J. Am. Chem. Soc. 1982, 104, 253-259

Quenching of the Singlet Excited States of Meso-Substituted Porphines by *p*-Benzoquinone under Unimolecular and Bimolecular Conditions: Evidence for Electron Transfer in Competition with Vibrational Relaxation

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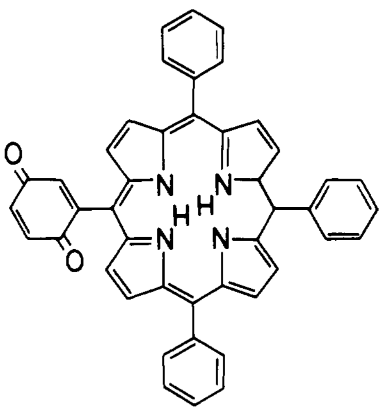
Abstract: Picosecond absorption spectroscopy was used to investigate the singlet excited-state (S_1) relaxations in two meso-substituted porphines, triphenyl(*p*-benzoquinone)porphine (P_3QP) and tetrakis(*p*-benzoquinone)porphine (Q_4P), and in solutions of *meso*-tetraphenylporphine with added amounts of *p*-benzoquinone. P_3QP and Q_4P have observable S_1 states with lifetimes of <6 ps which decay exclusively to triplet excited states (T_1) and ground states (S_0). The T_1 states decay in $\sim$30 ps to yield both long-lived triplet biradicals ($\tau > 5$ ns) and S_0 states. Since $\sim$90% of the T_1 states decay to ground states before forming relaxed electron-transfer (ET) products, reverse ET from a vibrationally unrelaxed triplet biradical to S_0 levels in competition with continued relaxation of the triplet biradical seems indicated. To the extent the rapid decay of the S_1 states results from ET to form a singlet biradical, the formation of T_1 states is also likely to result from a reverse ET while the singlet biradical is vibrationally relaxing. A working model of the multiple ET steps involved is proposed to summarize the above results and to guide future studies of unimolecular ET processes.

I. Introduction

Numerous flash kinetic studies have shown quinones to be facile electron acceptors.[1-11] In addition they are known to be intermediates in photosynthetic electron-transport chains.[12-14] Recently researchers[15-17] have linked quinone electron acceptors to porphyrin and chlorophyll electron donors to model the dynamics of photosynthetic electron transfers. The general conclusion of extensive studies of the quenching of excited states of porphyrins and chlorophylls by added quinones and nitroaromatic molecules is that ionic photoproducts can be observed when the quenching reaction proceeds from a triplet (T_1) excited state, but not when it proceeds from a singlet excited state (S_1).

It has been proposed[1,18,19] that the singlet states are quenched by the production of singlet radical pairs, but that the spin-allowed recombination of the electrons and holes exceeds their rate of dissociation. Thus ionic photoproducts are not seen. Triplet states, however, are quenched by the formation of triplet radical pairs. Apparently their spin-forbidden electron-hole recombination rate is less than their dissociation rate and ionic photoproducts are observable. In striking contrast to this behavior, recent studies[20,21] of a cofacial diporphyrin comprised of Mg-substituted and free-base subunits (Mg–H_2) have provided evidence of a <6 ps intramolecular ET reaction. The $Mg^{+}\cdot$–$H_2^{-}\cdot$ photoproduct is formed from the diporphyrin's S_1 state, yet it is stable for 0.2–1.3 ns depending on the solvent.[21]

The recent synthesis[22] of free-base porphyrins with either one or four *p*-benzoquinones substituted at the meso positions affords the possibility of studying the quenching of porphyrin excited states unencumbered by the diffusional and configurational uncertainties which plague bimolecular quenching studies. This paper reports the results of our picosecond spectroscopic investigation of these molecules. We also compare these results to those obtained for bimolecular quenching of the excited states of *meso*-tetraphenylporphine with various amounts of added *p*-benzoquinone.



I

II. Experimental Procedures

Modification of *meso*-tetraphenylporphine (TPP), which is being described elsewhere,[22] yielded *meso*-triphenyl(*p*-benzoquinone)porphine (P_3QP) as shown in structure I. Similarly[22] the three phenyl groups in I were replaced with *p*-benzoquinones (BQ) to yield *meso*-tetrakis(*p*-benzoquinone)porphine (Q_4P). The BQ (Aldrich) used for bimolecular quenching was purified by vacuum sublimation. Iodobenzene (Aldrich) was redistilled prior to use and stored in the dark. *N*,*N*-Dimethylform-

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amide, DMF (Aldrich), was purified[23] immediately prior to use and methylene chloride (Aldrich reagent grade) was used without purification.

Absorption spectra were measured on Cary 14 and Cary 17 spectrophotometers. Emission spectra and fluorescence quantum yields were measured on a Perkin-Elmer MPF-4 spectrofluorimeter equipped with a Hamamatsu R-446 multialkali photomultiplier tube and an automatic emission corrector. Fluorescence quantum yields were measured in deaerated, dilute solutions (absorbance <0.08 cm^{-1}) and are relative to a yield of 0.13 for TPP in deaerated benzene.[3,24] Fluorescence lifetimes were measured for deaerated samples in stoppered 2-mm path length cells. The emission was detected from the front surface of the sample with a Varian VPM-152 photomultiplier tube coupled to a 7A19 amplifier in a Tektronix 7844 oscilloscope. The response time of this system to a 6-ps laser pulse was 0.8 ± 0.2 ns. Red filters (Hoya O-56 and R-60) were used to discriminate against scattered 527-nm excitation light.

For picosecond kinetic measurements of change-in-absorbance (ΔA) spectra, the samples were degassed with three freeze-pump-thaw cycles and sealed in 2-mm path length cells. These samples were excited at 527 nm with a 6-ps laser pulse and the ΔA spectra of the resulting photoproducts were measured with an 8 ps (fwhm) white probe pulse. The entire system has been described elsewhere.[25]

The effects of time dispersion in the white probe pulse are important for several excited states in these systems because of their very short lifetimes ($\tau < 25$ ps). It is known that light of shorter wavelength travels more slowly in dense media such as water and glass than does light of longer wavelength. In other words if light at 775 nm is coincident in the sample with the excitation pulse, light at 600 nm will not get to the sample for several more picoseconds. In our apparatus there is about 1 ps of delay for each 35 nm of spectral increment in the 550–775-nm region. These delays are not significant for optical transients with lifetimes >25 ps. We have adopted the procedure of specifying the time of arrival of the 775-nm light at the sample relative to the excitation pulse. Negative time means that the 775-nm light arrived before or during the excitation pulse, while positive time means that it arrived after the excitation pulse. In order to tell the arrival time of any other wavelength, the delay at that wavelength must be added to the 775-nm arrival time. For example a ΔA spectrum labeled –4 ps is probing the 600-nm region + 1 ps after excitation.

