of purified major isomer **1** in its respective styrene as an external standard. Each reaction mixture and standard-containing solution was analyzed by GLC ($^1/_8$ in. × 10 ft, 20% DNP) 3–5 times, with the average being reported.

For all the reactions involving *p*-nitrostyrene and for the styrene/*p*-methoxystyrene competitive olefin experiment, the regioisomer ratios were determined by 282-MHz ^{19}F NMR in $CDCl_3$. Use of *m*-bromobenzotrifluoride as an internal standard allowed calculation of the percent yields. The samples were all degassed and sealed under vacuum. A T_1 population inversion experiment showed that the longest $T_1 \leq 6$ s for these compounds, and thus a 10-s pulse delay was used. The error in these results was estimated to be 2%.[28]

(*E*)- and (*Z*)-4-Deuterio-2,2-difluoro-3-phenyl-1-methylenecyclobutane (3) and (*E*)- and (*Z*)-2-Deuterio-3-phenyl-1-(difluoromethylene)cyclobutane (4). A representative procedure for the deuterated runs is given below. Into a clean, dry, 30-mL, Pyrex bulb containing a doubly degassed mixture of 2.00 mL (17.2 mmol) of 99.3% (*Z*)-β-deuteriostyrene and 41 mg of hydroquinone was condensed 7.9 mmol of previously triply degassed DFA. After being sealed under vacuum, the bulb was placed in a stirred oil bath at 79–81 °C for 7.5 h. The bulb was cooled and opened, and the regioisomer ratio **3**:**4** was determined by GLC with a $^1/_4$ in. × 10 ft 10% DNP column at 140 °C. The excess (*Z*)-β-deuteriostyrene was removed by vacuum transfer at 12 torr, along with some **4**.

Crude separation of the residue by flash chromatography with a 45 mm diameter column with 14 cm of 230–400 mesh silica gel with 25-mL fractions and hexane as the eluant afforded 77 mg (0.42 mmole) of **4** followed by 378 mg (2.09 mmol) of **3** for a combined isolated yield of 32%. The ratios of *Z* to *E* isomers of **3** and **4** were determined by 300-MHz ^{1}H NMR with a pulse delay of 30 s to ensure relaxation of the protons integrated. In this way the stereochemical ratios for the deuterium *Z* vs. *E* to the phenyl ring were determined to be 58:42 for regioisomer **3** and 79:21 for **4**. Analysis of each isolated regioisomer by GLC at conditions similar to those given above showed a single peak. Examination of the recovered (*Z*)-β-deuteriostyrene, which was also purified by flash chromatography, by 100-MHz ^{1}H NMR demonstrated that there was no isomerization of the starting material under the reaction conditions.

An additional control whereby 19.5 mg of **4** was heated in heptane at 100 °C for 6 h showed *no* isomerization of **4** to the more stable **3** and no change in the *Z* to *E* ratio of recovered 4.

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Registry No. **1a**, 96245-32-8; **1b**, 96245-33-9; **1c**, 96245-34-0; **2a**, 96258-18-3; **2b**, 96245-35-1; **2c**, 96245-36-2; (*E*)-**3**, 96245-37-3; (*Z*)-**3**, 96245-38-4; (*E*)-**4**, 96245-39-5; (*Z*)-**4**, 96245-40-8; (*Z*)-PhCH=CHD, 21370-59-2; PhC≡CD, 3240-11-7; DFA, 430-64-8; α-deuterio-β-phenylethenylboronic acid trimer, 96245-41-9; 2-((*Z*)-α-deuterio-β-phenyl)ethenyl-1,3,2-dioxaborolane, 96245-42-0; catecholborane, 274-07-7; ethylene glycol, 107-21-1; styrene, 100-42-5; *p*-vinylanisole, 637-69-4; *p*-nitrostyrene, 100-13-0.

Stereodynamics of Intramolecular Triplet Energy Transfer in Carotenoporphyrins

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Abstract: Carotenoporphyrins, consisting of carotenoid polyenes linked covalently to porphyrins, are known to mimic both the antenna function and the photoprotection from singlet oxygen damage provided by carotenoids in photosynthetic organisms. A series of carotenoporphyrins whose conformations, as determined from ^{1}H NMR studies, range from folded (with the carotenoid π-electron system stacked over that of the porphyrin) to extended (with the chromophores widely separated) has been prepared. Time-resolved spectroscopic studies have revealed intramolecular triplet energy transfer from porphyrin to carotenoid. Two distinct pathways for such transfer (presumably occurring via an electron-exchange mechanism) were observed: (a) static transfer which does not require significant intramolecular motions; (b) dynamic transfer mediated by intramolecular motions. The relative importance of these pathways is a function of molecular structure and dynamics. The results for this series of carotenoporphyrins help define the photochemical and photophysical requirements for protection from singlet oxygen damage both in photosynthetic organisms and in other biological systems.

Two of the important functions of carotenoid polyenes in photosynthetic organisms are protection from singlet oxygen damage and antenna function. Antenna function involves absorption of light by carotenoid polyenes and transfer of singlet excitation to chlorophyll where it can be used for photosynthetic work. Photoprotection, which is vital for the survival of the organism, involves limiting singlet oxygen damage by either quenching singlet oxygen or preventing its formation. Because singlet oxygen is produced by energy transfer from a chlorophyll triplet-state sensitizer, one of the most effective photoprotective mechanisms is the quenching of the chlorophyll triplet by carotenoids prior to any interaction with oxygen.

It has been well established that carotenoporphyrins, which consist of carotenoid polyenes covalently linked to porphyrins or chlorophyll derivatives, can mimic both the photoprotective and antenna functions of carotenoids.[1-5] Because photoprotection

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[∥] Paterson Laboratories.

(1) Dirks, G.; Moore, A. L.; Moore, T. A.; Gust, D. *Photochem. Photobiol.* **1980**, *32*, 277–280.
(2) Moore, A. L.; Dirks, G.; Gust, D.; Moore, T. A. *Photochem. Photobiol.* **1980**, *32*, 691–695.
(3) Bensasson, R. V.; Land, E. J.; Moore, A. L.; Crouch, R. L.; Dirks, G.; Moore, T. A.; Gust, D. *Nature (London)* **1981**, *290*, 329–332.
(4) Gust, D.; Moore, A. L.; Joy, A.; Tom, R.; Moore, T. A.; Bensasson, R. V.; Land, E. J. *Science (Washington, D.C.)* **1982**, *216*, 982–984.

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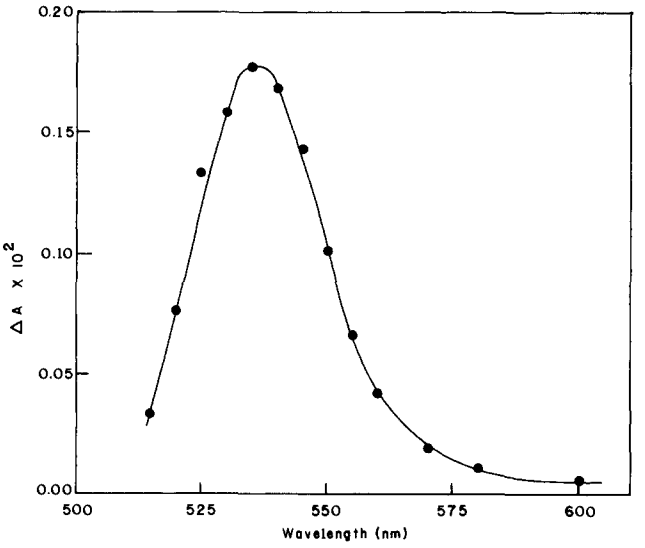


Figure 1. Change in absorption spectrum 6 μs after pulse radiolysis of 10^{-1} M biphenyl in the presence of 1.0×10^{-5} M **1** in benzene.

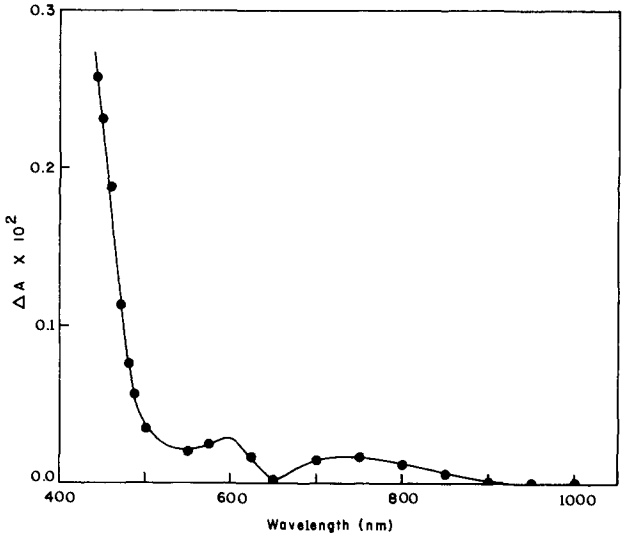


Figure 2. Change in absorption spectrum 6 μs after pulse radiolysis of 10^{-1} M biphenyl in the presence of 6.5×10^{-5} M **2** in benzene.

