$$CD_5^+ + c\text{-}C_4D_8 \longrightarrow C_4D_9^+ + CD_4 \quad (55)$$

$$C_4D_9^+ + i\text{-}C_5H_{12} \longrightarrow CD_3CDHCD_2CD_3 + C_5H_{11}^+ \quad (56)$$

is labeled in the secondary position indicates that the protonated cyclobutane ion isomerizes to the *sec*-butyl ion prior to or during reaction. The most probable route for this rearrangement is

$$c\text{-}C_4H_9^+ \longrightarrow [CH_3CH_2CH_2CH_2^+]^* \longrightarrow CH_3CH_2\overset{+}{C}HCH_3 \quad (57)$$

From the results given above (see Results section), it can be seen that when a proton is transferred to c-C_4D_8, the proton has approximately a statistical chance of ending up on a given carbon atom in the final reaction product. This indicates that a rapid shuffling of H (D) atoms in the protonated cyclobutane ion must have occurred, since according to the mechanism depicted above, and what is known about hydrogen shuffling in the *sec*-butyl ion (*i.e.*, 2–3 shifts should be strongly favored over 1–2 or 3–4 shifts), the proton would be expected to have a greater than statistical chance of ending up on a methyl group.

Excited State Donor–Acceptor Complexes. Olefin Isomerization as a Probe to Monitor Decay Processes[1]

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Abstract: The formation and reactions of excited state complexes (exciplexes) between excited states of metalloporphyrins or aromatic hydrocarbons and electron-deficient aromatic nitro compounds have been investigated. Various nitrostilbenes have been used as acceptors so that photoinduced geometric isomerization of the olefinic bond can provide information regarding possible fates of exciplex excitation energy. For zinc and magnesium porphyrins it is found that both excited singlets and triplets can form exciplexes with nitro compounds. The singlet and triplet exciplexes do not interconvert; in fact they have quite different reactivities. Exciplexes formed with the porphyrins do not decay *via* other excited states of porphyrin or acceptor; formation of ions from these exciplexes is evidently unimportant in nonpolar solvents. Triplet exciplexes are much more active in producing isomerization in the acceptor; evidence exists for a chain mechanism involving exchange of acceptor during the triplet exciplex lifetime. Excited singlets of tetracene and perylene form exciplexes with the nitrostilbenes that lead to isomerization of the acceptor with low efficiency. The triplet of tetracene is unreactive under the same conditions. Small changes in solvent or structure of the donor can produce large changes in exciplex formation constants as well as in the reactivity of the exciplex.

Photoassociation of electronically excited molecules in solution with ground states of the same species or other molecules is a well-established phenomenon.[4] Particularly well studied have been reactions of excited states with electron donors or acceptors.[5] Complexes between excited singlet states and electron donors or acceptors have been detected by the appearance of fluorescence from the complex concurrent with quenching of fluorescence from the free excited state.[5] Although singlet complexes have been perhaps better characterized due to their emission phenomena, triplet donor–acceptor complexes have also been detected.[6,7] In several cases excited complexes (exciplexes) of this sort have been suggested as intermediates in the course of chemical reactions.[8,9] It is probable that exciplexes involving photoexcited porphyrins and related compounds are involved in photosynthesis and related photobiological processes.

Despite the widespread occurrence of exciplexes, relatively little is known regarding mechanisms of exciplex decay. Often exciplex formation results simply in return of both partners to the ground state even in systems where one or both partners show distinctive emission or photochemistry in the absence of the other. Evidently in these cases exciplex formation provides a path for nonradiative decay, but the details of the mechanism are not clear.[10] In a recent review, Stevens[4] has discussed the possible fates of exciplexes formed by photoassociation. Chart I summarizes the several possibilities suggested by Stevens.

We have previously investigated the formation of exciplexes between excited states of metalloporphyrins and electron-deficient aromatic nitro compounds.[11] These complexes are nonfluorescent and in most cases

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[3] Alfred P. Sloan Foundation Fellow, 1970–1972; author to whom correspondence should be directed.

[4] B. Stevens, *Advan. Photochem.*, in press.

[5] A. Weller, *Pure Appl. Chem.*, 16, 115 (1968); H. Knibbe, K. Rollig, F. P. Schaffer, and A. Weller, *J. Chem. Phys.*, 47, 1183 (1967); H. Beens, H. Knibbe, and A. Weller, *ibid.*, 47, 1184 (1967), and references therein.

[6] H. Beens and A. Weller, Loyola International Conference on Molecular Luminescence, Chicago, Ill., 1968; reprinted in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

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[9] S. G. Cohen and N. Stein, *ibid.*, 91, 3690 (1969), and references therein.

[10] L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 16, 125 (1968).

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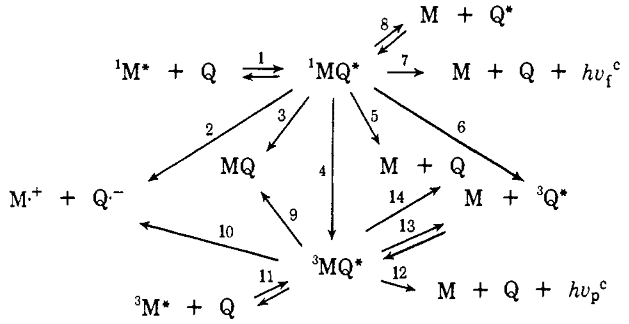
Chart I. Mechanisms for Decay of Exciplexes[a]



[a] Reference 4; M = donor; Q = electron deficient quencher; and MQ* = excited state complex.

evidently decay without chemical reaction. In the present paper we report an investigation of the fate of singlet and triplet exciplexes formed using photoexcited porphyrins and aromatic hydrocarbons as donors and aromatic nitro compounds as acceptors. By using various nitro and dinitrostilbenes which contain an isomerizable double bond as acceptors, we have been able to assess the importance of most of the paths outlined in Chart I. Results of this study include the findings that (a) for these systems triplet and singlet exciplexes do not interconvert, (b) singlet and triplet exciplexes have markedly different reactivities, and (c) small changes in the donor can cause relatively large changes in exciplex behavior. In particular we find that excited metalloporphyrins (as donors) can catalyze reactions in acceptor molecules with surprising efficiency.