III. Results

Previous studies[26-28] have shown that the quenching of the excited states of porphyrins and chlorophylls depends on the reduction potentials of the added electron acceptors. Similarly one-electron oxidation and reduction data for diporphyrins were shown to provide good estimates of the free energy, $\Delta E_{1/2}$, required to form intramolecular ET products from the diporphyrin's ground state.[20,21] The data in Table I compare singlet excited-state energies with estimates of $\Delta E_{1/2}$ for producing an ET product in P_3QP, Q_4P, and the molecular pair TPP/BQ.[29] In each case the S_1 states have 300 meV more energy than is required to drive an internal electron transfer to form an oxidized porphyrin and a reduced quinone. However, the energy stored in the T_1 state of TPP is nearly the same as the $\Delta E_{1/2}$ energies. In fact the results below show that the T_1 states of the molecular systems in Table I can be quenched in ≤100 ps. This suggests that the T_1 states are somewhat higher in energy than the ET product states.

Table I

molecular system	energy, eV		$\Delta E_{1/2}$,[b] eV
	S_1[a]	T_1	
TPP/BQ[c]	1.89	1.45[d]	1.58
P_3QP	1.80		1.49
Q_4P	1.77		[e]

[a] Energy of the lowest-energy ground-state absorption band about 20% up the long wavelength edge. [b] Estimated free-energy change for forming $TPP^{+}\cdot/BQ^{-}\cdot$ and $P_3Q^{-}\cdot P^{+}\cdot$ from their respective ground states. It was calculated from the following one-electron reductions in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate: $TPP^{+}\cdot/TPP$, $P_3QP^{+}\cdot/P_3QP$, $BQ/BQ^{-}\cdot$, and $P_3QP/P_3Q^{-}\cdot P$. [c] A pair of electron donor and acceptor molecules. [d] Reference 19. [e] Reversible cyclic voltamograms could not be obtained.

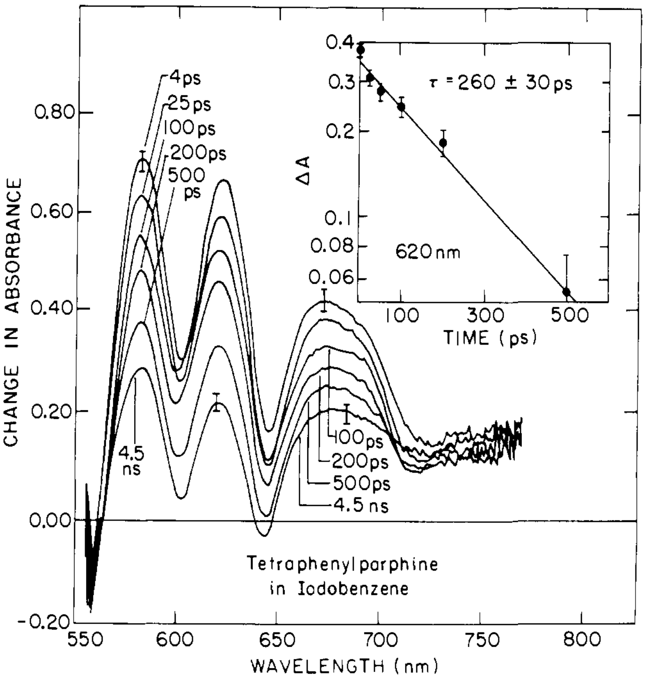

Figure 1. Change-in-absorbance spectra for 6 × 10^{-4} M TPP in iodobenzene. The errors in ΔA are the standard deviations of the mean ΔAs from a set of 15–20 ΔA measurements at each of the indicated times after excitation.

1. **TPP.** The fluorescence quantum yield ($\Phi_f = 0.13$) measured for TPP in CH_2Cl_2 is the same as that reported for TPP in toluene,[3] ethanol,[3] and deaerated benzene.[24,30] Solov'ev et al.[31,32] have determined the triplet quantum yield (Φ_T) of free base TPP to be 0.87. Therefore the sum of fluorescence and triplet quantum yields is near or equal to unity, a common occurrence for many aromatic molecules.[33] The fluorescence lifetime for TPP in CH_2Cl_2 is 6.3 ± 0.3 ns. In iodobenzene the low fluorescence quantum yield, $\Phi_f = 4 \times 10^{-3}$, is ascribed to a heavy-atom effect similar to that reported for several other porphyrins.[31,34,35] If the rate of radiative decay (k_f) in iodobenzene and CH_2Cl_2 is the same, the S_1 lifetime should be 0.20 ± 0.03 ns in iodobenzene. This value agrees well with the 0.26 ± 0.03 ns decay lifetime of the initial absorbance increase shown in Figure 1 for TPP in iodobenzene. Thus switching solvents has not significantly changed k_f for the

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Table II

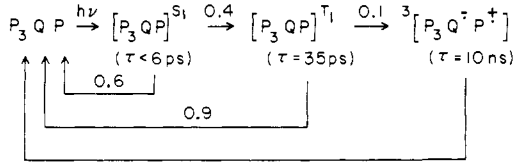
molecular system	τ_{S_1}	Φ_F[a]	$Y_T(\pm0.1)$	τ_{T_1}, ps	$Y_{ET}(\pm0.01)$[b]	τ_{ET}, ns
TPP in CH_2Cl_2 + 0.0 M BQ	6.3 ± 0.3 ns[c]	0.13	0.87[d]			
+ 0.03 M BQ	2.3 ± 0.2 ns[c,e]	0.03	0.3[f]			
+ 0.3 M BQ	<6, 20 ± 10ps[g,h]		0.7[f]	860 ± 30	0.05	>5
+ 1.0 M BQ	<6 ps[g]		0.5[f]	105 ± 15	0.05	>5
P_3QP in CH_2Cl_2	<6 ps[g]	7 × 10^{-4}	0.4[f]	35 ± 5	0.04	10 ± 3
in DMF	<6 ps[g]		0.4[f]	34 ± 10	0.03	>15
Q_4P in CH_2Cl_2	<6 ps[g]	<5 × 10^{-5}	0.45[f]	20 ± 9	0.06[i]	>5
in DMF	<6 ps[g]		0.5[f]	15 ± 10	0.04	>15
TPP in iodobenzene	260 ± 30 ps[g]	4 × 10^{-3}	1.0[d]	>15[j]		