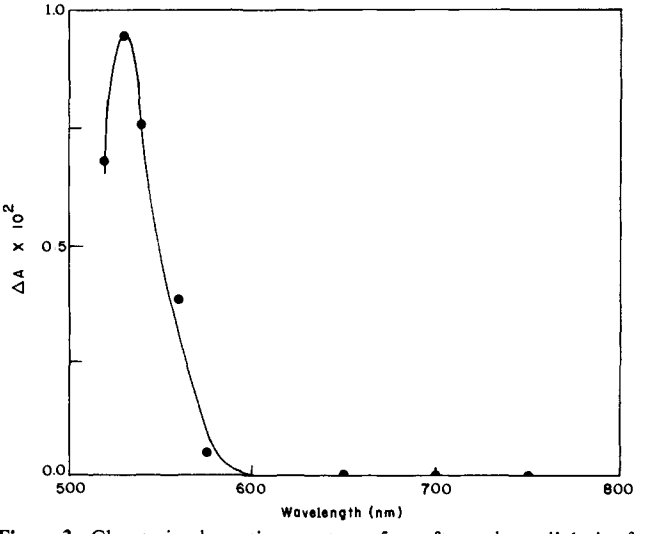


Figure 3. Change in absorption spectrum 5 μs after pulse radiolysis of 2.8×10^{-5} M **3** in benzene.

involves relatively long-lived triplet-state phenomena, it is amenable to study by time-resolved laser flash photolysis and pulse radiolysis

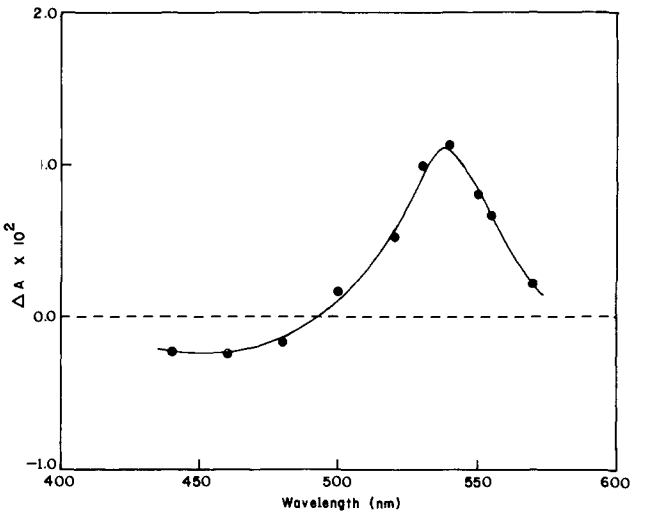


Figure 4. Change in absorption spectrum $\simeq$100 ns after nanosecond flash excitation (353 nm) of **4** in a deaerated polystyrene matrix.

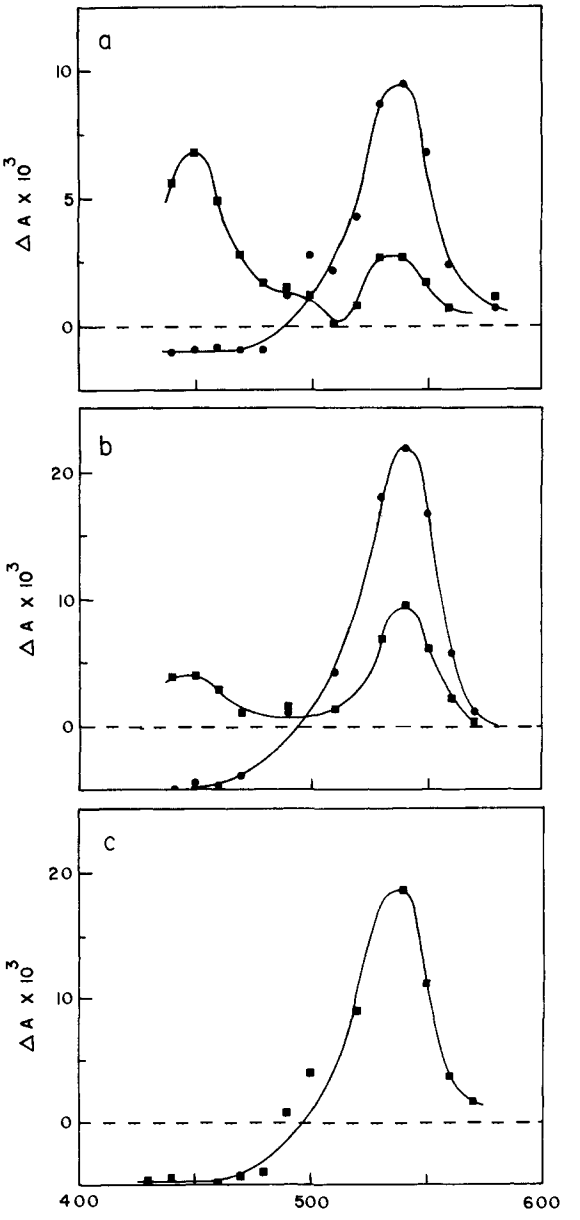
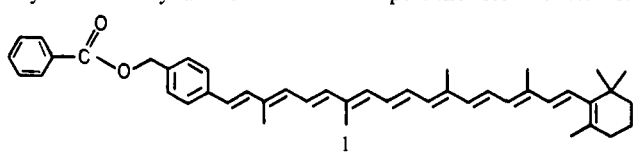


Figure 5. Changes in absorption spectrum in benzene (a) for 5.5×10^{-6} M **5**, (■), ~40 ns, (●), 800 ns; (b) for 5.1×10^{-6} M **6**, (■), ~40 ns, (●), 200 ns; and (c) 6.0×10^{-6} M **7**, (■), ~40 ns after nanosecond flash excitation (353 nm).

Chart I

techniques on the nanosecond time scale. Using these methods, we have previously found that triplet energy transfer and therefore photoprotection are sensitive functions of molecular stereochemistry and stereodynamics.[3,4] We now report the results of studies



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of a group of structurally related carotenoporphyrins and their precursors, **1–11**, which differ systematically in their structures, their static conformations, and their internal motions. These findings provide a more detailed understanding of the relationship of structure to triplet energy transfer and reveal that such transfer, which presumably occurs by an electron-exchange mechanism,[6] may be achieved by several distinct pathways.

Experimental Section

Synthesis of Carotenoporphyrins. The preparations of carotenoid **1**, porphyrin **2**, and carotenoporphyrin esters **3** and **4** have been previously described.[1,2,4,7] Unless otherwise specified, ^{1}H NMR spectra were obtained at 90 MHz with a Bruker WH-90 spectrometer and refer to ~1%

(5) Liddell, P. A.; Nemeth, G. A.; Lehman, W. R.; Joy, A. M.; Moore, A. L.; Bensasson, R. V.; Moore, T. A.; Gust, D. *Photochem. Photobiol.* **1982**, *36*, 641–645.

(6) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850.

(7) Dirks, G. W. Ph.D. Thesis, Arizona State University, Tempe, 1980.

solutions in chloroform-*d* with tetramethylsilane as an internal reference. The 500-MHz spectra were obtained with a Bruker WM-500 spectrometer. The standard carotenoid numbering system[8] is used to identify resonances. Mass spectra were obtained on a Varian MAT 311. Elemental analyses were performed by Galbraith Laboratories or MicAnal Laboratories.

Carotenoporphyrin 5. To a 50-mL round-bottomed flask equipped with a drying tube, magnetic stir bar, and argon inlet and containing 0.064 g (0.095 mmol) chlorin-free 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin[9] in 4.0 mL of dry dimethyl sulfoxide was added 1.0 mL of 0.095 M sodium methoxide in dimethyl sulfoxide. The reaction was stirred for 15 min at room temperature, after which 0.030 g (0.048 mmol) of 7′-apo-7′-(4-iodomethylphenyl)-β-carotene (prepared from the corresponding alcohol[1,2] with P_2I_4[10]) dissolved in 2.0 mL of toluene was added. After stirring for 30 min, the reaction was quenched by adding 30 mL of cold water. The aqueous suspension was extracted with ether (4 × 100 mL), and the combined extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was distilled under vacuum (room temperature) to yield a dark red crude product. Chromatography on silica gel (130 g) under anaerobic conditions with deaerated toluene gave 0.0527 g (93% yield) of the pure carotenoporphyrin. The ^{1}H NMR spectrum was consistent with the assigned structure with resonances at δ 1.04 (6 H, s, carotenoid 1-CH_3), 1.1–2.1 (6 H, m, carotenoid CH_2), 1.73 (3 H, s, carotenoid 5-CH_3), 1.99 (9 H, s, carotenoid, 9,13,13′-CH_3), 2.09 (3 H, s, carotenoid 9′-CH_3), 2.74 (9 H, s, tolyl CH_3), 5.33 (2 H, s, OCH_2), 6.1–7.0 (14 H, m, carotenoid vinylic H), 7.3–8.1 (20 H, m, ArH), and 8.86 (8 H, s, pyrrole H); mass spectrum (EI), *m/z* 1176 (M^+).

Carotenoporphyrin 6 was prepared as described for **5** by using 0.064 g 5-(3-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin[9] to yield 0.044 g (80%) of **6**. The ^{1}H NMR spectrum featured resonances at δ 1.05 (6 H, s, carotenoid 1-CH_3), 1.1–2.1 (6 H, m, carotenoid CH_2), 1.73 (3 H, s, carotenoid 5-CH_3), 1.99 (9 H, s, carotenoid 9,13,13′-CH_3), 2.06 (3 H, s, carotenoid 9′-CH_3), 2.71 (9 H, s, tolyl CH_3), 5.23 (2 H, s, OCH_2), 6.1–7.0 (14 H, m, carotenoid vinylic H), 7.4–8.1 (20 H, m, ArH), and 8.86 (8 H, m, pyrrole H); mass spectrum (EI), *m/z* 1176 (M^+).

Carotenoporphyrin 7 was prepared as described for **5** using 0.064 g 5-(2-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin[9] to yield 0.035 g of **7** (62%). The ^{1}H NMR spectrum was consistent with the assigned structure, with resonances at δ 1.03 (6 H, s, carotenoid 1-CH_3), 1.1–2.1 (6 H, m, carotenoid CH_2), 1.72 (3 H, s, carotenoid 5-CH_3), 1.88 (3 H, s, carotenoid 9′-CH_3), 1.94 (3 H, s, carotenoid 13′-CH_3), 1.98 (6 H, s, carotenoid 9,13-CH_3), 2.71 (9 H, s, tolyl CH_3), 4.92 (2 H, s, OCH_2), 6.1–6.6 (18 H, m, carotenoid vinylic and aromatic H), 7.0–8.1 (16 H, m, ArH), and 8.8–8.9 (8 H, m, pyrrole H); mass spectrum (EI), *m/z* 1176 (M^+).