Experimental Section

Fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer using RCA 1P21 and EMI 9558Q photomultiplier tubes. Fluorescence quenching studies were done in "true-bore" Pyrex ampoules degassed by three cycles of the freeze–pump–thaw method. Flash spectroscopic studies were performed on a flash photolysis apparatus consisting of a xenon–mercury flash tube (10–10% time 15 μsec) for initial excitation, a 75-W xenon arc lamp (Xenon Corporation Model G) or a GE 18 A Type CPG tungsten lamp as the analyzing light source, a Bausch and Lomb 500-mm grating monochromator, and a RCA 1P28 photomultiplier tube. A polished aluminum sample cavity in the shape of an ellipse was used with the sample cell located at one focus and the flash tube at the other. Transient signals were displayed on a Tektronix Type 585 oscilloscope and photographed on Polaroid Type 47 film. Samples for flash photolysis were degassed by up to six cycles of the freeze–pump–thaw method and sealed in cylindrical quartz cells (25-mm path).

Irradiations were carried out on samples in Pyrex ampoules degassed by three cycles of freeze–pump–thaw. Solutions of metalloporphyrins or perylene were irradiated in a merry-go-round apparatus[12] with light from a medium-pressure mercury lamp. Corning glass color filters were used to isolate the 546- and 577–579-nm lines for the metalloporphyrins and the 436-nm line for perylene. Tetracene solutions were irradiated with light from a super high pressure mercury lamp using a high-intensity Bausch and Lomb grating monochromator to isolate light centered at 472 nm. Light intensities were measured with the ferrioxalate actinometer.[13]

Photochemical esr studies were carried out by irradiating samples sealed in 4-mm Pyrex tubes in the cavity of a Varian E-3 esr spectrometer. The light from a super high pressure mercury lamp was passed through a high intensity Bausch and Lomb monochromator and focused on the sample with a condensing lens. Samples were degassed by three cycles of freeze–pump–thaw.

Materials. Etioporphyrin I was prepared by the condensation of kryptopyrrole.[14,15] Mesoporphyrin IX dimethyl ester was prepared by esterification of mesoporphyrin prepared by alkaline hydrogenation of protohemin.[16] Zinc etioporphyrin I and zinc mesoporphyrin IX dimethyl ester were prepared by the method of Calvin, *et al.*[15] Magnesium etioporphyrin I was prepared by the magnesium hexapyridine diiodide–pyridine method of Corwin, *et al.*[17] Purity of the etioporphyrin (*ca.* 99% or greater) was checked by liquid–liquid partition chromatography[18] and spectral techniques.

Tetracene and perylene were purified by column chromatography and recrystallization from benzene under minimum light conditions. *cis*- and *trans*-4-nitrostilbene were prepared by the Wittig reaction of *p*-nitrobenzaldehyde and benzyltriphenylphosphonium bromide.[19] The cis and trans isomers were separated by fractional recrystallization from hexane. The dinitro- and bromonitrostilbenes were prepared by the same method using the appropriately substituted benzyltriphenylphosphonium bromide. The cis and trans isomers of 4,4′-dinitrostilbene were separated by fractional recrystallization from ethanol. The cis and trans isomers of the bromonitrostilbenes were separated by column chromatography over alumina with hexane. Benzene was purified by treatment with sulfuric acid followed by distillation from P_2O_5. Dimethoxyethane (glyme) was purified by distillation from lithium aluminum hydride and stored under vacuum over sodium–potassium alloy. Other materials except spectrograde solvents were purified by distillation or chromatography.

Results

Exciplex Formation Constants. Excited singlet and triplet states of zinc and magnesium porphyrins are quenched by the various nitrostilbenes. For all of the quenchers studied, there is no spectral evidence of complex formation in the ground state. Charge-transfer complexes between porphyrins and aromatic nitro compounds produce a decrease in the extinction coefficients of the porphyrin visible transitions.[20] Quenching of the porphyrin fluorescence yields reasonably good linear Stern–Volmer plots at low quencher concentrations.[21] Singlet quenching rate constants (Table I) $k_q{}^s$ are calculated by dividing the Stern–Volmer slope by the singlet lifetime, τ_s, in the absence of quencher. Singlet lifetimes used in the calculations for etioporphyrin complexes were determined from fluorescence decay following excitation with a nanosecond flash lamp. The lifetimes for etioporphyrin and its metal derivatives are very close to those reported for the corresponding mesoporphyrins,[23] The values of $k_q{}^s$ for the nitrostilbenes are similar to those previously obtained for the same donors and other nitro compounds.[11] Although the values are near the diffusion-controlled limit there are still considerable differences between quenching constants for cis and

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(13) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 220, 104 (1953); G. Hatchard and C. A. Parker, *ibid., Ser. A*, **235**, 518 (1956).

(14) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. II, Part 1, Akademische Verlagsgesellschaft m.b.h., Leipzig, Germany, 1937, p 106.

(15) G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, 66, 2517 (1962).

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(18) E. W. Baker, M. Lachman, and A. H. Corwin, *Anal. Biochem.*, 8, 503 (1964).

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(20) M. Gouterman and P. E. Stevenson, *J. Chem. Phys.*, 37, 2266 (1962).

(21) Signficant positive deviations at higher quencher concentrations are probably due to "static" or nearest neighbor quenching[22] (*vide infra*).

(22) (a) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc., Ser. A*, **206**, 437 (1951); (b) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5715 (1967).

(23) G. P. Gurinovich, A. I. Patsko, and A. N. Sevchenko, *Dokl. Phys. Chem.*, **174**, 402 (1967).

Table I. Singlet Quenching Constants and Stern–Volmer Slopes for Various Donors with Nitrostilbenes[a]

Excited donor	Acceptor	Solvent	Slope	k_q^s, l. mol^{-1} sec^{-1}
Zn etio[b]	*cis*-4-NS[c]	Benzene	14.9	3.7×10^9
Zn meso[d]	*cis*-4-NS	Benzene	16.7	3.9×10^9
Zn etio	*trans*-4-NS	Benzene	35.8	8.9×10^9
Zn meso	*cis*-4,4′-DNS[e]	Benzene	35.0	8.1×10^9
Zn meso	*cis*-4-NS	Ethanol	31.1	7.2×10^9
Zn meso	*cis*-4,4′-DNS	Ethanol	54.7	12.7×10^9
Zn etio–pyridine	*cis*-4-NS	Benzene–pyridine[f]	18.1	4.2×10^9
Perylene[g]	*cis*-4-NS	Benzene	80.8	12.0×10^9
Tetracene[h]	*cis*-4-NS	Benzene	66.6	10.0×10^9
Mg etio[i]	*cis*-4-NS	Benzene	132	11×10^9

[a] Values used for singlet lifetimes are: zinc mesoporphyrin IX, $\tau_s = 4.3 \times 10^{-9}$ sec (see ref 23); zinc etioporphyrin I, $\tau_s = 4 \times 10^{-9}$ sec. [b] Zinc etioporphyrin I. [c] *cis*-4-Nitrostilbene. [d] Zinc mesoporphyrin IX. [e] *cis*-4,4′-Dinitrostilbene. [f] 0.005 *M* pyridine in benzene. [g] Singlet lifetime, $\tau_s = 6.9 \times 10^{-9}$ sec (see I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965). [h] Singlet lifetime, $\tau_s = 6.4 \times 10^{-9}$ sec (see Berlman, footnote *g*). [i] $\tau_s = 12 \times 10^{-9}$ sec.

trans isomers. *cis*-4,4′-Dinitrostilbene is a more efficient quencher than *cis*-4-nitrostilbene.