[a] Based on a reported value of 0.13 for Φ_F of TPP in benzene (ref 24 and 30). [b] Based on a molar absorptivity of 1 × 10^4 M^{-1} cm^{-1} (±20%) for TPP^+ in the 670-nm region (ref 37). [c] Emission decay measurement. [d] $\Phi_F + \Phi_T = 1$ (ref 24, 30, 31, and 32). [e] A small number of the S_1 states (<10%) decayed with a lifetime of 20 ± 10 ps. [f] Based on reported values of the molar absorptivity of the T_1 state of TPP (ref 36). [g] Lifetime obtained from the decay of an absorption transient. [h] ~50% of the absorbance increase due to S_1 states decayed during photolysis. [i] ±0.02. [j] ns.

S_1 state of TPP. Holten et al.[1] reported, in their study of bacteriopheophytin in (7/3) acetone/methanol and in methyl iodide, that switching to methyl iodide increased the triplet quantum yield from 0.54 to 0.91 without affecting the radiationless decay rate (k_{nr}) of S_1 to the ground state. If this is also true for TPP, the triplet yield in iodobenzene must be >0.99. These results are collected in Table II.

The most significant result of this experiment is the clear view of the ΔA spectra of the S_1 and T_1 states of TPP. The lack of absorbance increase at 642 nm agrees with the work of Pekkarinen and Linschitz[36] which showed that the S_0 and T_1 states of TPP have nearly the same molar absorptivity (ϵ) in this region. This feature makes it possible to distinguish clearly the several intermediates observed in the quenching experiments (see below).

2. P_3QP. The ΔA spectra produced during and after excitation of P_3QP in CH_2Cl_2 are shown in Figure 2. A large absorption increase is present during excitation (−8- and −4-ps spectra) in the 640-nm region. The state present immediately after excitation (+4-ps spectrum) does not absorb more than the ground state in this region. Comparison of these results with those for TPP in iodobenzene (Figure 1) shows that the state of P_3QP observed during laser excitation is its S_1 state (0.5 ps < τ < 4 ps) and the state populated after excitation is its T_1 state. The similarities of the ground-state absorption and excited-state difference spectra for P_3QP and TPP show that the perturbation of the low-energy TPP states in P_3QP due to the bound BQ is small and that the S_1 and T_1 states of P_3QP are overwhelmingly TPP in character. This conclusion is also supported by the observation that the fluorescence spectra for P_3QP and Q_4P are identical with that for TPP. To the extent the ϵ of T_1 in P_3QP is the same as that of TPP in toluene,[36] the yield of T_1 (Y_T) can be calculated to be 0.4 ± 0.1. Surprisingly the T_1 state of P_3QP has a lifetime of only 35 ± 5 ps. The broad absorbance increase corresponding to the formation of a decay product of the T_1 state is consistent with the formation of a free-base porphyrin radical cation such as $TPP^{+}\cdot$.[37] Bridge and Porter[6] have shown that the semiquinone radical ions ($Q^{-}\cdot$) of several substituted BQ molecules do not absorb appreciably beyond 500 nm. Therefore the decay of T_1 appears to produce $P_3Q^{-}\cdot P^{+}\cdot$. The ϵ for $TPP^{+}\cdot$ in this spectral region[37] is ~1 × 10^4 M^{-1} cm^{-1} (±20%). Thus the yield of $P_3Q^{-}\cdot P^{+}\cdot$ (Y_{ET}) is estimated to be 0.04 ± 0.01. The lifetime of the biradical, $P_3Q^{-}\cdot P^{+}\cdot$, is 10 ± 3 ns. Since it is formed from a T_1 state it is probably a triplet itself ($^3[P_3Q^{-}\cdot P^{+}\cdot]$ or $^3[^{+}\cdot{}^{-}\cdot]$). These kinetic pathways are summarized in eq 1.



$$P_3QP \xrightarrow{h\nu} [P_3QP]^{S_1} \xrightarrow{0.4} [P_3QP]^{T_1} \xrightarrow{0.1} {}^3[P_3Q^{\overline{\cdot}}P^{\dot{+}}] \qquad (1)$$