5-(2,3-Dimethoxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (12). To a solution of 2,3-dimethoxybenzaldehyde (5.2 g, 0.032 mol) and *p*-tolualdehyde (11.5 g, 0.096 mol) in refluxing propionic acid (500 mL) was added 8.6 g (0.13 mol) of pyrrole. After refluxing for 30 min, the solution was allowed to cool, and the crystallized porphyrins were collected by filtration and washed with methanol. The desired product was separated from other porphyrins (mainly *meso*-tetra-*p*-tolylporphyrin) by chromatography on silica gel (chloroform), and the chlorin impurity was oxidized by refluxing for 30 min with an excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in chloroform.[11] The solution was cooled and chromatographed over a short alumina column (chloroform). Distillation of solvent from the porphyrin fractions under vacuum yielded 0.44 g (2%) chlorin-free **12**. Anal. Calcd for $C_{49}H_{40}N_4O_2$: C, 82.10; H, 5.62; N, 7.82. Found: C, 81.72; H, 5.81; N, 7.69. The ^{1}H NMR spectrum featured resonances at δ 2.67 (9 H, s, CH_3), 3.20 (3 H, s, OCH_3), 4.08 (3 H, s, OCH_3), 6.8–7.3 (15 H, m, ArH) and 8.92 (8 H, s pyrrole H). Porphyrin ether **12** (0.020 g, 0.028 mmol) was dissolved in 2.0 mL of acetic acid mixed with 2.0 mL of 48% hydrobromic acid and heated at reflux for 2 h. After cooling, the solution was neutralized with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over sodium sulfate, and the solvent was distilled under vacuum to yield **5-(2,3-dihydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (13)** quantitatively. The ^{1}H NMR spectrum featured resonances at δ 2.69 (9 H, s, CH_3), 7.0–8.1 (15 H, m, ArH), and 8.8–8.9 (8 H, m, pyrrole H).

5-(2,6-Dimethoxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (14) was prepared by the method described above for **13** by using 5.32 g (0.032 mol) of 2,6-dimethoxybenzaldehyde to yield 0.21 g (1% yield) of pure porphyrin. Anal. Calcd for $C_{49}H_{40}N_4O_2$: C, 82.10; H, 5.62; N, 7.82. Found: C, 82.16; H, 5.47; N, 7.77. The ^{1}H NMR spectrum was consistent with the expected structure, with resonances at δ 2.69 (9 H, s, CH_3), 3.51 (6 H, s, OCH_3), 7.01 (2 H, d, *J* = 8.2 Hz, 5-phenyl *m*-H), 7.73 (1 H, t, *J* = 8.2 Hz, 5-phenyl *p*-H), 7.65 and 8.21 (12 H, AB quartet, *J* = 7.9 Hz, *p*-tolyl H), 8.79 and 8.83 (4 H, AB quartet, *J* = 5.0 Hz, pyrrole H) and 8.81 (4 H, s, pyrrole H).

5-(2,6-Dihydroxyphenyl)-10,15-20-tris(4-methylphenyl)porphyrin (15) was prepared from **14** as described for **13** by using 0.10 g (0.14 mmol) of **14**, 10 mL of acetic acid, and 10 mL of 48% hydrobromic acid. The yield was quantitative. The ^{1}H NMR spectrum featured resonances at δ 2.63 (9 H, s, CH_3), 6.8–8.0 (15 H, m, ArH), and 8.82 (8 H, m, pyrrole H).

Carotenoporphyrin 8. To a stirred solution of **15** (0.030 g, 0.044 mmol) in 2.0 mL of dry dimethyl sulfoxide, under argon, was added 1.0 mL of a 0.087 M soltuion of sodium methoxide in dimethyl sulfoxide. After stirring this mixture for 10 min at room temperature, 2.0 mL of a toluene solution of 7′-apo-7′-(4-iodomethyl)phenyl)-β-carotene (0.060 g, 0.096 mmol) was added, and stirring was continued for 30 min. The reaction was quenched by the addition of 30 mL of cold water. The aqueous suspension was extracted with ether (4 × 100 mL), and the combined ether extracts were dried over magnesium sulfate. Filtration, followed by evaporation of the solvent under reduced pressure, yielded a dark red crude product. This material was purified by chromatography on silica gel (130 g) under anaerobic conditions with degassed toluene to give 0.029 g (39% yield) of pure dicarotenoporphyrin. The ^{1}H NMR spectrum featured resonances at δ 1.03 (12 H, s carotenoid 1-CH_3), 1.1–2.1 (12 H, m, carotenoid CH_2), 1.72 (6 H, s, carotenoid 5-CH_3), 1.87 (6 H, s, carotenoid, 9′-CH_3), 1.98 (18 H, s, carotenoid 9,13,13′-CH_3), 2.70 (9 H, s, tolyl CH_3), 4.87 (4 H, s, OCH_2), 6.0–6.9 (28 H, m, carotenoid vinylic H), 7.0–8.2 (23 H, m, ArH), and 8.84 (8 H, m, pyrrole H).

Carotenoporphyrin 9 was prepared as described for **8** by using 0.030 g of **13** to yield 0.044 g (60%) of pure carotenoporphyrin. The ^{1}H NMR spectrum was consistent with the structure with resonances at δ 1.03 (12 H, s, carotenoid 1-CH_3), 1.1–1.7 (12 H, m, carotenoid CH_2), 1.72 (6 H, s, 5-CH_3), 1.76 (3 H, s, ortho carotenoid 9′-CH_3), 1.97 (18 H, s, carotenoid 9,13,13′-CH_3), 2.05 (3 H, s, meta carotenoid 9′-CH_3), 2.70 (9 H, s, tolyl CH_3), 4.52 (2 H, s, *o*-OCH_2), 5.37 (2 H, s, m-OCH_2), 5.8–6.7 (28 H, m, carotenoid vinylic H) 7.6–8.2 (23 H, m, ArH), and 8.13 (8 H, m, pyrrole H).

Carotenoporphyrin 10. To a 50-mL round-bottom flask equipped with a condenser, magnetic stir bar, and a nitrogen inlet and containing 0.262 g (0.36 mmol) of 5-(4-(3-hydroxypropoxy)phenyl)-10,15,20-tris(4-methylphenyl)-porphyrin[4] in 25 mL of dry toluene was added 0.64 g (2.3 mmol) of α-bromo-*p*-toluoyl chloride in 10 mL of dry toluene. The reaction was stirred at reflux for 48 h and then quenched with 2 mL of water. The solvents were removed under vacuum, and the product was dissolved in diethyl ether and washed with aqueous sodium carbonate. The ether layer was dried over sodium sulfate and evaporated under vacuum to give the crude product. This material, without further purification, was dissolved in 25 mL of *p*-xylene. To this was added 0.30 g (1.15 mmol) of triphenylphosphine. Heating at reflux for 24 h produced the desired phosphonium salt which was isolated by chromotagraphy on silica gel. To a 50-mL round-bottom flask containing 0.20 g (0.17 mmol) of phosphonium salt and 0.50 g (9.3 mmol) of sodium methoxide in 50 mL of dry toluene was added 0.075 g (0.18 mmol) of β-apo-8′-carotenal. The reaction was stirred at reflux for 24 h. The solvent was removed under vacuum, and the product was isolated by chromatography on silica gel with methylene chloride in 20% overall yield: ^{1}H NMR (500 MHz) δ 1.03 (6 H, s, 1-CH_3), 1.48 (2 H, m, 2), 1.68 (2 H, m, 3), 1.72 (3 H, s, 5-CH_3), 1.99 (9 H, s, 9,13,13′-CH_3), 2.00 (2 H, m, 4), 2.03 (3 H, s, 9′-CH_3), 2.47 (2 H, m, trimethylene CH_2), 2.70 (9 H, s, Ar-CH_3), 4.44 (2 H, t, *J* = 5.8 Hz, trimethylene CH_2), 4.68 (2 H, t, *J* = 5.8 Hz, trimethylene CH_2), 6.0–6.2 (3 H, m, 7, 8, 10), 6.25 (1 H, d, *J* = 10.5 Hz, 14), 6.29 (1 H, d, *J* = 9.1 Hz, 14′), 6.35 (1 H, d, *J* = 14.4 Hz, 10′), 6.38 (1 H, d, *J* = 10.7 Hz, 12), 6.43 (1 H, d, *J* = 14.7 Hz, 12′), 6.59 (1 H, d, *J* = 16.0 Hz, 8′), 6.60–6.70 (4 H, m, 11, 11′, 15, 15′), 7.01 (1 H, d, *J* = 16.0 Hz, 7′), 7.2–8.2 (20 H, m, ArH), 8.85 (8 H, s, pyrrole H); mass spectrum (EI), *m/z* 1246 (M^+).

5-(4-(2-Hydroxyethoxy)phenyl)-10,15,20-tris(4-methylphenyl)-porphyrin (16). To 0.040 g (0.060 mmol) of 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin in 5 mL of a mixture of chloroform and methanol (1:1 v/v) was added 0.5 g of sodium bicarbonate. The mixture was kept well stirred while ethylene oxide was gently bubbled through it for a period of approximately 2 h. Then 0.10 g of potassium carbonate was added, and the bubbling of the ethylene oxide

(8) "Chemical Abstracts, Tenth Collective Index Guide"; Chemical Abstracts Service: Columbus, OH, 1982; Appendix IV.
(9) Anton, J. A.; Loach, P. A. *J. Heterocycl. Chem.* **1975**, *12*, 573–576.
(10) Lauwers, M.; Regnier, B.; Van Zenoo, M.; Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1979**, 1801–1804.
(11) Fuhrhop, J.-H.; Smith, K. M. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; p 770.

was resumed for another 2 h. The reaction mixture was allowed to stand for 24 h and worked up by extraction with 20 mL of chloroform after the addition of 20 mL of water. The chloroform solution was dried with sodium sulfate and the solvent distilled under vacuum to yield quantitatively the desired porphyrin. The ^{1}H NMR spectrum (500 MHz in $CDCl_3$) was consistent with the expected structure, with resonances at δ 2.69 (9 H, s, $ArCH_3$), 4.13 (2 H, m, CH_2OH), 4.35 (2 H, t, J = 4.4 Hz, OCH_2), 7.27 (2 H, d, J = 8.5 Hz, 5′meta), 7.53 (6 H, d, J = 7.8 Hz, 10, 15, 20 meta), 8.08 (6 H, d, J = 7.8 Hz, 10, 15, 20 ortho), 8.10 (2 H, d, J = 8.5 Hz, 5 ortho), 8.89 (8 H, s, pyrrole H); mass spectrum (EI), m/z 716 (M^+).

