Figure 1. Upfield ^{13}C side band of *trans*-2,3-*trans*-5,6-dioxane-d_4 at $-103°$ (100 MHz, deuterium decoupled, computer enhanced, ten scans), showing the J_{aa} coupling of 11.7 Hz, and the unresolved J_{ee} coupling of $\sim$1 Hz (based on computer simulation).

Surprisingly, and to our delight, at low temperature the center proton resonance had separated into two peaks. This could only arise by the axial and equatorial protons on the carbons bearing deuterium having different chemical shifts, while in dioxane itself the resonances occur at (essentially) identical positions.

Further experiments indicated that in this solvent system at $-104°$, 1,4-dioxane-d_0 has a chemical shift of δ 3.67 while the two peaks of *trans*-2,3-*trans*-5,6-dioxane-d_4 have been shifted upfield to δ 3.66 and 3.63. (At room temperature, the relative shifts are δ 3.61 for dioxane-d_0 and δ 3.58 for the fast-exchange spectrum of the deuterated 1,4-dioxane.) By comparison with the unsymmetrical spectrum of the ^{13}C side band (the unresolved J_{ee} doublet is shifted downfield from the center of the J_{aa} doublet; see Figure 1), and assuming that $J_{^{13}C-H_{ax}} = J_{^{13}C-H_{eq}}$, the resonance at δ 3.66 was assigned to the equatorial protons and the resonance at δ 3.63 to the axial protons.

It now appeared that the inversion barrier could most simply be obtained by observing the changes in the spectrum of dioxane-d_7 with change in temperature. For this purpose dioxane-d_8 was prepared and mass spectral analysis showed the presence of 7% dioxane-d_7. This compound gives a sharp singlet at room temperature (deuterium decoupled), and at $-104°$ it appears as two sharp singlets (deuterium decoupled) with a separation of 3.34 Hz (Figure 2).

By observing the pmr spectrum at various temperatures and subjecting the data to computer analysis,[8] a barrier to inversion of $\Delta G^{\ddagger} = 9.70$ kcal/mol at $-93.6°$ is obtained. This barrier assumes a twist form as intermediate and represents the chair–twist barrier (eq 2).

(8) G. Binsch and D. A. Kleier, Program DNMR 3 obtained from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401.
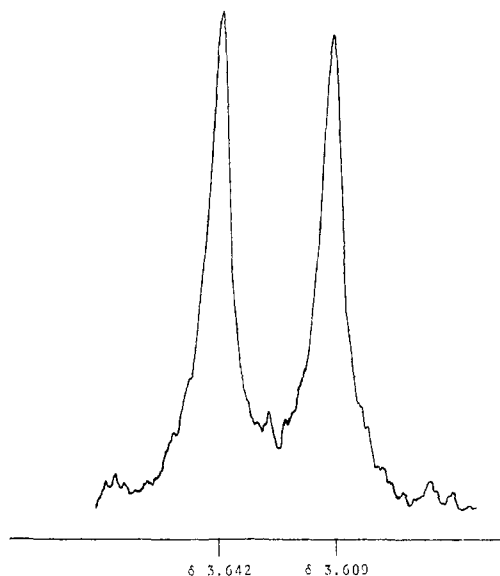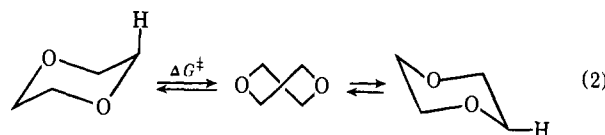

Figure 2. Dioxane-d_7 at $-107°$ (100 MHz, deuterium decoupled, TMS lock), showing the separate resonances of the equatorial (δ 3.642) and axial (δ 3.609) protons.

An effort is underway to determine $\Delta H^{\ddagger}$ for this process. However, it is likely that the major factor contributing to $\Delta S^{\ddagger}$ is the degeneracy of the reaction as is the case for

cyclohexane. A recent calculation of the chair–twist barrier of dioxane yielded a value of $\Delta G^{\ddagger} = 10.1$ kcal/mol.[9]

The magnitudes of the observed coupling constants in the ^{13}C side bands provide compelling evidence that dioxane exists in the chair form. The observed normal barrier for dioxane also supports this belief. X-Ray analysis of crystalline dioxane has previously demonstrated that it exists as the chair form in the solid state.[10]

Acknowledgment. This work was supported by the National Science Foundation under Grant No. GP6350.