Donors studied other than metalloporphyrins include perylene, tetracene, and free-base etioporphyrin. As data in Table I indicate, both aromatic hydrocarbon singlets are quenched in benzene by *cis*-4-nitrostilbene at rates which are essentially diffusion controlled. Fluorescence of free-base etioporphyrin I is not quenched by *cis*-4-nitrostilbene; however, *cis*-4,4′-dinitrostilbene produces slight quenching of etioporphyrin I fluorescence.

Rate constants for quenching of porphyrin-excited triplet states k_q^t were determined by monitoring the decay of triplet–triplet absorption as measured by flash spectroscopy (Table II). In contrast to singlet quenching phenomena, there is little difference in quenching efficiency between cis and trans isomers for the nitrostilbenes; k_q^t values in benzene are close to the diffusion-controlled limit. On the other hand, while addition of pyridine has little effect on singlet quenching, triplet quenching is retarded by nearly two orders of magnitude by addition of small amounts of pyridine. For magnesium etioporphyrin I-pyridinate (magnesium etioporphyrin with 0.005 *M* pyridine in benzene) k_q^t is reduced by only one order of magnitude. For zinc and magnesium etioporphyrin I in benzene, quenching of triplets is essentially complete for nitrostilbene concentrations of 10^{-3} *M*.

Table II. Quenching of Porphyrin Triplets by Nitrostilbenes

Porphyrin	Quencher	Solvent	k_q^t, l. mol^{-1} sec^{-1}
Zn etio[a]	*cis*-4-NS[b]	Benzene	1.7×10^9
Zn etio	*trans*-4-NS	Benzene	1.6×10^9
Zn etio	*cis*-4,4′-DNS[c]	Benzene	3.1×10^9
Zn etio	*trans*-4,4′-DNS	Benzene	2.7×10^9
Zn etio–pyridine	*cis*-4-NS	Benzene–pyridine[d]	2.6×10^7
Me etio[e]	*cis*-4-NS	Benzene	1.7×10^9
Mg etio–pyridine	*cis*-4-NS	Benzene–pyridine	2×10^8

[a] Zinc etioporphyrin I. [b] *cis*-4-Nitrostilbene. [c] *cis*-4,4′-Dinitrostilbene. [d] Benzene with 5×10^{-3} *M* pyridine. [e] Magnesium etioporphyrin I.

The perylene triplet was not detected in flash photolysis experiments; however, perylene is not expected to reach a triplet state under normal conditions since its fluorescence efficiency is reported to be 0.98.[24] The triplet of tetracene was easily detected in flash studies; however, the transients monitored at 433 and 490 nm (τ *ca.* 200 μsec) were not quenched by up to 0.02 *M* *cis*-4-nitrostilbene. This indicates that k_q^t for the tetracene–*cis*-4-nitrostilbene system in benzene is less than 3×10^4 l. mol^{-1} sec^{-1}. Similarly it was found that the triplet of free-base etioporphyrin I was not quenched by either *cis*-4-nitrostilbene or *cis*-4,4′-dinitrostilbene in benzene at olefin concentrations up to 0.01 *M*.

We have not been able to detect either triplet or singlet exciplexes spectroscopically. No new fluorescence appears out to 750 nm when nitrostilbene–porphyrin solutions are irradiated. The only long-lived species observed in the flash photolysis experiments are porphyrin triplet states. However, in these studies wavelengths greater than 600 nm could not be investigated with the phototube used and regions where the porphyrin absorbed could not be investigated with confidence.

Acceptor Isomerization in Exciplexes. When benzene solutions of zinc etioporphyrin and 4-nitrostilbene are irradiated with light absorbed only by the porphyrin, the only reaction observed is cis–trans isomerization of olefin. Even on prolonged irradiation an excellent mass balance is obtained. Quantum yields for isomerization are low in both directions but the energetically downhill $\varphi_{c \rightarrow t}$ is much higher than $\varphi_{t \rightarrow c}$. The stationary state is 99.5% trans. The value of $\varphi_{c \rightarrow t}$ is dependent on the concentration of *cis*-4-nitrostilbene (Figure 1).[25] The maximum value for $\varphi_{c \rightarrow t}$ of 0.017 is reached by 0.03 *M* *cis*-4-nitrostilbene where only about one-fourth of the excited singlets are quenched. When the concentration of *cis*-4-nitrostilbene is increased to 0.15 *M* where three-fourths of the singlets are captured (as indicated by the Stern–Volmer slope), $\varphi_{c \rightarrow t}$ drops to 0.007.

When the irradiations are carried out in solvents more polar than benzene, the isomerization efficiency drops (Table III). Zinc mesoporphyrin IX dimethyl ester was used as a donor instead of zinc etioporphyrin I due to the low solubility of the latter compound in polar solvents. (In benzene, replacement of zinc etioporphyrin with zinc mesoporphyrin IX dimethyl ester has no effect on the cis–trans isomerization.) In ethanol, photochemical reaction of the porphyrin and probably also of the nitrostilbene accompanies cis–trans isomerization. For 0.02 *M* *cis*-4-nitrostilbene in ethanol $\varphi_{c \rightarrow t}$ is 0.004. No decomposition of the porphyrin is observed in *N*-methylformamide but $\varphi_{c \rightarrow t}$ for 0.02 *M* *cis*-4-nitrostilbene is only 0.002.

Tollin, *et al.*,[26] observed an esr signal from semiquinone radicals on irradiation of solutions of quinones and porphyrins with visible light. Stilbene radical anions are known to undergo cis–trans isomerization

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(24) E. J. Bowen, *Advan. Photochem.*, 1, 23 (1963).