4-Carbomethoxybenzyltriphenylphosphonium bromide (17). To a 150-mL flask equipped with a condenser, magnetic stir bar, and nitrogen inlet was added 1.5 g (6.55 mmol) of methyl α-bromo-p-toluate, 1.72 g (6.55 mmol) of triphenylphosphine, and 50 mL of toluene. The solution was refluxed for 2 h, after which the reaction mixture was filtered and the residue washed with dry toluene. The resulting white solid was dried under vacuum to give 3.0 g (93%) of the required phosphonium salt. Anal. Calcd for $C_{27}H_{24}O_2BrP$: C, 66.00; H, 4.92; Br, 16.26. Found: C, 65.78; H, 5.02; Br, 16.00. ^{1}H NMR; δ 3.90 (3 H, s, CH_3), 5.71 (2 H, d, J = 16 Hz, CH_2), 7.2–8.0 (4 H, m, ArH); mass spectrum (FAB), m/z 411 (M^+ − Br).

7′-Apo-7′-(4-carbomethoxyphenyl)-β-Carotene (18). To a 50-mL flask equipped with a condenser, magnetic stir bar, and gas inlet tube was added 0.86 g (1.81 mmol) of **17**, 20 mL of toluene, 0.173 g (3.2 mmol) of sodium methoxide, and 0.5 g (1.2 mmol) of β-apo-8′-carotenal. The dark-colored solution was refluxed under an argon atmosphere for 3 h. TLC of the reaction mixture indicated that less than half of the carotenal had been consumed. An additional 0.5 g (1.05 mmol) of phosphonium salt and 0.1 g (1.85 mmol) of sodium methoxide was added, and refluxing was continued until all the carotenal had been consumed. After 4 h the reaction mixture was diluted with 100 mL of $CHCl_3$, washed several times with water, dried over $MgSO_4$, and filtered. The solvent was evaporated under vacuum, and the residue was chromatographed on silica gel (toluene) to give 410 mg (62%) of the methyl ester **18** (mp 168–170°): ^{1}H NMR; δ 1.03 (6 H, s, 1-CH_3), 1.1–1.8 (6 H, m, CH_2), 1.72 (3 H, s, 5-CH_3), 1.98 (9 H, s, 9,13,13′-CH_3), 2.06 (3 H, s, 9′, CH_3), 6.1–7.0 (14 H, m, vinyl H), 7.50 and 8.05 (4 H, AB quartet, J = 8.3 Hz, ArH); mass spectrum (EI), m/z 548 (M^+).

7′-Apo-7′-(4-carboxyphenyl)-β-carotene (19). Ester **18** (110 mg, 0.2 mmol) was dissolved in 16 mL of THF/CH_3OH (3:1). To this solution was added 2 mL of aqueous 10% KOH, and the solution was stirred under an argon atmosphere for 18 h. The solution was then partitioned between $CHCl_3$ and water (pH 1–2), and the aqueous layer was washed with $CHCl_3$ until all the carotene had been extracted. The combined $CHCl_3$ extracts were dried over Na_2SO_4 and filtered, and the solvent was evaporated to yield 98 mg (91%) of the pure carotene acid (**19**): ^{1}H NMR; δ 1.03 (6 H, s, 1-CH_3), 1.4–2.1 (6 H, m, 2, 3, 4), 1.72 (3 H, s, 5-CH_3), 1.99 (9 H, s, 9,13,13′-CH_3), 2.06 (3 H, s, 9′-CH_3), 6.0–7.0 (14 H, m, vinyl H), 7.4–8.1 (4 H, AB, ArH); mass spectrum (EI), m/z 534 (M^+).

Carotenoporphyrin 11. Porphyrin **16** (0.012 g, 0.017 mmol) was dissolved in 10 mL of dry dichloromethane and *N,N′*-dicyclohexylcarbodiimide (0.006 g, 0.029 mmol), carotenoid acid **19** (0.015 g, 0.028 mmol), and a trace amount of 4-(dimethylamino)pyridine were added. The reaction mixture was stirred under argon and kept at reflux temperature with an oil bath at 50 °C. After 3 h the solvent was evaporated and the crude product was redissolved in toluene and purified by column chromatography on silica gel with toluene to give 0.003 g (14%) of the pure carotenoporphyrin **11**. The ^{1}H NMR spectrum (500 MHz) was consistent with the assigned structure with resonances of δ 1.03 (6 H, s, 1-CH_3), 1.48 (2 H, m, 2), 1.68 (2 H, m, 3), 1.72 (3 H, s, 5-CH_3), 1.99 (9 H, s, 9,13,13′-CH_3), 2.00 (2 H, m, 4), 2.03 (3 H, s, 9′-CH_3), 2.69 (9 H, s, $ArCH_3$), 4.60 (2 H, m, CH_2), 4.85 (2 H, m, CH_2), 6.0–6.2 (3 H, m, 7, 8, 10), 6.25 (1 H, d, J = 10.5 Hz, 14), 6.29 (1 H, d, J = 9.1 Hz, 14′), 6.35 (1 H, d, J = 14.4 Hz, 10′), 6.38 (1 H, d, J = 10.7 Hz, 12), 6.43 (1 H, d, J = 14.7 Hz, 12′), 6.59 (1 H, d, J = 16.3 Hz, 8′), 6.60–6.70 (4 H, m, 11, 11′, 15, 15′), 6.98 (1 H, d, J = 16.3 Hz, 7′), 7.2–8.2 (20 H, m, ArH), 8.83 (8 H, s, pyrrole H); mass spectrum (EI), m/z 1232 (M^+).

Pulse Radiolysis and Laser Flash Photolysis. The pulse radiolysis equipment has been described by Keene.[12] Benzene solutions were argon flushed and irradiated in 1-cm quartz cells with 20-ns, ≃ 10-G pulses of 9–12-MeV electrons from a Vickers electron linear accelerator. Three different laser flash photolysis spectrometers were used. A time resolution of 2 ns was obtained with a Quantel frequency-doubled YAG laser providing 30-ps pulses of 533-nm light. The measuring light was provided by a 20-μs xenon flash. The signal was detected by an XP1141 photomultiplier[13] and digitized with a Tektronix R-7912 transient digitizer. Slower kinetics (100 ns–1 ms) were measured by using a Quantel YAG-pumped dye laser providing 10-ns pulses of ~ 600-nm broad-band light[14] or a CILAS neodymium-doped glass laser providing 30-ns pulses of 353-nm light.[15] All experiments in fluid solution were carried out with a 1-cm optical path length cell for the analyzing light. In all cases, the laser pulse was attenuated so that the change in absorbance was linear vs. laser pulse energy.

Results

Photophysical Properties of Nonlinked Precursors. The triplet–triplet absorption spectrum ($T_1 \rightarrow T_n$) of polyene **1** was determined by pulse radiolysis by using energy transfer from a biphenyl triplet donor. Pulse radiolysis of a 0.1 M solution of biphenyl in the presence of $\simeq 1 \times 10^{-5}$ M **1** yielded the triplet absorption spectrum shown in Figure 1. The polyene triplet has a maximum at 535 nm, where $\epsilon_T - \epsilon_G \simeq 1.4 \times 10^5$ M^{-1} cm^{-1}, measured against the biphenyl triplet as a standard[16] (ϵ_T and ϵ_G are the extinction coefficients of the triplet and ground states, respectively). The spectrum of the triplet state of porphyrin **2** (Figure 2), obtained in the same way, had a maximum at 440 nm, with $\epsilon_T - \epsilon_G \simeq 6.8 \times 10^4$ M^{-1} cm^{-1}.

Photophysical Properties of Carotenoporphyrin Esters 3 and 4. Pulse radiolysis of **3** in benzene solution yielded the transient spectrum shown in Figure 3. The transient absorption with a maximum at 535 nm (shown here 5 μs after the pulse) is due to the carotenoid triplet. This peak grew in after the pulse, reached a maximum at ≃ 5 μs, and decayed with $\tau \simeq 10$ μs. Laser flash photolysis studies of **3** in benzene solution have previously shown[3] that triplet–triplet energy transfer from the porphyrin moiety to the carotenoid occurs with a transfer rate constant $k \sim 5 \times 10^5$ s^{-1}. The growth of the carotenoid peak observed by pulse radiolysis occurs at the same rate and may be ascribed to the same process.

Isomeric ester **4**, in which the carotenoid is linked to the ortho position of a meso aromatic ring, shows a carotenoid $T_1 \rightarrow T_n$ absorption in the visible region immediately (100 ns) after a radiolysis pulse in benzene solution. The triplet–triplet energy transfer rate constants derived from laser flash photolysis experiments for **4** and the other carotenoporphyrins are summarized in Table I. Such experiments with **4** in benzene solution revealed the appearance of the carotenoid triplet spectrum with approximately the response time of the instrument ($k \geq 200 \times 10^6$ s^{-1}). No porphyrin triplet spectrum was observed. Thus, quenching of the porphyrin triplet in **4** by the attached carotenoid is much faster than in **3**. Flash photolysis (2-ns resoltuion) of **4** in a deoxygenated polystyrene film also shows immediate ($k \geq 130 \times 10^6$ s^{-1}) formation of the carotenoid triplet. A spectrum taken 100 ns after the laser flash reveals only the carotenoid triplet state (Figure 4). The decay of this triplet ($k \sim 1 \times 10^5$ s^{-1}) is similar to that observed in fluid benzene.[3]

Carotenoporphyrin Ethers. Ethers **5**, **6**, and **7** are isomeric structures which differ only in the position of attachment of the carotenoid moiety (para, meta, or ortho) to the porphyrin aryl ring. Benzene solutions of these molecules were studied by 353- and 600-nm laser flash photolysis as described above. The measured lifetimes (Table I) were independent of excitation wavelength. The spectral features observed (Figure 5) were similar for all of these compounds and were essentially the same as those for **3** and **4**. However, the rates of triplet energy transfer varied greatly. The spectrum of **5** (Figure 5a) features a typical porphyrin triplet absorbance immediately (~40 ns) after flash photolysis with a relatively small contribution from the carotenoid triplet at ~535 nm. After 800 ns, this porphyrin spectrum has disappeared, and only the carotenoid triplet spectrum remains. This time dependence ($k = 3.6 \times 10^6$ s^{-1}, Figure 6), coupled with the well-known extremely low intersystem crossing efficiencies of carotenoid polyenes, indicates that triplet energy transfer from

(12) Keene, J. P. *J. Sci. Instrum.* **1964**, *41*, 493–496.