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Importance of ^{1}n,π^* States in N-Heterocycles. Internal Conversion, Intersystem Crossing, and Isomerization in Azastilbenes

Sir:

Previously, we reported photoaddition and photoreduction reactions of acridine and 1,2-bispyridylethylenes originating from low-lying ^{1}n,π^* states.[1,2] We now report results which more clearly delineate the

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(2) D. G. Whitten and Y. J. Lee, *ibid.*, **93**, 961 (1971).

Table I. Quantum Efficiencies for Fluorescence, trans → cis Isomerization, and Photoreduction for 1,2-Bispyridylethylenes[a]
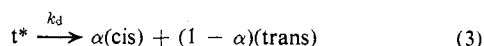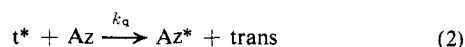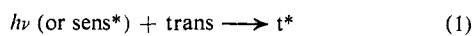
Compound	Process	Benzene	Methyl-cyclohexane	Solvent 2-Propanol	tert-Butyl alcohol	Acetonitrile-Water[b]
4,4'BPE	$\phi_{t \to c}$	0.003	0.005	0.04	0.08	0.25
	ϕ_f	0.0004	0.0004	~0.0004	~0.0004	~0.0004
	ϕ_{red}		0.0004	0.02		
3,3'BPE	$\phi_{t \to c}$	0.1		0.23	0.24	0.38
	ϕ_f	0.04		0.12	0.14	0.12

[a] Degassed solutions, $\lambda = 313$ nm, olefin concentration 0.005 M. [b] 70% acetonitrile by volume.

role of $^1n,\pi^*$ states for the bispyridylethylenes and stilbazoles. Evidence is presented suggesting that rates of internal conversion from $^1\pi,\pi^*$ states to $^1n,\pi^*$ states in N-heterocyclic compounds may depend on nitrogen placement in aromatic skeletons in a predictable manner.

Three processes occur on direct irradiation of trans isomers of azastilbenes (stilbazoles and 1,2 bispyridylethylenes): fluorescence, trans → cis isomerization, and photoreduction reactions. Triplets of these compounds undergo only trans → cis isomerization. Table I compares quantum efficiencies for the various processes in several solvents for 1,2-bis(4-pyridyl)ethylene (4,4'BPE) and 1,2-bis(3-pyridyl)ethylene (3,3'BPE). Fluorescence shows only slight solvent effects. In contrast, photoreduction occurs with measurable efficiency only for 4,4'BPE and only in solvents having readily donatable hydrogen atoms. Both compounds show increased isomerization efficiencies with increasing solvent polarity; however, the increase is much greater for 4,4'BPE. Isomerization yields for 4,4'BPE are lower in 2-propanol, where reduction occurs, than in tert-butyl alcohol, where no reduction occurs, suggesting that the state responsible for reduction precedes the isomerizable species.

Studies of the differential quenching of direct and sensitized photoisomerization of stilbene have been used by Saltiel[3,4] to demonstrate that stilbene isomerizes by separate singlet and triplet paths and that intersystem crossing to the triplet is unimportant. Selective quenching of trans to cis isomerization by azulene (where only one state is involved) can be described by

$$h\nu \text{ (or sens*)} + trans \longrightarrow t^* \qquad (1)$$

$$t^* + Az \xrightarrow{k_q} Az^* + trans \qquad (2)$$

$$t^* \xrightarrow{k_d} \alpha(cis) + (1 - \alpha)(trans) \qquad (3)$$

where sens* = excited sensitizer and t^* = a common olefin excited state or isomerization precursor which normally decays via (3) but is quenched by azulene to trans olefin. From these equations, the usual Stern–Volmer relationship (eq 4) can be derived. Azulene

$$\phi_{t \to c}^0/\phi_{t \to c} = 1 + (k_q/k_d)[Az] \qquad (4)$$

quenching of sensitized isomerization of bispyridylethylenes[5] in tert-butyl alcohol yie'ds good linear plots whose slopes (k_q/k_d) are 250 and 280 M^{-1} for 3,3'BPE and 4,4'BPE, respectively. Direct isomerization quan-

tum yields also yield good linear plots for azulene quenching; slopes are 90 and 70 M^{-1} for 3,3'BPE and 4,4'BPE, respectively. Examination of kinetic possibilities for isomerization[7] indicates the linear plots of eq 4 for direct isomerization with smaller slopes than obtained for the corresponding sensitized isomerization can be accounted for only by a singlet path for direct isomerization. Therefore, we conclude that for 3,3'-BPE and 4,4'BPE, as with stilbene, intersystem crossing does not occur on direct irradiation.