(25) Values in Figure 1 are slightly different from those reported earlier.[11]

(26) R. A. White and G. Tollin, *J. Amer. Chem. Soc.*, 89, 1253 (1967); A. K. Bannerjee and G. Tollin, *Photochem. Photobiol.*, 5, 315 (1966).

Table III. Maximum Quantum Yields of Isomerization for Various Donor–Acceptor Pairs

Donor	Acceptor	[Acceptor], *M*	Solvent	$\varphi_{c \to t}^{max}$
Zn etio[a]	*cis*-4-NS[b]	0.025	Benzene	0.017
Zn etio	*cis*-4-NS	0.020	Ethanol	0.004
Zn etio	*cis*-4-NS	0.020	*N*-Methylformamide	0.002
Zn etio–pyridine	*cis*-4-NS	0.025	Benzene–pyridine[c]	0.650
Zn etio–pyridine	*cis*-4,4′-DNS[d]	0.005	Benzene–pyridine[c]	1.90
Zn etio	*cis*-4,4′-DNS	0.010	Benzene	0.130
Zn etio	*cis*-4,4′-BNS[e]	0.020	Benzene	0.020
Zn etio	*cis*-2,4′-BNS[f]	0.020	Benzene	0.008
Mg etio[g]	*cis*-4-NS	0.010	Benzene	0.056
Mg etio	*cis*-4,4′-DNS	0.005	Benzene	0.088
Me etio–pyridine	*cis*-4-NS	0.010	Benzene–pyridine[c]	0.018
Mg etio–pyridine	*cis*-4-NS	0.025	Pyridine	0.004
Tetracene	*cis*-4-NS	0.100	Benzene	0.006
Perylene	*cis*-4-NS	0.03[h]	Benzene	0.004

[a] Zinc etioporphyrin I. [b] *cis*-4-Nitrostilbene. [c] Benzene with 0.005 *M* pyridine. [d] *cis*-4,4′-Dinitrostilbene. [e] *cis*-4-Bromo-4′-nitrostilbene. [f] *cis*-2-Bromo-4′-nitrostilbene. [g] Magnesium etioporphyrin I. [h] Highest acceptor concentration studied.

to yield the trans isomer preferentially.[27] We find that the radical anions of 4-nitrostilbene produced by potassium metal reduction in 1,2-dimethoxyethane also undergo cis–trans isomerization. In an attempt to determine the importance of electron transfer (reactions 2 and 10 of Chart I) to form the nitrostilbene radical anion, solutions of zinc porphyrins and 4-nitrostilbene or 4,4′-dinitrostilbene were irradiated in an esr cavity. No signal was detected when the solvent was benzene or benzene with 5×10^{-3} *M* pyridine. A weak, unresolved spectrum was seen in ethanol. Under the same conditions solutions of zinc porphyrin and *p*-benzoquinone gave a well-resolved spectrum of the semiquinone radical when the solvent was ethanol and no signal when the solvent was benzene. This is in agreement with Tollin's work.[26]

Irradiation of zinc etioporphyrin I in the presence of nitrostilbenes was also carried out in benzene containing 0.005 *M* pyridine. At this pyridine concentration the zinc porphyrin exists as a monopyridinate in both the ground and excited singlet state.[11] The rate of singlet quenching (Table I) is little affected by the addition of pyridine; however, the rate constant for triplet quenching (Table II) is about two orders of magnitude lower with pyridine present. The isomerization quantum yields for *cis*-4-nitrostilbene under these conditions show a concentration dependence similar to that observed in pure benzene; there is a decrease in $\varphi_{c \to t}$ at high *cis*-4-nitrostilbene concentration. Olefin isomerization is much more efficient in the presence of pyridine: $\varphi_{c \to t}^{max}$ is 0.65 (0.025 *M* olefin); $\varphi_{c \to t}$ drops to 0.48 at 0.1 *M* 4-nitrostilbene. The stationary state is greater than 99% trans; again no by-products were observed on long irradiation.

When solutions of zinc porphyrins and 4,4′-dinitrostilbene are irradiated with light absorbed only by the porphyrin, the results are very similar to those observed for 4-nitrostilbene. The same trends on changing solvent and on varying the concentration of olefin are observed. However, the efficiencies of excited state quenching (Tables I and II) and of cis–trans isomerization (Table III) are higher for 4,4′-dinitrostilbene than for 4-nitrostilbene. The fact that $\varphi_{c \to t}^{max}$ for *cis*-4,4′-dinitrostilbene and zinc etioporphyrin–pyridinate is greater than 1 suggests the presence of a chain process such as exchange of acceptor–olefin within the exciplex.[28]

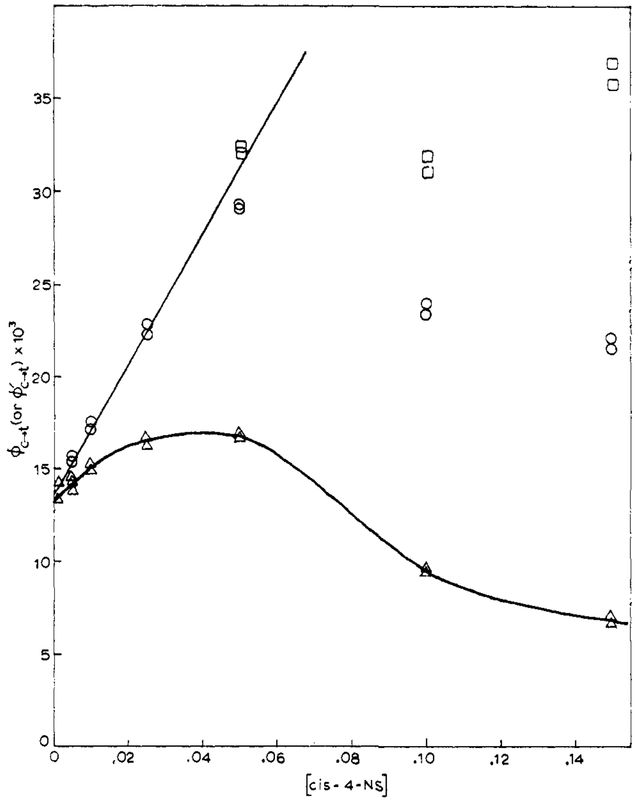

Figure 1. Variation of $\varphi_{c \to t}$ (△), φ' (○), and ϕ', corrected for "static" quenching (□), with concentration of *cis*-4-nitrostilbene for zinc etioporphyrin I–*cis*-4-nitrostilbene in benzene at 28°.