(13) Mathis, P. In "Primary Processes of Photosynthesis"; Barber, J., Ed.; Elsevier: New York, 1977; pp 269–302.

(14) Kramer, H.; Mathis, P. *Biochim. Biophys. Acta*, **1980**, *593*, 319–329.

(15) Bensasson, R. V.; Chachaty, C.; Land, E. J.; Salet, C. *Photochem. Photobiol.* **1972**, *16*, 27–37.

(16) Bensasson, R. V.; Dawe, E. A.; Long, D. A.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1319–1325.

Table I. Rate Constants and Distances for Intramolecular Triplet Energy Transfer from Porphyrin to Carotenoid

	carotenoporphyrin								
	3 (para ester)	**4** (ortho ester)	**5** (para ether)	**6** (meta ether)	**7** (ortho ether)	**8** (ortho,ortho ether)	**9** (ortho,meta ether)	**10** (-(C-$H_2)_3$-)	**11** (-(C-$H_2)_2$-)
				Rate Constant k, s^{-1}					
benzene	0.5×10^6	$\geq 200 \times 10^6$ [b]	3.6×10^6	22×10^6	100×10^6	$>30 \times 10^6$ [b]	$>30 \times 10^6$ [b]	9.7×10^6	15×10^6 [a]
polystyrene	$\sim 0.7 \times 10^6$	$\geq 130 \times 10^6$ [b]	2.2×10^6	3.1×10^6	4.4×10^6			≤ 800	≤ 800
				Chromophore Separation, Å					
center-to-center[c]	23	13	~ 23	~ 22	16				
edge-to-edge[d]	5	5	4	4	4				
stacked		4							

[a] This measurement was made in toluene. [b] These numbers are lower limits because triplet transfer was as fast or faster than the response time of the particular spectrometer involved. In the case of **8** and **9**, transfer rates may in fact be comparable to those measured for **7** by using a spectrometer with ~2-ns time resolution. [c] This is the approximate distance from the center of the carotenoid (C-15′) to the center of the porphyrin ring, based on the solution time average conformation derived from ^{1}H NMR studies.[20] [d] This is the approximate distance between the carotenoid aryl carbon atom bearing the methylene group and the porphyrin aryl carbon bearing the linkage oxygen or carboxyl carbon, based upon the ^{1}H NMR derived time average conformation.[20]

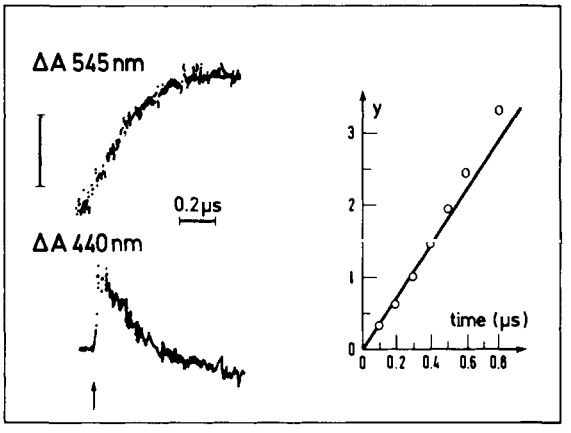

Figure 6. Change in absorption with time following picosecond flash excitation (530 nm) of a ca. 5×10^{-6} M solution of **5** in benzene. The oscilloscope trace at 545 nm (vertical bar = 2.5×10^{-2} absorbance units) shows the growth of the carotenoid triplet, whereas the trace at 440 nm (vertical bar = 1.25×10^{-2} absorbance units) shows the decay of the porphyrin triplet and the appearance of carotenoid ground-state bleaching. Each trace is an average of eight flashes. The kinetic plot used to derive the rate constant in Table I from the 545-nm trace is also shown; $y = \ln (A_f/A_f - A)$ where A_f is the maximum absorbance increase.

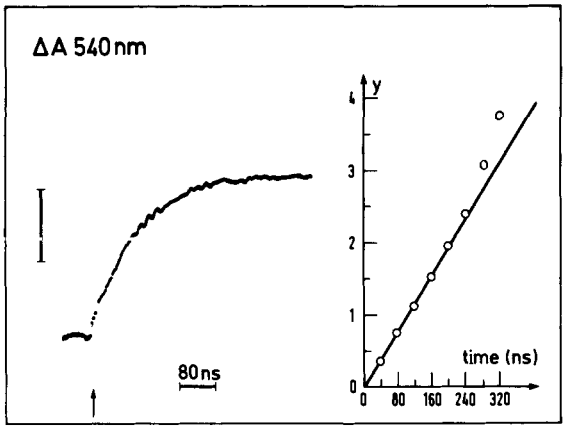

Figure 7. Change in absorption of a ca. 5×10^{-6} M solution of **10** in benzene following nanosecond flash excitation (600 nm). The trace is the average of four flashes, and the vertical bar indicates 2.9×10^{-2} absorbance units. The rate constant for the formation of the carotenoid triplet by energy transfer from the porphyrin triplet (Table I) was calculated from the plot shown (y as in Figure 6).

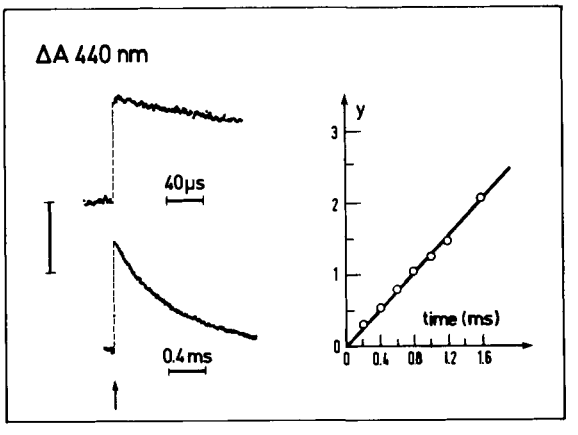

Figure 8. Decay of the porphyrin triplet absorption following nanosecond flash excitation (600 nm) of **10** in polystyrene plastic. The trace is the average of four flashes, and the vertical bar represents 2.0×10^{-2} absorbance units. No carotenoid triplet was observed. The rate constant for triplet decay (Table I) was calculated by using the plot shown; $y = \ln (A_0/A)$ where A_0 is the absorbance immediately after the flash.

porphyrin to polyene is occurring. Similarly (Figure 5b), triplet transfer in **6** takes place with $k = 22 \times 10^6$ s^{-1}. In the case of **7**, the carotenoid triplet is formed still more rapidly ($k = 100 \times 10^6$ s^{-1}), and no porphyrin triplet spectrum remains at 40 ns. Pulse radiolysis of **5** and **7** in benzene in the presence of 1×10^{-1} M biphenyl resulted in the observation of transient spectra whose wavelength maxima (535 nm), extinction coefficients ($\simeq 1.4 \times 10^5$ M^{-1} cm^{-1}), and decay rates confirmed that the triplet excitation was ultimately localized on the carotenoid moiety.

In a polystyrene matrix, the large differences in triplet-transfer rates among the ethers **5**, **6**, and **7** disappear, and transfer rate constants $k = 2.2 \times 10^6$, 3.1×10^6, and 4.4×10^6 s^{-1}, respectively, were found for these compounds.

The effects of linking multiple carotenoids to the same porphyrin moiety were evaluated by using **8** and **9**. With excitation at 353 nm and a flash duration of ~30 ns, only carotenoid triplet spectra were detected after excitation (λ_{max} = 535 nm, with concomitant carotenoid ground-state bleaching). Thus, quenching of the porphyrin triplet state by carotenoid must occur within 30 ns of excitation ($k > 3 \times 10^7$ s^{-1}).

Carotenoporphyrins 10 and 11. Carotenoporphyrin **10** also demonstrates triplet transfer in benzene solution. A porphyrin $T_1 \rightarrow T_n$ absorption spectrum is observed immediately after a 600-nm laser flash. This absorption disappears with time, and a carotenoid triplet spectrum appears. The rate of triplet transfer was determined by following the rise of the carotenoid triplet and was found to be 9.7×10^6 s^{-1} (Figure 7). This is comparable to transfer rates observed previously for a related molecule.[4] In polystyrene plastic, however, only the porphyrin triplet spectrum was observed, and this absorption decayed very slowly ($\tau \sim 1.3$ ms, Figure 8). This decay rate is close to that observed for porphyrins alone in this plastic. Thus, triplet transfer under these conditions must have $k \leq 800$ s^{-1}.

Similarly, the rate constant for triplet transfer for **11** in toluene solution was $k = 1.5 \times 10^7$ s^{-1}, but in polystyrene this rate slowed to $k \leq 800$ s^{-1}.

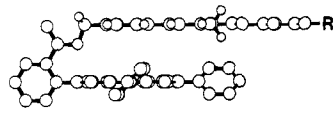

Figure 9. Time-average solution conformation of **4** as determined from ^{1}H NMR studies.[20] For clarity, part of the carotenoid chain and most of the hydrogen atoms have been omitted. Note that the carotenoid is folded over the porphyrin π system, with a separation of ~4 Å between the center of the porphyrin macrocycle and the center of the carotenoid aryl ring.