Investigation of the isomerization path leads to different results for the two azastilbenes. For stilbene, azulene quenching likely involves long-range energy transfer from the fluorescent singlet.[3] Theoretical and experimental treatments for stilbene yield values for R_0, the distance at which the transfer rate equals the normal decay rate, of 16 Å.[3] For 4,4'BPE, where the fluorescence yield is low and the corresponding decay rate very high,[6] the theoretical $R_0 = 7$ Å in tert-butyl alcohol.[8] However, the slope for azulene quenching is much larger than that for stilbene, and the experimental relationship ($R^0 = 6.32(k_q/k_d)^{1/3})^9$ yields $R_0 = 26$ Å, far from the value predicted for the fluorescent singlet. For 4,4'BPE, isomerization likely proceeds via internal conversion of the fluorescent state to a $^1n,\pi^*$ state and subsequent activated conversion to a twisted $^1\pi,\pi^*$ state which decays with isomerization. Quenching of the fluorescent state is probably unimportant; however, quenching of the $^1n,\pi^*$ state competes with isomerization. Polar solvents could increase energy of $^1n,\pi^*$ states, lowering the activation energy to the twisted $^1\pi,\pi^*$ state. The finding that fluorescence efficiency of 4,4'BPE increases little (less than five times) on changing from a fluid solution (25°) to a glass (77°K) in EPA reinforces this scheme.

Apparently the isomerizat on precursor for 3,3'BPE is the fluorescent singlet. The relatively high efficiencies for fluorescence in all solvents (comparable to stilbene) suggest radiationless decay to the $^1n,\pi^*$ state is rather inefficient. The low reduction yields support this result. Theoretical ($R_0 = 20$ Å) and experimental ($R_0 = 28$ Å) values for R_0 for azulene quenching are in reasonable agreement. In contrast to results with 4,4'BPE but in agreement with stilbene results,[10] isomerization and fluorescence are evidently coupled for 3,3'BPE. Changing from fluid solution (25°) to a glass (77°K)

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(4) J. Saltiel, ibid., 89, 1036 (1967); 90, 6394 (1968).
(5) Quantum yields are obtained using benzophenone-1,2-diphenyl-propene–azulene solutions as actinometers.[6]
(6) D. G. Whitten and M. T. McCall, J. Amer. Chem. Soc., 91, 5097 (1969).

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in EPA raises the fluorescence quantum efficiency for 3,3'BPE to unity.

The remaining isomeric 1,2-bispyridylethylenes and 2- and 4-stilbazole show behavior similar to that of 4,4'BPE on direct irradiation; fluorescence yields are low,[6] and decay via a lower energy $^1n,\pi^*$ state is suggested by photoreduction reactions and/or low cis–trans isomerization efficiencies. The only azastilbene behaving similarly to 3,3'BPE is 3-stilbazole, which, like 3,3'BPE, has nitrogen only in a position meta to the ethylenic linkage. CNDO and INDO calculations suggest that nitrogen location causes little difference in energies of n,π^* excited states for isomeric stilbazoles and 1,2-bispyridylethylenes.[11,12] However, both the highest bonding π MO's as well as the lowest antibonding π MO's of stilbene and the azastilbenes (those involved in π,π^* excitation) have near nodes at the 3 or meta position (coefficients from HMO calculations on stilbenes: π, 0.079; π^*, 0.079;[13] these are similar to coefficients from CNDO and INDO calculations).[12] The location of nitrogen at a near node in the π MO may possibly render the n,π^* excited states inaccessible from the initially formed $^1\pi,\pi^*$ state. Rates of radiationless decay are predicted to depend on an electronic integral between the initial and final states;[14] therefore, it is reasonable that for N-heterocycles with nitrogen at a near node in the π MO, the electronic integral $\beta_{el} = \langle\psi_{\pi,\pi^*}|H'|\psi_{n,\pi^*}\rangle$[14] is small enough to reduce rates of radiationless interconversion.[15,16]

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(15) To test the hypothesis, we have carried out INDO calculations on the 1-, 2-, and 3-azaphenanthrenes (nitrogen occurs at a near node in 2-azaphenanthrene). While the results are not as gratifying as hoped, the direction of fluorescence yields is roughly in line with the hypothesis. Since several additional factors could influence both radiationless decay as well as fluorescence yields (e.g., vibronic coupling, lifetime of the $^1n,\pi^*$ state, and reversible population of the $^1\pi,\pi^*$ state), it is not at all clear that a quantitative correlation would be expected.