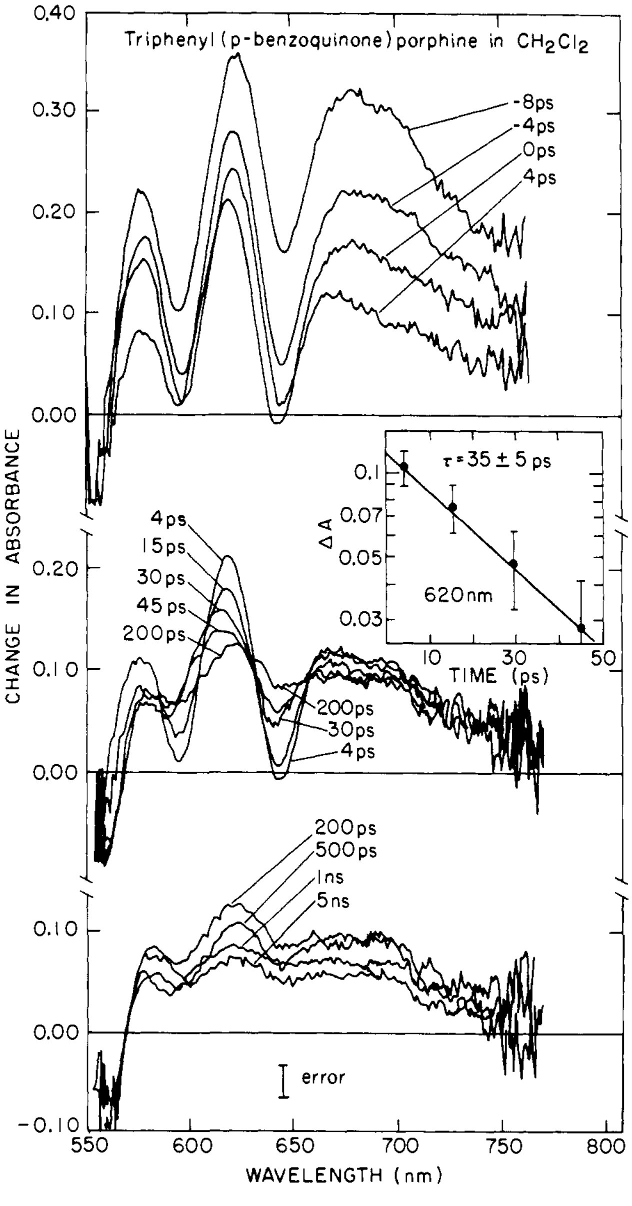


Figure 2. Change-in-absorbance data at the indicated times after excitation for 4.6 × 10^{-4} M P_3QP in CH_2Cl_2. Negative time refers to measurements during photolysis. See the text for a discussion of time dispersion effects for short-lived transients.

The photochemistry of P_3QP in *N,N*-dimethylformamide (DMF) is summarized in Table II. The patterns of reactivity found in DMF and CH_2Cl_2 differ only in that the final product's lifetime in DMF is increased to ≫15 ns. A similar stabilization of a biradical ET product was found for a Mg–H_2 diporphyrin

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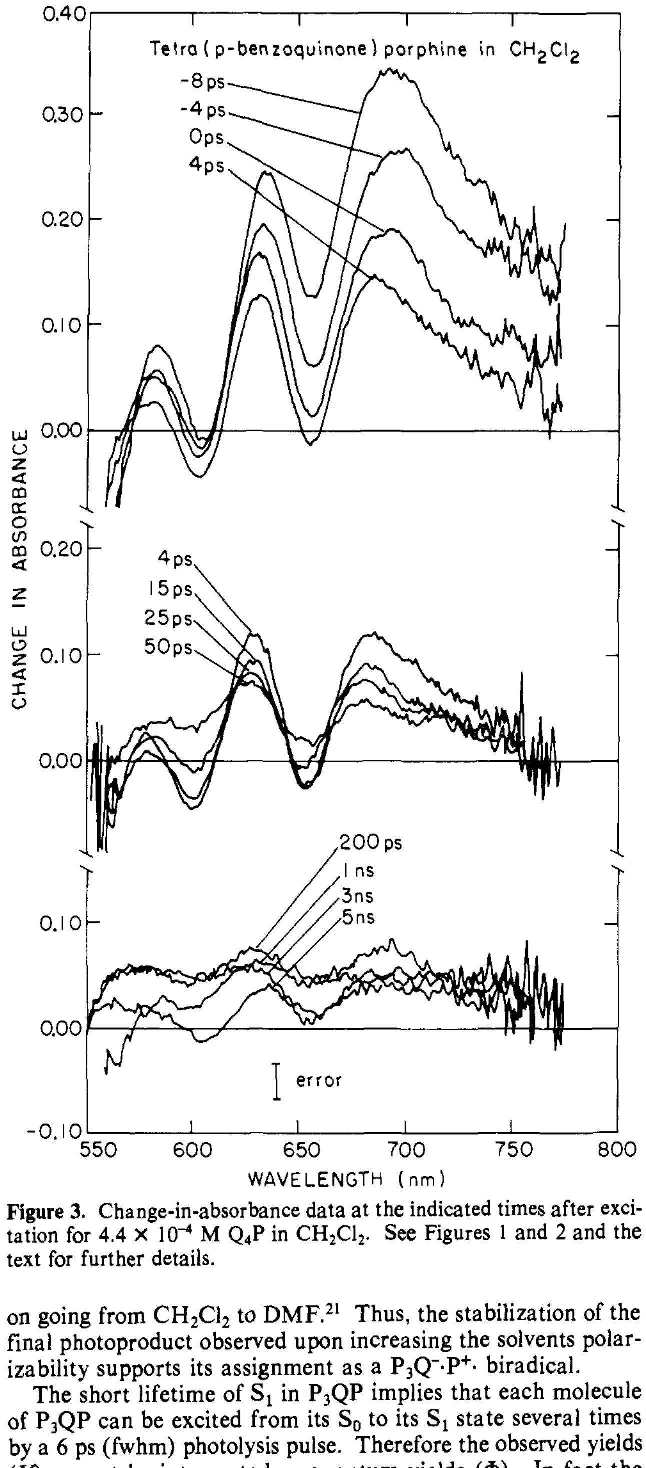

Figure 3. Change-in-absorbance data at the indicated times after excitation for 4.4 × 10^{-4} M Q_4P in CH_2Cl_2. See Figures 1 and 2 and the text for further details.

on going from CH_2Cl_2 to DMF.[21] Thus, the stabilization of the final photoproduct observed upon increasing the solvents polarizability supports its assignment as a $P_3Q^{-}\cdot P^{+}\cdot$ biradical.

The short lifetime of S_1 in P_3QP implies that each molecule of P_3QP can be excited from its S_0 to its S_1 state several times by a 6 ps (fwhm) photolysis pulse. Therefore the observed yields (Y) cannot be interpreted as quantum yields (Φ). In fact the shortest S_1 state lifetimes consistent with the ready observation of S_1 are also consistent with a Φ_T as low as 3–5%. In contrast, the longest S_1 state lifetimes consistent with the decay of S_1 during the pulse imply that the upper range of Φ_T values is 15 to 20%. The particular Y_T and Y_{ET} values reported in this work are a consequence of our photolysis pulse energy and the true triplet quantum yields of the complexes studied.