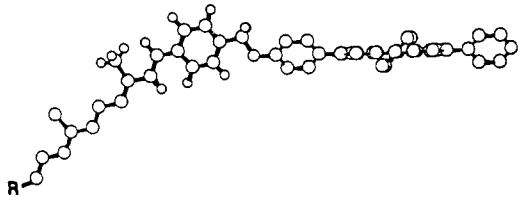

Figure 10. Time-average solution conformation of **5** as determined from ^{1}H NMR studies.[20] Part of the carotenoid chain and most of the hydrogen atoms have been omitted for clarity. The carotenoid chain is extended away from the porphyrin with a distance of ~13 Å between the center of the porphyrin π system and the center of the carotenoid aryl ring.

Molecular Conformations. The spectroscopic studies described above have shown that in benzene solution, all these carotenoporphyrins (**3–11**) demonstrate porphyrin to carotenoid triplet energy transfer. In all cases, the carotenoid triplet states, once formed, decay at roughly the same rate ($\tau \simeq 6$–10 μs). However, the rates of intramolecular triplet energy transfer span several orders of magnitude. The reason for the divergent behavior of these closely related molecules may be understood only after we have some knowledge of their solution conformations. Such knowledge may be obtained from their ^{1}H NMR spectra. The aromatic porphyrin moieties of carotenoporphyrins give rise to large diamagnetic "ring currents". These effects, in turn, cause substantial perturbations of the chemical shifts of protons in the immediate vicinity of the porphyrin ring.[17-19] Quantitative calculations of molecular conformation based on these ring current shifts have been reported for carotenoporphyrins **4–7**.[20] Relevant interchromophore distances are reported in Table I. Ortho ester **4** is found to exist in a tightly folded conformation with the carotenoid π-electron system stacked about 4 Å above the porphyrin plane (Figure 9). In the case of para ether **5**, the carotenoid moiety lies roughly in the plane of the porphyrin and is extended away from the porphyrin, rather than folded over it (Figure 10). Thus, the two π-electron systems are widely separated, with a distance of ~13 Å between the center of the porphyrin ring and the center of the carotenoid aryl ring. Calculations for para ester **3** show that it assumes a similar conformation. Satisfactory fits to the experimentally observed chemical shift changes for **6** and **7** required significant populations of two conformers (Figure 11 and 12), and the resulting detailed structures are probably not as reliable as those found for **4** and **5**.[20] However, it can be stated with confidence that ortho ether **7** adopts partially folded conformations with an interchromophore distance (as defined for **5**) of ~6–7 Å, whereas meta ether **6** is more extended, with a separation of ~11 Å between the chromophores. Thus, molecules **3–7** form a series with a range of conformations from tightly folded (**4**) through partly folded (**7**) and partly extended (**6**) to fully extended (**3**, **5**).

High-resolution ^{1}H NMR spectra have also been obtained for **10** and **11**. Although detailed analyses of these spectra in terms of ring current effects have not been carried out, the chemical shift changes observed for these molecules are all small and downfield. Based upon the known distance and angle dependence of the ring current field,[17-20] it can be stated that these molecules exist in time-average solution conformations which are extended as in **3** and **5**, rather than folded as in **4**, and, to some extent, **7**.

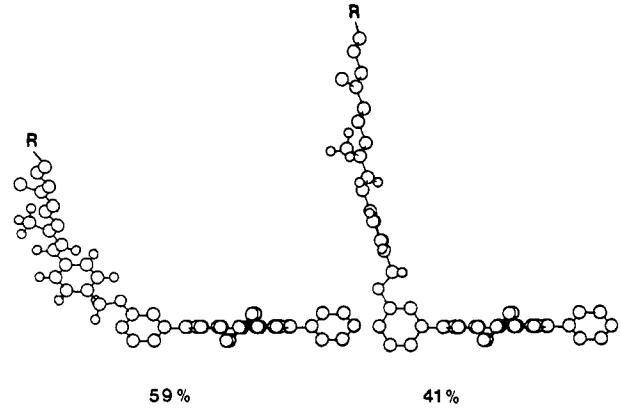

Figure 11. Solution conformations of meta ether **6** as determined from ^{1}H NMR studies.[20] The two conformers are calculated to be present in the ratio indicated. For clarity, part of the carotenoid chain and most of the hydrogen atoms have been omitted.

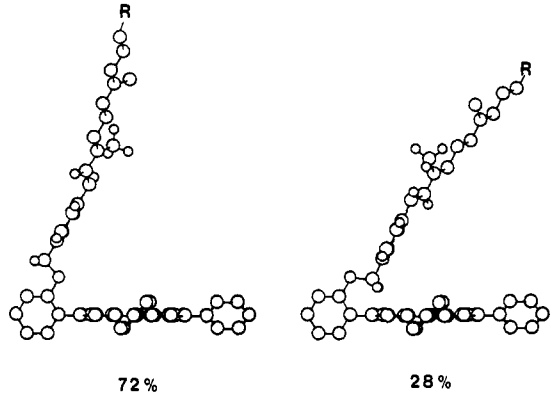

Figure 12. Solution conformations of ortho ether **7** as determined from ^{1}H NMR studies.[20] The two conformers are calculated to be present in the indicated ratio. For clarity, parts of the carotenoid chain and most of the hydrogen atoms have been omitted.

Discussion

No clear general picture has been drawn[21-24] from the numerous observations of intramolecular triplet energy transfer between nonconjugated donor and acceptor chromophores.[25-37] For instance, no rule analogous to Hirayama's $n = 3$ rule[38] has been

(17) Shulman, R. G.; Wüthrich, K.; Yamane, T.; Patel, D. J.; Blumberg, W. E. *J. Mol. Biol.* **1970**, *53*, 143–157.
(18) Abraham, R. J.; Fell, S. C. M.; Smith, K. M. *Org. Magn. Reson.* **1977**, *9*, 367–373.
(19) Abraham, R. J.; Bedford, G. R.; McNeillie, D.; Wright, B. *Org. Magn. Reson.* **1980**, *14*, 418–425.
(20) Chachaty, C.; Gust, D.; Moore, T. A.; Nemeth, G. A.; Liddell, P. A.; Moore, A. L. *Org. Magn. Reson.* **1984**, *22*, 39–46.
(21) Wagner, P. G.; Hammond, G. S. *Adv. Photochem.* **1968**, *5*, 21–156.
(22) De Schryver, F.; Boens, N. *Adv. Photochem.* **1977**, *10*, 359–465.
(23) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: New York, 1978; pp 338–375.
(24) Lamola, A. A. In "Technique of Organic Chemistry"; Leermakers, P. A., Weissberger, A., Ed.; Wiley-Interscience: New York, 1969; Vol. XIV, pp 17–132.
(25) Lamola, A. A.; Leermakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322–2332.
(26) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777.
(27) Filipescu, N.; DeMember, J. R.; Minn, F. L. *J. Am. Chem. Soc.* **1969**, *91*, 4169–4173.
(28) Breen, D. E.; Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1935–1940.
(29) Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1940–1944.
(30) Keller, R. A.; Dolby, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 1293–1299.
(31) Bunting, J. R.; Filipescu, N. *J. Chem. Soc. B* **1970**, 1750–1755.
(32) Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153–1162.
(33) Schäfer, F. P.; Zhang, F. G.; Jethwa, J. *Appl. Phys.* **1982**, *B28*, 37–41.
(34) Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1975**, *58*, 397–415.
(35) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1060–1062.
(36) Zimmerman, H. E.; Golman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951.
(37) Kilp, T.; Gillet, J. E. *Macromolecules* **1981**, *14*, 1680–1688.
(38) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.

Discussion

No clear general picture has been drawn[21-24] from the numerous observations of intramolecular triplet energy transfer between nonconjugated donor and acceptor chromophores.[25-37] For instance, no rule analogous to Hirayama's $n = 3$ rule[38] has been

found. This rule is valid for intramolecular singlet excimers and exciplexes and is based on the fact that an optimum sandwich configuration between the chromophores can be reached via a trimethylene chain taking a gauche–gauche conformation.[22,38] In the case of benzophenone and naphthalene chromophores separated by a polymethylene chain $-(CH_2)_n-$ with n = 1, 2, and 3, the rate of energy transfer from the benzophenone triplet to the naphthalene is higher than 10^{10} s^{-1} and is not measurably dependent on n.[25] However, in other cases such as acetophenone linked to a *trans*-β-methylstyryl group (n = 2, 3, and 4)[32] or bifluorophoric laser dyes with methylene linkages (n = 1, 2, and 3),[33] the triplet energy transfer rate decreased regularly with increasing length of the link.

The carotenoporphyrins studied here are good candidates for the investigation of intramolecular triplet energy transfer because the porphyrin triplet donor has a high quantum yield of intersystem crossing[39] while the vanishingly small intersystem crossing yield of the carotenoid precludes any triplet formation which does not occur via energy transfer from the porphyrin moiety.[40] Moreover, reverse energy transfer is not significant in these carotenoporphyrins. The triplet energy level of the acceptor (<1 eV)[41-43] is lower than that of the donor[39] by at least 0.5 eV.[44] This means that even in the case where $k_{^3PC \rightarrow ^3C} \sim 10^8$ s^{-1}, $k_{^3CP \rightarrow ^3C}$ must be less than or equal to ~ 0.4 s^{-1}. Because $k_{^3CP \rightarrow CP}$ is $\sim 1 \times 10^5$ s^{-1}, $k_{^3CP \rightarrow ^3C}/k_{^3CP \rightarrow CP}$ must be $\sim 4 \times 10^{-6}$.