To study the effect of introduction of a heavy atom into the acceptor, 2-bromo-4′-nitrostilbene and 4-bromo-4′-nitrostilbene were studied with zinc etioporphyrin I. The quantum yields for isomerization are somewhat lower for both compounds than for corresponding 4-nitrostilbene solutions and there is still a decrease in $\varphi_{c \to t}$ as the concentration of acceptor increases to levels producing extensive fluorescence quenching. Rate constants for fluorescence quenching

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(27) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, 46, 2314 (1967).

(28) D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, 91, 3393 (1969).

are in the same range for the bromonitrostilbenes as those for 4-nitrostilbene and 4,4′-dinitrostilbene. Here again the trans isomer of the olefin has a higher $k_q{}^s$ than the cis.

We have studied the isomerization of the nitrostilbenes in complexes with donors other than zinc porphyrins. For magnesium etioporphyrin I in benzene the quantum yields of isomerization for both *cis*-4-nitrostilbene and *cis*-4,4′-dinitrostilbene show the same dependence on concentration observed with the zinc porphyrin; $\varphi_{c \rightarrow t}$ decreases as higher concentrations of quencher are approached. Isomerization efficiencies are in approximately the same range for both zinc and magnesium porphyrins as donors in pure benzene. For 4,4′-dinitrostilbene $\varphi_{c \rightarrow t}$ is slightly lower ($\varphi_{c \rightarrow t}^{\max}$ is 0.088) while for 4-nitrostilbene $\varphi_{c \rightarrow t}$ is two to three times as high ($\varphi_{c \rightarrow t}^{\max}$ is 0.056) with the magnesium etioporphyrin. However, in contrast to the situation with zinc porphyrins, addition of pyridine to magnesium etioporphyrin–nitrostilbene solutions in benzene reduces the efficiency of isomerization of the acceptor olefin. In benzene with 0.005 *M* pyridine, where the magnesium etioporphyrin is present mainly as the monopyridinate, $\varphi_{c \rightarrow t}^{\max}$ for *cis*-4-nitrostilbene is 0.018. With pyridine as solvent, where about 40% of the magnesium etioporphyrin is in the form of the dipyridinate complex,[29] $\varphi_{c \rightarrow t}^{\max}$ has fallen to 0.004.

Although excited singlets of tetracene and perylene are quenched efficiently by the nitrostilbenes, the aromatic hydrocarbons are relatively inefficient in catalyzing isomerization of the acceptor olefin. Irradiation of benzene solutions of perylene and *cis*-4-nitrostilbene with 436-nm light leads to very inefficient isomerization; the maximum value for $\varphi_{c \rightarrow t}$ of 0.004 was obtained with 0.03 *M cis*-4-nitrostilbene, the highest concentration investigated. Isomerization of the bromonitrostilbenes, where an acceptor heavy-atom effect might be anticipated, with excited perylene as donor was also extremely inefficient. Tetracene, which fluoresces with an efficiency of between 0.1[30] and 0.21,[31] is little better than perylene at catalyzing acceptor isomerization. The quantum yield of *cis*-4-nitrostilbene isomerization increases steadily as olefin concentration increases going from 0.0021 at 0.01 *M* olefin to 0.0061 at 0.1 *M* olefin.

Discussion

Possible mechanisms for quenching of either excited state of the donor include formation of an excited state complex (see Chart I, 1 or 11) or electron transfer to form radical ions (eq 15). It has been suggested

$$M^* + Q \longrightarrow M\cdot^+ + Q\cdot^- \qquad (15)$$

that quenching of pyrochlorophyll fluorescence by various nitrobenzenes in ethanol–pyridine proceeds *via* electron transfer.[32] Our earlier work[11] with substituted nitrobenzenes which shows that fluorescence quenching is related to the "oxidizing ability" of the quencher and that $k_q{}^s$ values increase slightly with increase in solvent polarity suggests that there is some transfer of charge. Because values of $k_q{}^s$ are slightly lower than the diffusion-controlled limit and are somewhat dependent on steric factors, fluorescence quenching in benzene probably occurs through initial formation of a collision complex. The fact that fluorescence quenching increases only slightly on going from nonpolar solvents such as benzene and cyclohexane to polar solvents such as *N*-methylformamide and ethanol would seem to support formation of an exciplex with some polar character over complete electron transfer as a quenching mechanism. It is probable that triplet quenching also proceeds *via* exciplex formation. It is noteworthy that cis and trans isomers of the various nitrostilbenes are equally efficient triplet quenchers, but in each case the trans isomer has a higher $k_q{}^s$ value than the corresponding cis olefin. This may reflect a difference in exciplex geometry for singlet and triplet (*vide infra*). The reason for the drastic drop in $k_q{}^t$ for zinc etioporphyrin on addition of pyridine while $k_q{}^s$ remains almost unchanged is not known.

As shown in Chart I there are several routes by which singlet and triplet exciplexes might decay. All of our work has been carried out in solution and in no case have we detected emission from the exciplex (eq 7 and 12 of Chart I). In benzene the only chemical reaction observed is cis–trans isomerization of the nitrostilbene. Therefore reactions 3 and 9 can be neglected for benzene solutions. Studies on the direct and sensitized photoisomerization of nitrostilbenes[33] and other olefins[34] indicate that excited states of nitrostilbenes should yield a decay ratio close to 50/50 cis/trans. Here, however, we obtain stationary states greater than 99% trans. This suggests that either cis exciplex decays to free excited states of the nitrostilbenes much more rapidly than does the trans exciplex or, more likely, excited states of the nitrostilbenes are not formed to any appreciable extent. If the latter is true, then reactions 6, 8, and 13 are not important for these exciplexes. The reverse of reaction 11 and other reactions leading from $^1MQ^*$ to $^3M^*$ do not occur for any of the systems studied. For tetracene–nitrostilbene, for example, the triplet lifetime was unchanged at moderate nitrostilbene concentration and the triplet–triplet absorption intensity was much reduced, indicating simply a reduced yield of tetracene triplet by the normal route.[35]

When solutions of zinc porphyrins and nitrostilbenes were irradiated in an esr cavity no signal was seen when the solvent was benzene or benzene–pyridine and only an unresolved signal when the solvent was ethanol. Absence of an esr signal does not mean that radicals are not involved in the reaction being investigated. If the radical ions produced by electron transfer in the exciplex recombine at a rate limited only by diffusion it would be difficult to build up an observable concen-

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(29) C. B. Storm, A. H. Corwin, R. Arellano, M. Martz, and R. Weintraub, *J. Amer. Chem. Soc.*, 88, 2525 (1966).