A word of caution should be mentioned concerning the biradical description, $[^{+}\cdot{}^{-}\cdot]$, of the final photoproduct. Since the ionic components are close to each other, their electron exchange interaction may be large enough to split the $^1[^{+}\cdot{}^{-}\cdot]$ and $^3[^{+}\cdot{}^{-}\cdot]$ levels as much as 0.1–0.2 eV. Also, other molecular excited states (such as the nearly isoenergetic T_1 state of TPP) may be mixed with the biradical states. However, the $[^{+}\cdot{}^{-}\cdot]$ label will be useful as long as it is remembered that it may not be a complete description of the states of the electron-transfer product.

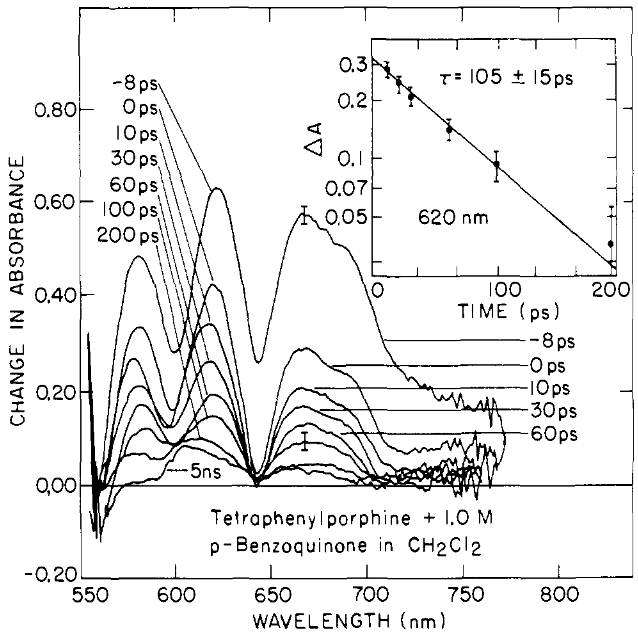

Figure 4. Change-in-absorbance data at the indicated times after excitation for 5.7 × 10^{-4} M TPP in CH_2Cl_2 with 1.0 M *p*-benzoquinone. See Figures 1 and 2 and the text for further details.

3. **Q_4P.** The fluorescence quantum yield of Q_4P in CH_2Cl_2 is <5 × 10^{-5}. The ΔA spectra obtained after exciting Q_4P (Figure 3) show that the same states found after photoexciting P_3QP are also seen here: S_1, observed during the pulse (τ < 6 ps); T_1, observed after the excitation pulse (τ = 20 ± 9 ps), and $Q_3Q^{-}\cdot P^{+}\cdot$. The lifetimes and yields of these states are summarized in Table II. Also, exciting Q_4P in DMF produces essentially the same results as in CH_2Cl_2, including a low yield of a long-lived ET product (τ > 15 ns).

It is important to note that the kinetic data for P_3QP and Q_4P clearly show that the ET products are formed from T_1 states. Yet, the lifetimes of both the S_1 and T_1 states are quenched relative to their values in TPP. Also, since the longest lived photoproducts are the $^3[P_3Q^{-}\cdot P^{+}\cdot]$ and $^3[Q_3Q^{-}\cdot P^{+}\cdot]$ biradicals, it is reasonable to assume that they are lower in energy than the T_1 states. These biradicals last sufficiently long that they may be in thermal equilibrium with the T_1 levels. Although the precise free-energy differences are unknown, they appear to be large enough (>50 meV) to significantly favor population of the biradical ET products over the T_1 levels.

4. **TPP + BQ.** P_3QP and Q_4P offer the advantage of a known structure and therefore freedom from configurational and diffusional ambiguities that complicate analogous bimolecular quenching reactions. However, it is worth discovering whether their excited-state dynamics are uniquely their own or are also typical of the bimolecular quenching of porphyrin excited states by added quinones. The ΔA spectra obtained after exciting TPP with 1.0 M BQ in CH_2Cl_2 are shown in Figure 4.

A transient absorption due to the S_1 state of TPP is seen during photolysis. An absorption due to the T_1 state is seen immediately after photolysis; its lifetime is 105 ± 15 ps. Thus the excited-state kinetics observed for P_3QP and Q_4P are nearly reproduced. The data in Table II show that the yields of the various photoproducts are also similar for the unimolecular and bimolecular systems. Finally, the ΔA spectra in Figure 4 for times >200 ps show a broad absorbance characteristic of $TPP^{+}\cdot$ formation; its lifetime is >5 ns. This absorbance appears to grow in at 642 nm after the T_1 state is formed as was the case for P_3QP and Q_4P.

As the concentration of added BQ is reduced, both the S_1 and T_1 lifetimes of TPP increase (see Table II). With 0.03 M BQ, the S_1 state lifetime (τ = 2.3 ± 0.2 ns) measured by emission spectroscopy agrees well with the lifetime measured by absorption spectroscopy. The intersystem crossing rate (1.3 × 10^8 s^{-1}) for this case is about the same as that of TPP without added BQ (1.4

$\times 10^8\ s^{-1}$). Thus dynamic quenching of S_1 returns it predominantly to the ground state. In contrast, the static quenching of S_1 with 1.0 M BQ added and the internal quenching in P_3QP and Q_4P populate both T_1 and ground-state levels in nearly equal amounts. This apparent mechanistic difference between the two types of quenching is most likely due to the fact that complexes with S_1 state lifetimes (τ_s) <6 ps can build up T_1 photoproducts due to multiple excitations of their ground states during photolysis while those with $\tau_s > 30$ ps cannot. While dynamic quenching predominates for TPP with 0.03 M BQ, the nonhomogeneous nature of the solution is reflected in the fact that a small fraction (<10%) of TPP excited-singlet states are quenched with a lifetime of 20 ± 10 ps. For TPP with 0.3 M BQ, about half of the absorbance increase due to S_1 states decays during photolysis with time <6 ps; the remainder decays after photolysis with time of 20 ± 10 ps.