The triplet transfer rates measured for **3–11** (Table I) are higher than the intermolecular energy transfer rate calculated by using the maximum expected diffusion-controlled rate constant and micromolar concentrations. Thus, the measured rate constants represent intramolecular processes. They may be related to molecular structure in general and to conformation in particular if one knows the mechanism of transfer. Triplet–triplet energy transfer may in theory occur by either an electrostatic or an electron-exchange mechanism.[6,21-24,45] Due to vanishingly small dipole–dipole and higher multipole terms, the exchange mechanism is usually assumed. However, recent reports have shown that under some circumstances, dipole–dipole coupling does mediate triplet–triplet energy transfer at relatively large distances.[45] Therefore, efforts were made to fit the observed rate constants for the series **5**, **6**, and **7** in polystyrene (Table I) to the expected[23,24,25] R^{-6} distance dependence, using the "center-to-center" distances in the table. Energy transfer in **7** is found to be about 10 times slower than predicted by the R^{-6} dependence, based on rates for **5** and **6**. Since the orientation factor (κ) changes markedly from **5** to **7**, the observed rate constants could be fit to a $\kappa^2 R^{-6}$ function. However, two factors mitigate strongly against the dipole–dipole mechanism. Firstly, in these and analogous carotenoids, the $S_0 \rightarrow T_1$ transition has not been reported, and the transition moment is expected to be extremely small due to the absence of heteroatoms. Secondly, the phosphorescence yield of the free-base porphyrin is also extremely low, probably less than 10^{-4}.[39] Thus, the dipole–dipole mechanism is not likely to make an important contribution, and it appears reasonable to assume that triplet transfer in these systems occurs via an electron-exchange mechanism.

Perusal of the data in Table I reveals that in the carotenoporphyrins, two distinct classes of triplet energy transfer phenomena are represented: (a) static energy transfer which does not require significant intramolecular motion (Electronically, this involves significant exchange coupling between the π systems of the carotenoid and porphyrin in the highly populated conformer(s). In some cases, especially if the geometry of the σ systems is correct, the σ-bond framework linking the chromophores could be involved in this exchange interaction,[34-36] although we have no evidence regarding this point.) and (b) dynamic energy transfer mediated by intramolecular motion (This mechanism requires large scale intramolecular motion to bring the two chromophores into momentary contact. This case is analogous to conventional collisional transfer of triplet excitation.[6,21-24]).

Energy transfer in ortho ester **4** is extremely rapid both in solution and in a plastic matrix. A motional component to the transfer (case b) is ruled out by the rapid transfer in viscous media. Thus, the observed triplet transfer must be a static process (case a) in both media. For para ester **3**, the observed transfer rate in benzene solution ($k = 4.5 \times 10^5$ s^{-1}), although much slower than that for **4**, is also essentially unchanged in polystyrene where large-scale intramolecular motions must be slow. Thus, triplet transfer in **3** can also be assigned to case a in both benzene and polystyrene. Similarly, triplet transfer rate constants for ethers **5–7** in polystyrene (Table I) are all roughly comparable and can also be assigned to static transfer in this viscous solvent.

In solution, ethers **6** and **7** show a dramatic increase in triplet transfer rate compared to the results in polystyrene ($k = 22 \times 10^6$ and 100×10^6 s^{-1}, for **6** and **7**, respectively). This increase may be ascribed to dynamic triplet transfer (case b) mediated by motions which bring the carotenoid π system into momentary contact with the porphyrin π-electron system. Although the degrees of freedom around the linkage bonds would, of course, be similar for the three ethers, it is reasonable to conclude that as one goes from **5** to **6** to **7**, an increasingly larger fraction of the intramolecular excursions are effective in achieving the requisite conformation for energy transfer, because of the change in distance and angle parameters. Ethers **8** and **9**, which feature two carotenoid chromophores linked to the same porphyrin, both have rapid solution energy transfer rates, as was the case for **7** (Table I). This is not surprising, because all three molecules feature an ortho ether linkage.

Carotenoporphyrin **10** undergoes triplet transfer very slowly or not at all in a polystyrene matrix. Similar behavior has been observed for related molecules in frozen glasses or plastics.[4] The extended conformation and relatively long saturated trimethylene linkage evidently preclude the orbital overlap of the π-electron systems necessary for static transfer (case a), and the high viscosity of the medium prevents the rapid, large-scale intramolecular motions necessary for dynamic transfer (case b). In benzene solution, on the other hand, dynamic transfer is fast ($k = 9.7 \times 10^6$ s^{-1}), because rapid intramolecular folding motions momentarily produce conformations suitable for triplet transfer (case b).[4] Similarly, in **11**, dynamic transfer in toluene is rapid ($k = 1.5 \times 10^7$ s^{-1}), but in polystyrene, transfer is not significant. Thus, the dimethylene linkage is also an efficient insulator between the π-electron systems.

Conclusions

Static Triplet Energy Transfer. Two main conclusions can be drawn from the correlation of the NMR results with the triplet energy transfer rates in the carotenoporphyrins. First, we will consider the results in polystyrene plastic where large-scale intramolecular motions are very slow. According to the theory of Dexter,[6] triplet energy transfer by an electron-exchange mechanism should obey the relationship

$$k = Y \exp(-2R/L) \quad (1)$$

where k is the triplet energy transfer rate constant, R is the interchromophore separation, Y represents a variety of factors including orientation effects, and L is typically ~ 1 Å.[46] Using the various NMR-derived distances (Table I), one may attempt to fit the carotenoporphyrin data to the above relationship.

Because the dimensions of the π-electron systems are large compared to interchromophore separations, the choice of distance parameters is not straightforward. The most reasonable set of

(39) Moore, T. A.; Benin, D.; Tom, R. *J. Am. Chem. Soc.* **1982**, *104*, 7356–7357.
(40) Dallinger, R. F.; Woodruff, W. H.; Rodgers, M. A. J. *Photochem. Photobiol.* **1981**, *33*, 275–277.
(41) Mathis, P. Thèse de Doctorat es-Sciences Physiques, Orsay, France, 1970.
(42) Mathis, P.; Kleo, J. *Photochem. Photobiol.* **1973**, *18*, 343–346.
(43) Bensasson, R.; Land, E. J.; Maudinas, B. *Photochem. Photobiol.* **1976**, *23*, 189–193.
(44) Sandros, K. *Acta Chem. Scand.* **1974**, *18*, 2355–2374.
(45) Morgan, J. R., El Sayed, M. A. *J. Phys. Chem.* **1983**, *87*, 2178–2185.
(46) Wagner, P. J.; McGrath, J. M.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6883–6886.

distances would appear to be the distances of closest approach of the π-electron systems of the carotenoid and the porphyrin. For ethers **6**, **7**, and **8** and para ester **3**, this is the "edge-to-edge" distance as defined in Table I. For ortho ester **4**, this is the 4-Å separation of the π-electron systems in the stacked conformation. Qualitatively, the distances and rates for **3**, **5**, **6**, and **7** are in agreement with eq 1. The distances for ethers **5**–**7** are approximately equivalent, as are the k values. Para ester **3** is further from the porphyrin, and its rate constant is reduced accordingly. Quantitatively, a linear least-squares fit of ln k vs. R using the data for **3**, **5**, **6**, and **7** yields a line of slope −1.4, which in turn yields $L = 0.7$ Å in eq 1. This is in fair agreement with literature values.[46] However, the least-squares fit predicts a rate constant of 3.1×10^6 s^{-1} for ortho ester **4**, whereas the measured rate constant is at least 40 times larger ($>130 \times 10^6$). The departure of **4** from the behavior predicted from eq 1 is much too large to rationalize on the basis of inaccuracies in the NMR-determined distances. In addition, attempts to fit the data by using other combinations of distances from the table yield similar results: The data for **3**, **5**, **6**, and **7** are roughly in accord with eq 1 but with values for $L \ll 1$ Å, and with the predicted rate constant for ortho ester **4** much too small.

There are several conceivable explanations for this discrepancy. It is possible that the ester linkage joining the chromophores in **4** permits rapid "through-bond" transfer, relative to the ether linkages. However, this is unlikely because the rate constant for **3**, which has an identical linkage, is smaller than those for the ethers and is in accord with eq 1 with $L \sim 1$ Å. There are two other effects which probably do play an important role. The rate of triplet transfer by an exchange mechanism depends upon the interchromophore exchange integral.[6,23,24] Strictly speaking, the magnitude of this orbital overlap term is a function not only of separation R but also of the number of interacting orbitals and the relative orientations of these orbitals.[47-49] In the case of para ester **3** and ethers **5**, **6**, and to some extent **7**, the main orbital overlap interaction would be expected to involve the carotenoid π orbitals near the CH_2O group and the porphyrin π orbitals in the meso aromatic ring and perhaps that part of the porphyrin macrocycle in the vincinity of C-5. With ortho ester **4**, however, the molecule exists in a stacked conformation with all the π orbitals of the carotenoid aryl ring and the adjacent π bond in face-to-face contact with a large number of porphyrin macrocycle orbitals (Figure 9). This large increase in total orbital overlap could account at least in part for the increase in rate seen for **4**. Similar many-electron-exchange effects have been observed in electron-transfer reactions occurring by an exchange mechanism.[47,50,51]

It has also been pointed out that for a given separation R, changes in the relative angular orientations of the chromophores may theoretically affect the exchange integral by up to several orders of magnitude.[48,49] Perusal of the NMR-derived structures for **3**–**7** (Figures 9–12) shows not only that the average interchromophore angle differs greatly among these molecules but also that the optimal parallel arrangement[49] is best achieved for **4**.

The results for the carotenoporphyrins in polystyrene illustrate the fact that when one is dealing with highly nonspherical chromophores whose dimensions are large relative to their separation, and whose relative orientations are severely restricted, application of energy transfer theories which focus only upon the separation distance can be a serious oversimplification.

Role of Intramolecular Motions. Secondly, the results of this study demonstrate that the role of intramolecular motion in triplet energy transfer between linked chromophores can be an extremely important one. The rate constants for triplet transfer in molecules **6**, **7**, **10**, and **11** in benzene solution are much larger than the corresponding values in polystyrene. To a first approximation, these two aromatic solvents would be expected to have rather similar properties, and the molecular conformations of a solute in the two solvents should be similar. However, large-scale inter- and intramolecular motions will be relatively slow in a rigid polystyrene glass but rapid in fluid benzene. Thus, the increase in transfer rate in going from polystyrene to benzene may be ascribed to the influence of intramolecular motions which allow the molecule to momentarily assume conformations favorable for energy transfer. This is particularly apparent in the series of ethers **5**, **6**, and **7** where the rate constants are nearly equal in polystyrene but differ by up to a factor of 30 in benzene, and in **10** and **11** where the rates in benzene increase by ca. 10^4 over those in plastic. Thus, the rate constants for **6**, **7**, **10**, and **11** in benzene reflect the rates of intramolecular motions, rather than simply static structural features.