(30) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 276, 125 (1963).

(31) See Berlman, Table I, footnote *g*.

(32) G. R. Seely, *J. Phys. Chem.*, 73, 125 (1969).

(33) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 90, 3907 (1968); D. Schulte-Frohlinde, N. Blume, and H. Gusten, *J. Phys. Chem.*, 66, 2486 (1962).

(34) G. S. Hammond, *et al.*, *J. Jap. Chem.*, 18, 1464 (1965); *J. Amer. Chem. Soc.*, 86, 3197 (1964).

(35) Although irradiation of a ground-state charge-transfer complex of anthracene with trinitrobenzene is reported to result in emission from the anthracene triplet,[36] conversion of $^1MQ^*$ to $^3M^*$ *via* $^3MQ^*$ certainly does not appear to be general as has been asserted.[37]

(36) S. P. McGlynn and J. D. Boggus, *J. Amer. Chem. Soc.*, 80, 5096 (1958).

(37) G. H. Schenck and N. Radke, *Anal. Chem.*, 37, 910 (1965).

tration of spins (10^{-7}–10^{-8} *M*). With the light intensity used (*ca.* 10^{-5} einsteins/min) and the low absorbance of the sample (*ca.* 0.1) even a concentration of only 10^{-8} *M* spins appears to be out of reach. Rough calculations predict a spin concentration closer to 10^{-9} *M* if recombination occurs at a diffusion-limited rate. In ethanol, where an esr signal is observed, the isomerization quantum yield is much lower than in benzene. Also other reactions besides isomerization are seen in ethanol but not in benzene. The isomerization of nitrostilbene radical anions produced by potassium metal reduction in glyme is also accompanied by side reactions. It would seem therefore that electron transfer (reactions 2 and 10) is not the major route to isomerization and that electron transfer is insignificant in benzene.

Perhaps the most striking aspect of our studies is the surprising effect of acceptor concentration on the quantum efficiency of isomerization of the acceptor. For 4-nitrostilbene and zinc etioporphyrin $\varphi_{c\rightarrow t}$ has reached its maximum value by 0.03 *M* nitrostilbene. As the concentration of quencher is increased above 0.03 *M*, singlet quenching becomes more important but $\varphi_{c\rightarrow t}$ decreases. This suggests that isomerization proceeds more efficiently through the porphyrin triplet state and that intersystem crossing in zinc porphyrin singlet exciplexes (reaction 4) is not very important. The lack of any isomerization enhancement due to a "heavy atom effect" when the bromonitrostilbenes are used as acceptors reinforces this conclusion. The increase in $\varphi_{c\rightarrow t}$ with increasing concentration of *cis*-4-nitrostilbene below 0.03 *M* acceptor may be due to exchange of acceptor within the lifetime of the triplet exciplex (eq 16). Taking the above results into consideration we can now write a much simplified scheme for exciplex decay in metalloporphyrin systems, where M = metalloporphyrin, Q = cis quencher, Q′ = trans quencher, β = fraction of singlet exciplexes which decay with isomerization of acceptor, and α = fraction of triplet exciplexes which decay with isomerization of quencher (see Chart II). Using the above reactions we have attempted to derive expressions which will agree with the experimental data on variation of isomerization quantum efficiency with acceptor concentration.

Chart II

$$^1\mathrm{M}^* + \mathrm{Q} \xrightarrow{k_s^q} {}^1\mathrm{MQ}^* \qquad (1)$$

$$^1\mathrm{MQ}^* \xrightarrow{k_s^e} \beta\mathrm{Q}' + (1-\beta)\mathrm{Q} + \mathrm{M} \qquad (5')$$

$$^3\mathrm{M}^* + \mathrm{Q} \xrightarrow{k_q^t} {}^3\mathrm{MQ}^* \qquad (11)$$

$$^3\mathrm{MQ}^* \xrightarrow{k_e^t} \alpha\mathrm{Q}' + (1-\alpha)\mathrm{Q} + \mathrm{M} \qquad (14')$$

$$^3\mathrm{MQ}^* + \mathrm{Q} \xrightarrow{k_c} {}^3\mathrm{MQ}^* + \mathrm{Q}' \qquad (16)$$

As a first possibility it can be assumed that isomerization occurs only through the triplet exciplex (β in reaction 5′ is 0) and that exchange of acceptor within the exciplex (eq 16) occurs. The equation for the quantum yield of isomerization of Q to Q′ then becomes

$$\varphi = \frac{k_{isc}}{k_0^s + k_q^s[\mathrm{Q}]}\,\frac{k_q^t[\mathrm{Q}]}{k_0^t + k_q^t[\mathrm{Q}]}\,\frac{\alpha k_e^t + k_c[\mathrm{Q}]}{k_e^t} \qquad (17)$$

where k_{isc} = rate constant for intersystem crossing of M, k_0^s and k_0^t are the reciprocals of the lifetimes of the singlet and triplet states, respectively, of M in the absence of acceptor, and k_q^s and k_q^t are rate constants for formation of singlet and triplet exciplexes. Even at 0.001 *M* acceptor, the lowest concentration studied, $k_q^t[\mathrm{Q}]$ is so much greater than k_0^t that the second fraction in eq 17 may be neglected to give eq 18. The

$$\varphi = \frac{k_{isc}}{k_0^s + k_q^s[\mathrm{Q}]}\,\frac{\alpha k_e^t + k_c[\mathrm{Q}]}{k_e^t} \qquad (18)$$

introduction of $\gamma = k_{isc}/k_0^s$ and $\tau_s = 1/k_0^s$ gives on rearranging terms eq 19. To obtain an expression

$$\varphi = \frac{\gamma}{1 + k_q^s\tau_s[\mathrm{Q}]}\,\frac{\alpha k_e^t + k_c[\mathrm{Q}]}{k_e^t} \qquad (19)$$

easier to work with, a new quantity φ' is defined as $\varphi' = (1 + k_q^s\tau_s[\mathrm{Q}])\varphi$. In this case φ' becomes