(16) Support of this work by the Army Research Office (Durham) (Grant No. DA-AROD-31-124-G1097) and the Research Corporation is gratefully acknowledged.

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Iron(IV) Porphyrins

Sir:

Tetravalent heme iron has been evoked[1] to explain the course of oxidation in catalase, horse radish peroxidase, and cytochrome-c peroxidase. Recently it was proposed[2] that the catalytically active primary compounds of catalase and horse radish peroxidase are π-cation radicals of Fe(IV) porphyrins. We now show that stable, one-electron oxidation products of ferric por-

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(2) D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, Proc. Nat. Acad. Sci. U.S., 68, 614 (1971).

phyrins can be prepared, and that the oxidation is best characterized as electron abstraction from the metal in contrast to removal of an electron from the porphyrin π system.

Cyclic voltammetry of tetraphenylporphyrin iron-(III) chloride, FeTPPCl, or octaethylporphyrin iron-(III) chloride, FeOEPCl, in dichloromethane–tetrapropylammonium perchlorate (TPAP) solutions showed reversible one-electron oxidation to occur at $\epsilon_{1/2} = 1.13$ and 0.99 V vs. sce (aqueous), respectively. One-electron, reversible half-wave potentials at $\epsilon_{1/2} = 0.84$ and 1.09 V were observed for the dimer, μ-oxo-bis-(tetraphenylporphyrin iron(III)),[3] $(FeTPP)_2O$, and at $\epsilon_{1/2} = 0.66$ and 0.96 V for μ-oxo-bis(octaethylporphyrin iron(III)), $(FeOEP)_2O$.

Controlled potential electrolyses of the ferric porphyrins were carried out at the plateau of their first oxidation wave. Spectral changes occurring during oxidation are shown in Figures 1 and 2. Simultaneous coulometry indicated that one-electron oxidations had taken place: 1.0 ± 0.1 electron per FeTPPCl or FeOEPCl, or per $(FeTPP)_2O$ or $(FeOEP)_2O$ dimer. The parent iron(III) porphyrins were recovered in yields exceeding 95% by either electrochemical or iodide reduction. In CH_2Cl_2 the oxidized ferric porphyrins decay at a rate of a few per cent per hour. The oxidized $(FeTPP)_2O$ was isolated in crystalline form as the perchlorate salt (ClO_4^- ir absorptions[4] at 1090 and 620 cm^{-1} in KBr) by washing the solid isolated from the electrolysis with boiling water to remove TPAP and then with benzene to remove the parent compound. The crystalline solid $(FeTPP)_2O^+,ClO_4^-$ redissolved in CH_2Cl_2 exhibited a polarographic reduction potential of 0.84 V and a spectrum identical with that of Figure 2, thus demonstrating that no change had occurred during isolation. The presence of positive charge was established by a moving boundary experiment performed as previously described.[5]

The pmr spectrum of $(FeTPP)_2O$ was compared with that of the isolated oxidized material. In the former compound two resonances were observed: a broad ($\sim$50 Hz) signal at 13.6 ppm downfield from TMS[6] and a resonance at 7.6 ppm with width $\sim$20 Hz. Relative intensities are 1:2.5, and we assign[7] them to β-pyrrole and phenyl protons, respectively. At 40° the oxidized dimer in $CDCl_3$ displayed absorptions (widths) at 3.4 ($\sim$25 Hz), 11.4 ($\sim$25 Hz), and 12.2 ppm ($\sim$50 Hz). Relative intensities are approximately 1:1.5:1. As the concentration ratio of oxidized porphyrin to parent porphyrin was decreased by addition of iodide, the 11.4- and 3.4-ppm lines coalesced into the 7.6-ppm resonance of $(FeTPP)_2O$, and the 12.2- ppm resonance moved to 13.6 ppm. The pmr spectra are consonant with a fast electron exchange between $(FeTPP)_2O^+$ and $(FeTPP)_2O$ giving rise to a number-averaged spectrum. In accord with these data, the following assignments of the $(FeTPP)_2O^+$ lines are made: β-pyrrole protons,

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