IV. Discussion

Several studies of the quenching of porphyrin and chlorophyll S_1 and T_1 states by added quinones and nitroaromatics have demonstrated that the amount of quenching is a strong function of the reduction potential of the added quencher.[27,28] When T_1 states are quenched, yields of ionic products as high as 50–60% are observed[3] in solvents with dielectric constants above ~10. When S_1 states are quenched, ionic products are not observed.[1,2] The proposed S_1 state quenching mechanism[1,18,19] involves formation of a singlet radical pair, ${}^{1}[{}^{+}\cdot{}^{-}\cdot]$. Presumably the reason ionic products are not observed is that the spin-allowed recombination of the opposite charges in ${}^{1}[{}^{+}\cdot{}^{-}\cdot]$ is much faster than their rate of separation. The S_1 state quenching data reported here are consistent with this mechanism, but also show that triplet states can be produced in competition with S_0 formation during the charge recombination of ${}^{1}[{}^{+}\cdot{}^{-}\cdot]$. This latter step appears to provide a demonstration of ET in competition with continued vibrational relaxation (see below).

If a critical nuclear displacement coordinate can be defined such that motions along it govern the observed ET reactions, only this dimension of the relevant potential energy surfaces need by explicitly discussed. One goal of ET studies on unimolecular complexes is to explore the appropriateness of such an approximation. With this in mind, it is useful to discuss the excited-state dynamics of P_3QP and Q_4P in terms of a likely arrangement of potential-energy curves. This serves not only to summarize current experimental results but also to guide future experiments.

The primary experimental observations to be modeled are the following: (1) <6 ps production of only T_1 and S_0 states; (2) a measurable T_1 lifetime of ~30 ps; (3) an ET product yield of ~10% from T_1; and (4) a final ET product whose lifetime is >5 ns.

Four mechanisms could produce the very short S_1 and T_1 lifetimes observed in P_3QP and Q_4P: (1) energy transfer from porphyrin states to BQ states and back to lower porphyrin states; (2) mixing BQ states with porphyrin states to provide fast radiationless decay routes; (3) spin orbit (SO) coupling of ${}^{1}(\pi,\pi^*)$, ${}^{3}(\pi,\pi^*)$, and S_0 porphyrin states due to quinone attachment; and (4) quenching due to formation of biradical intermediates.

Energy transfer from the porphyrin S_1 (1.8 eV) and T_1 (1.5 eV) states to the lowest BQ states is too endothermic to be important. The lowest BQ excited states are (n,π^*) type and the ${}^{1}(n,\pi^*)$ level is 2.6 eV in solution.[38] If the S_1–T_1 separation in solution is similar to its gas-phase value,[39] 0.17 eV, the ${}^{3}(n,\pi^*)$ level of BQ should be ~2.4 eV. These energy differences between the BQ and porphyrin levels also appear large enough to prevent them from mixing.

If the short S_1 and T_1 lifetimes of the (π,π^*) levels of P_3QP are due to increased SO coupling, the similar results for the bimolecular quenching of the excited states of TPP by BQ would have to be explained in the same way. Yet, it seems unlikely that collision with BQ would induce more SO coupling than that induced by using iodobenzene as a solvent. In iodobenzene, the S_1 state of TPP still lasted 260 ps and its T_1 state longer than 15 ns (Table II). Also relevant are studies of the S_1 and T_1 quenching of porphyrins by quinones which show that the efficiency of the process depends on the ease of reduction of the quinone and on the ease of oxidation of the porphyrin.[26-28] This result is unexpected if quenching collisions are inducing a large SO coupling among the porphyrin's states, but is expected if the quenching is due to ET and the formation of radical pair intermediates. We therefore feel that the most reasonable explanation for the shortness of the lifetimes of the S_1 and T_1 states of P_3QP and Q_4P is the rapid creation of biradical ET products. The fact that the S_1 state is shorter lived than the T_1 state is consistent with the ET reaction from S_1 being ~0.4 eV more exothermic than the one from T_1.

Figure 5 presents a model of excited-state interactions in P_3QP that is consistent with the above data. The minima of the S_1 and T_1 potential-energy curves are shown as only slightly displaced relative to that of the S_0 curve, because the Stokes shift between the fluorescence and absorption maxima is small for porphyrins[24,40] and because the nuclear arrangements for the porphyrin singlet and triplet (π,π^*) states should be similar.[41] In contrast, a large nuclear displacement is shown for the formation of the ET product $P_3Q^{-}\cdot P^{+}\cdot$ (symbolized as ${}^{1,3}[{}^{+}\cdot{}^{-}\cdot]$). This displacement arises predominantly from reduction of the quinone rather than oxidation of the porphyrin. X-ray[42] and Raman[43] measurements on neutral and ionic porphyrins show that their bond lengths, bond angles, and frequencies are very similar. However, reduction of quinones is thought to cause significant nuclear changes.[18,44] The energy of the singlet level was determined from absorption data (see Table I).[29] The energy of the T_1 state of TPP is 1.45 eV,[19] a value which we use for the T_1 state of P_3QP as well. Finally, electrochemical measurements show that the free energy required to form $P_3Q^{-}\cdot P^{+}\cdot$ from P_3QP, $\Delta E_{1/2}$, is about 1.49 eV. The quenching results for this compound suggest that the actual energy of ${}^{3}[P_3Q^{-}\cdot P^{+}\cdot]$ is below that of the T_1 state.

If all of the T_1 levels are quenched by biradical formation, the conclusion that S_0 is populated by reverse ET from unrelaxed biradical states is inescapable since the relaxed triplet biradical lives >5 ns and T_1 states last only ~30 ps. As discussed above, no other mechanism for shortening the T_1 lifetime appears reasonable. The assumption that all of the S_1 levels are quenched by biradical formation is insufficient to conclude that S_0 is populated by reverse ET from an unrelaxed ${}^{1}(P_3Q^{-}\cdot P^{+}\cdot)$ intermediate since the lifetime of the relaxed ${}^{1}(P_3Q^{-}\cdot P^{+}\cdot)$ product is unknown. However, the reasonable assumptions that the minima of the singlet and triplet biradical potential-energy curves have nearly the same nuclear configuration and that the S_1, T_1, and S_0 porphyrin states are nested make population of T_1 by ET from an unrelaxed biradical during the decay of S_1 as likely as a similar population of S_0 during the decay of T_1 (see above).