$$\varphi' = \gamma\alpha + (\gamma k_c[\mathrm{Q}]/k_e^t) \qquad (20)$$

Equation 19 predicts that a plot of φ' *vs.* [Q] should give a straight line with an intercept of $\gamma\alpha$ and a slope equal to $\gamma(k_c/k_e^t)$. For zinc etioporphyrin I and *cis*-4-nitrostilbene in benzene, to obtain φ' the experimental values of $\varphi_{c\rightarrow t}$ are multiplied by $1 + k_q^s\tau_s[\mathrm{Q}]$. The value of $k_q^s\tau_s$ is given by the Stern–Volmer slope for fluorescence quenching (Table I). The values of φ' for *cis*-4-nitrostilbene fall along a straight line with an intercept of 0.0136 and a slope of 0.354 (Figure 1). Gurinovich, *et al.*,[23] found for zinc mesoporphyrin that the value of γ (the intersystem crossing yield) is 0.28. Using this value and the intercept we obtain a value α = 0.05 indicating that most of the triplet exciplexes decay to the ground state without isomerization of the acceptor. Deviation of φ' values from the line for high concentrations of 4-nitrostilbene are discussed later.

A second possible expression for $\varphi_{c\rightarrow t}$ can be derived if one assumes that isomerization can take place from both singlet and triplet exciplexes (eq 5′ and 11′), but that exchange of acceptor within the exciplex (eq 16) is unimportant. These assumptions lead to the following equation

$$\varphi = \frac{k_q^s[\mathrm{Q}]}{k_0^s + k_q^s[\mathrm{Q}]}\,\frac{\beta k_e^s}{k_e^s} + \frac{k_{isc}}{k_0^s + k_q^s[\mathrm{Q}]}\,\frac{k_q^t[\mathrm{Q}]}{k_0^t + k_q^t[\mathrm{Q}]}\,\frac{\alpha k_e^t}{k_e^t} \qquad (21)$$

When the same substitutions and simplifications that were made on eq 17 and 18 are carried out on eq 21, the result is eq 22.

$$\varphi = \frac{\beta k_q^s\tau_s[\mathrm{Q}]}{1 + k_q^s\tau_s[\mathrm{Q}]} + \frac{\gamma\alpha}{1 + k_q^s\tau_s[\mathrm{Q}]} \qquad (22)$$

This leads to an expression for φ' (eq 23) of the same

$$\varphi' = \gamma\alpha + \beta k_q^s\tau_s[\mathrm{Q}] \qquad (23)$$

form as before, except that here the slope of the straight line equals $\beta k_q^s\tau_s$. If the slope (0.354) is divided by $k_q^s\tau_s$ (14.9), β is found to be 0.024. Thus if isomerization from the singlet is completely responsible for the rise in φ on going from 0.001 to 0.03 *M* *cis*-4-nitrostilbene, the singlet exciplex is only half as efficient as the triplet in causing acceptor isomerization. If

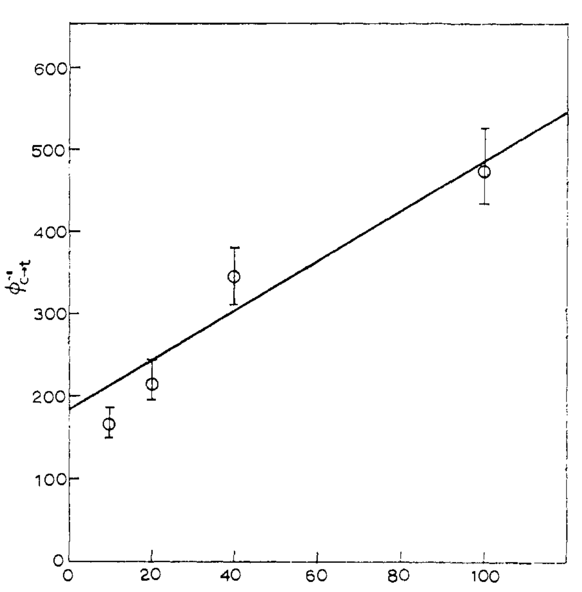

Figure 2. Plot of reciprocal of $\varphi_{c\rightarrow t}$ *vs.* reciprocal of *cis*-4-nitrostilbene concentration for tetracene-*cis*-4-nitrostilbene in benzene at 28°. Error bars show uncertainty due to a 10% error in φ.

reactions 5′, 11′, and 16 are all important, a straight line with an intercept of $\gamma\alpha$ is still predicted but the slope would equal the sum $\gamma(k_c/k_e^t) + \beta k^s\tau_s$.

None of the expressions derived so far predict a drop in φ' at the higher concentrations of *cis*-4-nitrostilbene. We observed that the drop in φ' occurs over the same range of nitrostilbene concentrations in which positive deviations from the straight line Stern-Volmer plot for fluorescence quenching were found. The positive deviation indicates that fluorescence quenching is greater than that predicted by the Stern-Volmer relationship: "extra" quenching can be attributed to "static" quenching.[21,22] Since "static" quenching produces the same singlet exciplex produced by "normal" diffusion-controlled quenching of the porphyrin singlet, one would not expect the large drop in φ (or φ') if the singlet exciplex leads to isomerization. In fact one might anticipate positive deviation for φ' at high acceptor concentrations. If isomerization proceeds only through the triplet exciplex, the higher than predicted singlet quenching leads to a lower than predicted yield of porphyrin triplet and therefore a lower yield of triplet exciplex. When φ' is corrected for the "static" quenching the points for 0.10 and 0.15 *M* *cis*-4-nitrostilbene are closer to the line but still below it (Figure 1). Possibly the remaining negative deviation is due to a change in solvent properties at high quencher concentration which might affect the rate of reaction 16.

The other metalloporphyrin-nitrostilbene systems show similar behavior. When *cis*-4,4′-dinitrostilbene was used as the acceptor in benzene solutions of zinc etioporphyrin I a plot of φ' *vs.* [Q] gave a straight line with the points at highest quencher concentrations below the line. From the intercept of 0.13, α is found to be 0.47; this is over ten times as large as α for *cis*-4-nitrostilbene. The slope of 4.96 for *cis*-4,4′-dinitrostilbene is also much higher than the value of 0.354 obtained for *cis*-4-nitrostilbene. A plot of φ' *vs.* [Q] for zinc etioporphyrin I pyridinate as donor and *cis*-4-nitrostilbene gives a slope of 23.9 and an intercept of 0.35; these values are much higher than those obtained in the absence of pyridine. The value of γ for zinc etioporphyrin pyridinate is not known. However since neither α not γ can be greater than 1, an intercept of 0.35 requires that the value of α, the efficiency of triplet exciplex isomerization, be between 0.35 and 1. For magnesium etioporphyrin I-4-nitrostilbene the slope is *ca.* 3 and the intercept is 0.026. Since γ is estimated to be 0.3 for the magnesium porphyrin,[23] α must be *ca.* 0.09 for the magnesium porphyrin triplet exciplex.

