}\text{B}]$ at $t = -50\text{ }^\circ\text{C}$: monoclinic (alternate setting), space group $P2_1/a$, $a = 17.841$ (9) Å, $b = 17.007$ (7) Å, $c = 18.294$ (8) Å, $\beta = 98.18$ (4) $^\circ$, $V = 5494$ (8) Å³, and $Z = 8$. Diffraction data: Enraf-Nonius CAD4 automated κ -axis diffractometer, Mo radiation ($\lambda(\text{K}\alpha) = 0.71073$ Å), range $2.0 < 2\theta < 15.0^\circ$ for $\pm h \pm k \pm l$ and $15.0 < 2\theta < 40.0^\circ$ for $+h - k \pm l$, 6446 reflections (5101 unique, $R_i = 0.026$, 857 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, Lorentz and polarization effects. Solution: direct methods (SHELXS-86). Refinement: tetramethylammonium cation and aromatic rings refined as rigid idealized groups, H atoms included as idealized contributors and remaining atoms independently refined (SHELX). Final: difference Fourier map (range $-0.40 < e/\text{Å}^3 < 0.42$) showed no significant features; variance between observed and calculated structure factors showed no apparent systematic errors; agreement factors, $R = 0.115$, $R_w = 0.098$, and $E = 1.99$. Refinement of the proposed model was limited by the paucity of data. Recrystallization failed to improve crystal quality, presumably due to the fluxional nature of the compound. A complete report of the X-ray structure determination prepared by Dr. Scott Wilson of this department is available as Supplementary Material to this paper.

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(9) In addition to the peaks for **1**, this spectrum shows the following: **3**, δ 5.47 (d, $J = 6$ Hz), 6.23 (dd, $J_1 = 6$ Hz, $J_2 = 9$ Hz), 4.99 (dd, $J_1 = 6$ Hz, $J_2 = 9$ Hz); **4**, δ 5.41 (d, $J = 6$ Hz), 6.23 (dd, $J_1 = 6$ Hz, $J_2 = 9$ Hz), 4.99 (dd, $J_1 = 6$ Hz, $J_2 = 9$ Hz).

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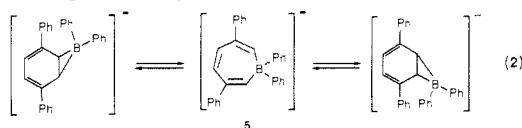
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(-20 °C, 500 MHz) reveal that **5** must be less than ca. 10 kcal/mol higher energy than **1**.



The electronic structure of **1** is unusual. In particular, its strong absorption in the visible region is unexpected by analogy with related norcaradienes¹⁵ and by comparison with *trans*-1,1,2,3-tetraphenylboratirane ($\lambda_{\max} = 280$ nm).¹² The 510-nm absorption of **1** therefore must be due to interaction of the strained three-membered borate ring with the diene chromophore. Some insight into this interaction comes from molecular orbital calculation (Gaussian 86, 3-21G basis set)¹⁶ on parent boratanorcaradiene ($C_6H_8B^-$). Its HOMO is formed from combination of the diene Ψ_2 with the appropriate Walsh-like¹⁷ orbital of the borate ring. For comparison, the HOMO of norcaradiene, calculated at the same level of approximation, has the same nodal properties but is much lower in energy. Clearly, the "excess" electronic charge that results from replacement of a neutral carbon by a negative borate group alters properties profoundly. We are continuing to explore the extent of this perturbation.

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Supplementary Material Available: Drawings of **1** and **2** containing atom numbering and tables of atomic coordinates, calculated positions, and thermal parameters for $[(CH_3)_4N][C_{30}H_{24}B]$ (7 pages); observed and calculated structure factors for $[(CH_3)_4N][C_{30}H_{24}B]$ (4 pages). Ordering information is given on any current masthead page.

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Free Standing Polydiacetylene Films Cast from Bilayer Membranes

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The formation of supramolecular assemblies of monolayers, bilayers, and/or multilayers is of considerable interest. Monolayers and multilayers are frequently prepared by Langmuir-Blodgett techniques. Recently Kunitake and co-workers introduced an alternative approach to ordered multilayers.¹⁻⁵ The molecular ordering present in bilayers was transformed to macroscopic ordering in multilayer films by the casting of aqueous dispersions of bilayers onto solid supports.