The individual steps in the excited-state relaxations shown in Figure 5 are given in eq 2–6. α, β, and γ are ET product yields; open arrows indicate a spin-allowed ET; hatched arrows indicate a spin-forbidden ET; solid arrows indicate continued vibrational relaxation; and $[{}^{+}\cdot{}^{-}\cdot]'$ represents a vibrationally unrelaxed biradical. The ET in reaction 2 may be activationless since S_1 can only be observed during laser excitation. However, the possibility of ET from unrelaxed vibrational levels of S_1 cannot be ruled out until experiments with longer wavelength photolysis pulses ($h\nu \sim 1.9$ eV) are done. Given the extremely short singlet state lifetime and

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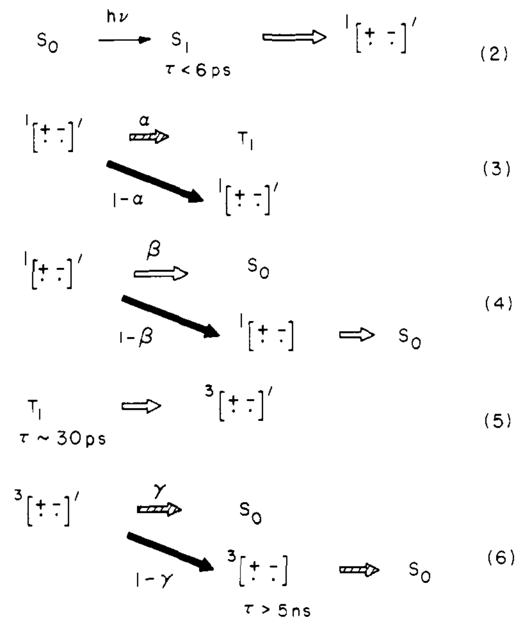

the finite triplet yield, all of the relaxations in reactions 3 and 4 have rates $>2 \times 10^{11}$ s^{-1}. Reactions 3, 4, and 6 each have steps that involve ET in competition with continued vibrational relaxation. Jortner has recently developed a theoretical description of ET reactions whose rates are faster than medium-induced vibrational relaxation times and noted that his description is similar to models developed earlier to explain fluorescence quenching of the excited electronic states of F centers in solids.[45]

The observation that α is greater than zero suggests than an unequilibrated distribution of T_1 sublevels may be produced by the decay of S_1. The short lifetimes of the T_1 states of P_3QP and Q_4P in CH_2Cl_2 preclude epr studies of them. However, we have found that the T_1 state of P_3QP in (7/3) acetone/methanol solution is formed in high yield in <6 ps and persists for >15 ns. Thus epr investigations of this system's T_1 state may be possible. The observation of polarized electron (or possibly polarized nuclear) resonances would strongly support the above described quenching mechanism.

The measurable lifetime of the T_1 state in reaction 5 is probably due to a nuclear barrier. As noted above, the reduction of the quinone is expected to require nuclear reorganization. After $^3[^{+\cdot,-\cdot}]$ is formed, it crosses the S_0 potential energy curve (Figure 5, panel II, and reaction 6) as it vibrationally relaxes. In spite of the fact that ET to the S_0 curve is spin forbidden, the low yield of relaxed $^3[^{+\cdot,-\cdot}]$, ~0.05, implies that γ in reaction 6 is ~0.9. The long lifetime of the relaxed $^3[^{+\cdot,-\cdot}]$ is probably a consequence both of a nuclear barrier and reduced electronic coupling between it and the S_0 state. Temperature-dependence studies may be able to measure the magnitudes of the kinetic barriers in reactions 5 and 6. Also, it will be interesting to see if changing the temperature will affect the ET yields, α, β, and γ.

V. Conclusion

The attachment of BQ directly to a free-base porphyrin to form P_3QP and Q_4P affords an opportunity to examine quenching of porphyrin excited states without the complications of diffusional processes. Comparing the excited-state relaxations in P_3QP and Q_4P to those observed for bimolecular quenching of TPP excited states by added BQ shows no differences except those ascribable to diffusion. The quenching of S_1 states to yield some T_1 states and a much larger number of S_0 states is readily explained in terms of the rapid formation and decay of a singlet biradical ET product. For P_3QP and Q_4P, the T_1 states live for ~30 ps (see Table II) before producing triplet biradical ET products. However, the yield of relaxed triplet biradicals is only ~0.05. This implies that ~90% of the T_1 states decay to the ground state first. This latter step appears to involve ET from an unrelaxed triplet biradical to the S_0 potential energy surface in competition with continued vibrational relaxation of the triplet biradical (see the spin-forbidden ET step in reaction 6).

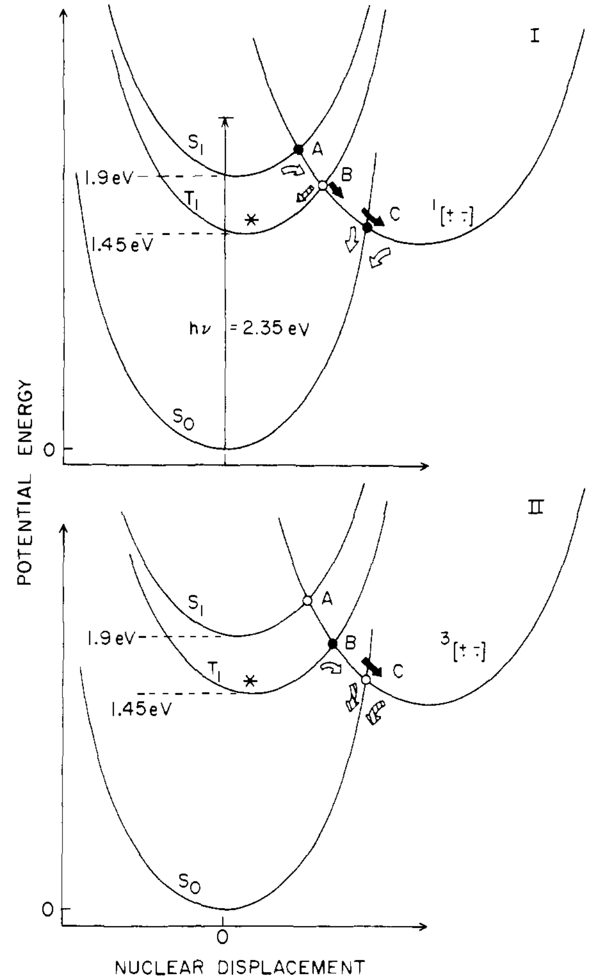

Figure 5. An arrangement of potential energy curves consistent with the ET reactions and excited-state quenchings observed in P_3QP and Q_4P: solid circle, a spin-allowed electronic coupling; open circle, a spin-forbidden electronic coupling; open arrow, a spin allowed ET; hatched arrow, a spin forbidden ET; solid arrow, continued vibrational relaxation; asterisk, population of T_1 states formed in panel I and relaxing in panel II; A, B, and C, electronic coupling regions; $h\nu$, a photon.[29]