The tetracene-4-nitrostilbene system presents an interesting contrast to the donor-acceptor pairs where the donor is a metalloporphyrin. Although the tetracene singlet is quenched very efficiently, the tetracene triplet is not quenched at all by the stilbene. Therefore all isomerization must come from the singlet-state exciplex. The expression for $\varphi_{c\rightarrow t}$ should be

$$\varphi = \frac{ak_q^s[Q]}{k_0^s + k_q^s[Q]} \tag{24}$$

where a is the fraction of singlet exciplexes which decay with isomerization of the quencher. A more useful form of eq 24 is

$$1/\varphi = 1/a + (k_0^s/ak_q^s[Q]) \tag{25}$$

or

$$1/\varphi = 1/a + (1/ak_q^s\tau_s)(1/[Q]) \tag{26}$$

A plot of $1/\varphi$ against $1/[Q]$ should give an intercept of $1/a$ and a slope of $1/(ak_q^s\tau_s)$. The plot is shown in Figure 2. The line drawn through the points was determined by a least-squares approximation which did not consider the value of φ for 0.1 *M* quencher since the Stern-Volmer plot for tetracene fluorescence quenching showed considerable "static" quenching at this concentration. The intercept divided by the slope gives $k_q^s\tau_s$; the value obtained here is 62.2 which agrees well with the value of 66.6 obtained from the Stern-Volmer plot. The value of a from the reciprocal of the intercept indicates that fewer than 1% of the tetracene singlet exciplexes decay with isomerization of the acceptor.

The striking differences in reactivity of singlet and triplet exciplexes could be attributable to several factors. As mentioned previously, comparison of k_q^s and k_q^t values for different cis-trans pairs of acceptor olefins suggests that the exciplexes have different geometries. It is quite possible that lifetimes for the triplet exciplexes might be considerably longer than those for singlet exciplexes; however, we have no information concerning this since we have been unable to observe either exciplex spectroscopically. Several reports have suggested that triplet biradicals may have much longer lifetimes than corresponding singlet biradicals.[38-40] "Spin memory" effects have also been ascribed to ion-pair and charge-transfer intermediates formed *via* photoassociation.[7] For example, although triethylamine quenches both singlets and triplets of fluorenone with high efficiency *via* charge-transfer complex formation, photoreduction occurs much more

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(39) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

(40) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

efficiently from triplet fluorenone.[41,42] Similar phenomena have been reported for pyrochlorophyll-sensitized photoreduction of nitro compounds in ethanol.[32,43] The fact that exchange of acceptor occurs within the triplet exciplex lifetime suggests that the triplet may be longer lived with perhaps considerable electron localization on the acceptor. Presumably the triplet exciplex comes very close to being an ion pair.

The differences between 4-nitrostilbene and 4,4′-dinitrostilbene as acceptors can be attributed to the greater electron affinity of the latter compound. The k_q values indicate that 4,4′-dinitrostilbene forms both singlet and triplet exciplexes faster than 4-nitrostilbene. The larger α values for the triplet exciplex suggest greater electron localization on the acceptor in the 4,4′-dinitrostilbene complexes.

The differences in reactivity between the various donors are not readily explainable. The failure of tetracene and free base etioporphyrin to form triplet exciplexes is a little surprising. Tetracene has a low ionization potential (6.95 eV)[44] and its excited singlet is clearly more reactive as a donor than the excited singlet of zinc etioporphyrin (Table I). However the triplet energy of tetracene (29.3 kcal/mol)[45,46] is somewhat lower than the *ca.* 40 kcal/mol triplets of the porphyrins. In forming ground state charge-transfer complexes with trinitrobenzene, free-base tetraphenylporphine is much more reactive than the zinc complex.[20] It is tempting to suggest that even though excitation and fluorescence clearly involve π,π^* states of the porphyrin, the metal plays the dominant role in exciplex formation. The effect of pyridine on reactivity of zinc and magnesium porphyrins is even more surprising. Both porphyrin pyridinates form triplet exciplexes with lower k_q^t values than in the absence of pyridine. The drastic reduction in k_q^t for zinc etioporphyrin pyridinate is much too great to be explained as a steric effect since the porphyrin is complexed on only one side. The lowering of k_q^t for magnesium etioporphyrin I pyridinate is less dramatic and it may or may not be related to steric factors or geometry of the magnesium. It is most surprising that pyridine enhances catalysis of acceptor isomerization by zinc but retards the same in the case of magnesium. Here again, exciplex lifetime may be a contributing factor. However, the more than tenfold increase in α, the fraction of exciplexes decaying with acceptor isomerization, indicates that pyridine specifically enhances isomerization. Participation of pyridine by interaction through d orbitals of the zinc may be a possibility, but no simple mechanism can be advanced at this time.

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Molecular Structure of Bicyclo[2.1.0]pentane

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Abstract: The molecular structure of bicyclo[2.1.0]pentane has been determined from electron diffraction studies of the vapor. The cyclobutane ring is planar and the interatomic distances are: C_1–C_4 = 1.439 ± 0.015, C_2–C_3 = 1.622 ± 0.016, C_1–C_2 = 1.543 ± 0.011, C_1–C_5 = 1.521 ± 0.011, and C–H_{av} = 1.121 ± 0.009 Å. The dihedral angle between the two rings is 109.4 ± 0.4° and the average H–C–H angle is 108.8 ± 3.6°. The salient features of the structure are the planar cyclobutane ring, the remarkably short distance, 1.439 Å, for the reactive zero-membered bridge bond, and the long 1.622-Å carbon–carbon bond length opposite the short bond in the cyclobutane ring.

The conformation of a four-membered ring can be puckered or planar. Results of structural studies on many compounds related to cyclobutane have been tabulated by Adman and Margulis.[2] Prior to this study only puckered equilibrium configurations have been observed in free molecules of cyclobutane and derivatives containing neither cyclic nor exocyclic double bonds.[3] In the solid state, some of these molecules have planar rings.[4] It appears likely, however, that the planar conformations are due to a dominance of crystal packing forces over intramolecular forces. On the other hand, four-membered ring compounds containing cyclic or exocyclic double bonds have planar

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