It is well known that the topotactic photopolymerization of diacetylenes is acutely sensitive to the molecular order of crystals and supramolecular assemblies. Monolayers of diacetylenic fatty

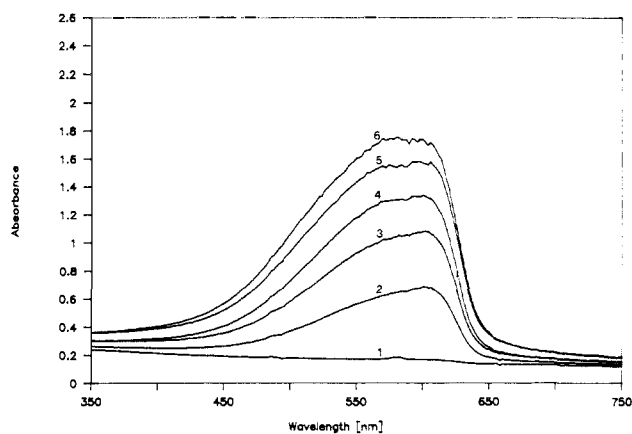
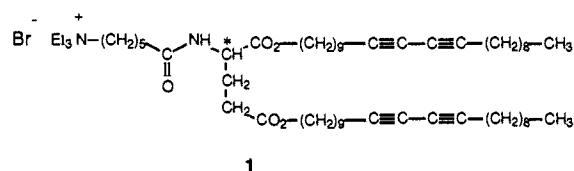


Figure 1. Absorption spectra of a cast multilayer film of **1**. The spectra were recorded after exposure to 254 nm light for the following times: curve 1, 0 s; 2, 10 s; 3, 30 s; 4, 60 s; 5, 120 s; and 6, 180 s.

acids are polymerizable only in close packed solid-like monolayers.^{6,7} Bilayer membranes of lipid diacetylenes are neither photopolymerizable above the lipid phase transition temperature (T_c) of the membrane⁸ nor in small sonicated vesicles where the lipid chain packing is disordered by the sharp radius of curvature of the membrane.⁹ The stringent requirements for efficient photopolymerization of diacetylenes provide an excellent test of the ordering in cast multilayer films.

We describe here a new diacetylenic lipid (**1**) based on a glu-



1

tamate backbone, the formation of cast multilayers from bilayers of pure **1**, and the successful photopolymerization of the multilayers to yield free standing polydiacetylene (PDA) films. The rigid, all-conjugated polymer structure renders most PDAs insoluble. Therefore the preparation of films of PDA heretofore has been accomplished only from a few chloroform soluble PDA (i.e., poly-3BCMU, poly-4BCMU)¹⁰ or from amphiphilic diacetylenes via L-B techniques.^{11,12}

Lipid **1** was synthesized (detailed procedure will be described elsewhere) by condensation of *N*-Cbz-L-glutamic acid and docosa-10,12-diyne-1-ol, removal of the protecting group with iodotrimethylsilane, reaction of the free amino group with 6-bromohexanoyl chloride, and finally amination with triethylamine.¹³

Bilayer membrane vesicles of **1** were prepared from a thin film of 5 μ mol of **1**, which was hydrated with 1 mL of water (Milli-Q, Millipore Corp) and subsequently sonicated for 30 s at room

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(13) Compound **1** was characterized by IR, NMR, TLC, and elemental analysis: IR (KBr) 3302, 2922, 2849, 2180, 2140, 1726, 1644, 1532, 1463 cm^{-1} ; ¹H NMR ($CDCl_3$) δ 0.88 (t, 6 H), 1.26-1.85 (m, 75 H), 2.24 (t, 8 H), 2.53 (t, 2 H), 3.55 (q, 8 H), 4.04 (t, 2 H), 4.06 (t, 2 H), 4.45 (m, 1 H), 7.92 (d, 1 H). Anal. Calcd for $C_{61}H_{105}N_2O_3Br$: C, 71.41; H, 10.24; N, 2.73. Found: C, 71.64; H, 10.77; N, 2.74. Mp: t_m 35 °C, t_i 85 °C (thermotropic liquid crystalline behavior observed at this temperature range on a hot-stage polarizing microscope).

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