Triplet energy transfer rates can therefore be excellent probes for motional processes. It must be noted that the probe is a selective one in that only a particular subset of motions, those leading to conformations suitable for triplet transfer, is detected. This is clearly a different subset of motions from those detected by other methods. In addition, these results demonstrate that the interpretation of triplet transfer rates determined in fluid solution for flexible molecules in terms of static structural features *only* can lead to significant errors.

Implications for Biological Photoprotection. These triplet energy transfer results have relevance for photoprotection in photosynthetic organisms. As mentioned above, chlorophyll triplet states are excellent singlet oxygen sensitizers. Carotenoids can in principle provide photoprotection from singlet oxygen damage by several mechanisms, including interception of the chlorophyll triplet prior to its interaction with oxygen, or quenching of singlet oxygen itself by energy transfer or chemical reaction. Carotenoporphyrins have been found to mimic natural photoprotective behavior by the first of these mechanisms.[3,4] Typically, porphyrin triplet states will react with oxygen in organic solutions at an approximately diffusion-controlled rate of roughly (10^{-3} M O_2) × (10^9 M^{-1} s^{-1}) = 10^6 s^{-1}. The degree of photoprotection provided by a carotenoid in a carotenoporphyrin solution will therefore depend upon the intramolecular triplet energy transfer rate constant (k). Thus, **4**, with $k > 10^8$ s^{-1}, should provide complete photoprotection for aerated solutions, and this has been observed.[3,4] The current results suggest that unlike carotenoid-to-porphyrin singlet energy transfer (antenna function), which requires a folded carotenoporphyrin conformation prior to generation of the short-lived ($\leq 10^{-12}$ s) carotenoid singlet state,[2,3,4] photoprotection can in principle tolerate molecular motion during the long porphyrin triplet lifetime. Thus, although **3** ($k = 4.5 \times 10^5$ s^{-1}) provides only a small amount of photoprotection,[3] **10**, with $k = 9.7 \times 10^6$ s^{-1}, is nearly completely photoprotective under similar conditions in aerated benzene. The data reported above suggest that carotenoporphyrin ethers **7**, **8**, and **9** will be completely photoprotective in aerated solution and photoprotection with **6** will be very great. Ether **5**, however, should be intermediate between **3** and **10**.

In photosynthetic membranes, efficient triplet transfer from chlorophyll to carotenoids takes place with a high rate ($\sim 1 \times 10^8$ s^{-1})[14] in the absence of a covalent linkage between the chlorophyll and the carotenoid. Large-scale molecular motions of the type discussed here could in principle be involved in natural photoprotection in photosynthetic membranes. In these membranes the chlorophyll and carotenoid pigments are bound to various proteins in highly specific arrangements. Although dynamic structural fluctuations of these proteins, if rapid enough, could mediate triplet energy transfer and therefore photoprotection, it is important to remember that antenna function (singlet energy transfer) by carotenoid pigments requires intimate association of the carotenoid and chlorophyll chromophores prior to excitation.[1-5] It is reasonable to assume that such antenna carotenoids will also be able to provide photoprotection by triplet energy transfer with no necessity for large-scale motion.

These photophysical prerequisites for carotenoid photoprotection from singlet oxygen damage will also apply to other biological

(47) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860–4867.
(48) Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676–6686.
(49) Warshel, A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3105–3109.
(50) Katz, J. L., Choi, S. I., Rice, S. A., Jortner, J. *J. Chem. Phys.* **1963**, *39*, 1683–1697.
(51) Silbey, R., Jortner, J., Rice, S. A., Vala, M. T. *J. Chem. Phys.* **1965**, *42*, 733–737.

systems where $^1O_2$ may be involved including erythropoietic protoporphyria[52] and hematoporphyrin photochemotherapy.[53-55]

The relatively precise distance and angle information for **4-7** provided by NMR studies coupled with the triplet energy transfer rate constants determined by flash photolysis provide correlations among structural, dynamical, and photophysical parameters which will be useful in developing or testing quantitative theories of energy transfer between chromophores within a single molecule. For example, it appears that a quantum mechanical calculation of orbital overlap would be necessary in order to correlate the above-mentioned electron transfer in polystyrene with structure. These molecular systems are also potentially useful for studying intramolecular electron transfer reactions; in fact, a carotenoporphyrin linked to a quinone has recently been found to form a long-lived charge-separated state upon excitation with visible light.[56]

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Registry No. 6, 95998-78-0; **7**, 95998-79-1; **8**, 95998-80-4; **9**, 95998-81-5; **10**, 95998-82-6; **11**, 95998-83-7; **12**, 95998-84-8; **13**, 95998-85-9; **14**, 95998-86-0; **15**, 95998-87-1; **16**, 95998-88-2; **17**, 1253-46-9; **18**, 90652-11-2; **19**, 90447-13-5; 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 57412-08-5; 7′-apo-7′-(4-(iodomethyl)-phenyl)-β-carotene, 95998-89-3; 5-(3-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 57412-06-3; 5-(2-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 57412-07-4; 5-(4-(3-hydroxypropoxylphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 95998-90-6; α-bromo-*p*-toluoyl chloride, 52780-16-2; 2,3-dimethoxybenzaldehyde, 86-51-1; *p*-tolualdehyde, 104-87-0; pyrrole, 109-97-7; propionic acid, 79-09-4; 2,6-dimethoxybenzaldehyde, 3392-97-0; ethylene oxide, 75-21-8; methyl α-bromo-*p*-toluate, 2417-72-3; β-apo-8′-carotenal, 1107-26-2; oxygen, 7782-44-7.

(52) Mathews-Roth, M. M. *J. Natl. Cancer Inst.* (*U.S.*) **1982**, *69*, 279-285.
(53) Weishaupt, K. R.; Gomer, C. J.; Dougherty, T. J. *Cancer Res.* **1976**, *36*, 2326-2329.
(54) Poletti, A.; Murgia, S. M.; Cannistraro, S. *Photobiochem. Photobiophys.* **1981**, *2*, 167-172.
(55) Bensasson, R. V.; Moore, T. A.; Gust, D.; Moore, A. L.; Joy, A.; Tom, R.; Nemeth, G. A.; Land, E. J. "Proceedings of the International Symposium on Tumour Phototherapy"; Andreoni, A., Cubeddu, R. Eds.; Plenum Press: New York, 1984; pp 93-94.
(56) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature* (*London*) **1984**, *307*, 630-632.

Acid-Catalyzed Enolization and Aldol Condensation of Acetaldehyde

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Abstract: The condensation of acetaldehyde (**1**) to an equilibrium mixture of aldol (**2**) and crotonaldehyde (**3**) is second order in **1**. An excess acidity analysis reveals that a water molecule is also involved in the rate-limiting step; the reaction is actually the *base-assisted* addition of vinyl alcohol to protonated **1**, even in concentrated H_2SO_4. A previous report of a kinetically first-order conversion of **1** to **3** is shown to be due to the presence of a fast-reacting oligomer of **1**. The reaction of **1** in D_2SO_4 leads to partially deuterated **3**, a result ascribed to partial conversion of vinyl alcohol to deuterated **1**. Hydrogen isotope exchange of **3** was also observed, but at a slower rate. The rates of enolization of **1** were studied by iodination and are consistent with previous results and the proposed mechanism. The interconversion of **2** and **3** is shown to proceed via the enol of **2**; in this case the rate-limiting step is water attack on/water loss from protonated **3**/**2**, not proton transfer at carbon.

The acid-catalyzed condensation of acetaldehyde (**1**) to aldol (**2**) and the subsequent dehydration of **2** to crotonaldehyde (**3**) is the simplest example of this fundamental class of organic reactions (eq 1). This reaction sequence is of particular relevance to a study in our laboratory of the acid-catalyzed hydration of acetylene to acetaldehyde[2] because **1** is converted to **3** under these conditions. Surprisingly, however, although enolization is well studied,[3] and the mechanism of the acid-catalyzed aldol reaction is sometimes discussed,[4] the only thoroughly investigated example of the latter process involves ketones and aromatic aldehydes.[5] The transformation of **1** to the equilibrium mixture of **2** and **3** has only once been the object of quantitative study.[6] However, there was not only a discrepancy found between these results[6] and an examination of acetaldehyde enolization using bromination rates,[7] but also there was a puzzling indication[6] that the reaction shown in eq 1 was first order in acetaldehyde, contrary to expectation.[4]

$$\underset{\mathbf{1}}{2CH_3CH{=}O} + H^+ \xrightarrow{k_2}$$

$$\underset{\mathbf{2}}{CH_3CH(OH)CH_2CH{=}O} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathbf{3}}{CH_3CH{=}CHCH{=}O} + H_2O \qquad (1)$$

Thus McTigue and Gruen[6] reported that **1** in H_2SO_4 gave first-order formation of the characteristic UV absorption of **3**,

(1) (a) Scarborough College and Department of Chemistry. (b) Department of Chemistry. Mechanistic Studies in Strong Acids. X. Part IX is ref 12a.
(2) Baigrie, L. M.; Slebocka-Tilk, H.; Tencer, M.; Tidwell, T. T., manuscript in preparation.
(3) (a) Bell, R. P. "The Proton in Chemistry"; 2nd ed.; Chapman and Hall: London, 1973. (b) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1-77.
(4) (a) Nielsen, A. T.; Houlihan, W. J. *Org. React.* **1968**, *16*, 1-444. (b) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; 2nd ed.; Cornell: New York, 1969; pp 828-834 and 1003-1006. (c) Liler, M. "Reaction Mechanisms in Sulfuric Acid"; Academic Press: London, 1971; pp 231-232.
(5) Noyce, D. S.; Snyder, L. R. *J. Am. Chem. Soc.* **1959**, *81*, 620-624.
(6) McTigue, P. T.; Gruen, L. C. *Aust. J. Chem.* **1963**, *16*, 177-179.
(7) McTigue, P. T.; Sime, J. M. *Aust. J. Chem.* **1967**, *20*, 905-910.

0002-7863/85/1507-3640$01.50/0