Future studies involving modifications of the quinone or porphyrin chromophores in P_3QP can explore whether or not the production of T_1 states is a general phenomenon or due to the near degeneracy of the T_1 and biradical levels in this system. For example, MgTPP is 0.5 eV easier to oxidize than TPP.[19] Presumably the $\Delta E_{1/2}$ for ET in P_3Q(MgP), *meso*-triphenyl(*p*-benzoquinone)porphinatomagnesium(II), would be similarly smaller than the $\Delta E_{1/2}$ for ET in P_3QP. Also, substituting another electron acceptor for BQ (e.g., naphthoquinone) may alter the nuclear displacements between the potential-energy curve for the ET product and those for the porphyrin's S_1 and S_0 states.

Study of the ET pathways in unimolecular complexes such as P_3QP and Q_4P can provide insight into the relative importance of the key factors known to govern ET reactions: electronic couplings, electron vibration couplings (nuclear displacements), and free-energy differences.[44-47] Study of similar systems as functions of structure, redox parameters, and temperature offers hope of providing a refined picture of ET reactions suitable for

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testing ET theories.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences (Contract No. DE-AC02-76CHE00016) at Brookhaven National Laboratory. We would also like to thank Drs. J. Fajer and I. Fujita for advice and assistance in making the electrochemical measurements.

Registry No. I, 79664-53-2; TPP, 917-23-7; BQ, 106-51-4; Q_4P, 72695-45-5.

Antiallergenic 8-Azapurines. 3. Structural Characterization of 2-(2-Propoxyphenyl)-8-azahypoxanthine, 2-(2-Propoxy-5-(propylsulfonyl)phenyl)-8-azahypoxanthine, and 2-(2-Propoxy-5-(*N*-methyl-*N*-isopropylsulfamoyl)phenyl-8-azahypoxanthine

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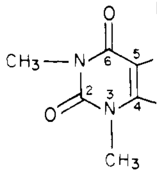
Abstract: The crystal and molecular structures of 2-(2-propoxyphenyl)-8-azahypoxanthine, $C_{13}H_{13}N_5O_2$, 2-(2-propoxy-5-(propylsulfonyl)phenyl)-8-azahypoxanthine methanolate, $C_{16}H_{19}N_5O_4S\cdot CH_4O$, and 2-(2-propoxy-5-(*N*-methyl-*N*-isopropylsulfamoyl)phenyl)-8-azahypoxanthine, $C_{17}H_{22}N_6O_4S$, have been determined from three-dimensional counter X-ray data using Mo Kα radiation. The 2-propoxyphenyl compound crystallizes in the orthorhombic space group *Pnma* with four molecules in a cell of dimensions a = 9.293 (2) Å, b = 6.671 (2) Å, c = 21.020 (7) Å; the structure has been refined to a final value of the conventional R factor (on F) of 0.043 based on 1029 independent intensities. The propylsulfonyl derivative, which crystallizes with 1 mol of methanol/mol of purine in the monoclinic space group $P2_1/c$ with four molecules in a cell of dimensions a = 12.521 (15) Å, b = 5.816 (8) Å, c = 28.388 (40) Å, β = 108.21 (5)°, has been refined to an R factor of 0.105 based on 918 observations. The *N*-methyl-*N*-isopropylsulfamoyl derivative also crystallizes in space group $P2_1/c$ with four molecules in a cell of dimensions a = 12.129 (8) Å, b = 10.680 (9) Å, c = 16.958 (11) Å, β = 116.74 (4)° and has been refined to an R factor of 0.050 based on 1771 observations. In the 2-propoxyphenyl and propylsulfonyl derivatives, the entire ring systems are held approximately planar (exactly planar in the former case) by a strong N(1)–H···O(2) intramolecular hydrogen bond, where O(2) is the oxygen atom of the propoxy group. In the *N*-methyl-*N*-isopropylsulfamoyl derivative, the purine and phenyl rings are inclined at an angle of 52.6°. The 2-propoxy and *N*-methyl-*N*-isopropylsulfamoyl derivatives are present as the N(9)–H tautomers, but the propylsulfonyl compound exhibits the N(8)–H tautomer. CNDO/2 molecular orbital calculations show that, in all three cases, atom N(3) is very electron rich while the triazole atoms have smaller residual charges.



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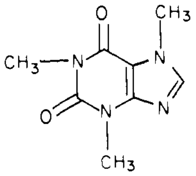

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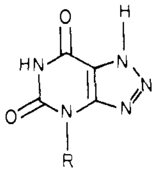

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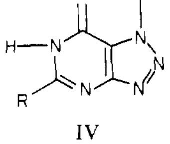

IV

As a result of the discovery that common methylxanthines such as theophylline (I) and caffeine (II) show certain antiallergic properties,[2] efforts are being made to determine the structural basis for the biochemical properties of these compounds in order to facilitate the production of more potent antiallergic drugs.[3,4] Substitution of a nitrogen atom for the carbon atom in the 8-position of the imidazole ring to yield 8-azaxanthines (III) has been shown to consistently increase the potency of the drugs with respect to their xanthine analogues;[5] this observation is especially true with bulky substituents at the 3-position of the pyrimidine ring. Numerous 8-azahypoxanthines with exocylic substituents at the 2-position of the pyrimidine ring (IV) were examined,[3-5] and the compounds with the most potent antiallergic properties were found to be those with ortho-substituted phenyl groups at C(2). It has been postulated that activity of the drugs is increased when the 2-substituent contains a group that is capable of forming a hydrogen bond to the N(1)–H group of the purine ring.[3,4] In order to test this hypothesis, we have undertaken the X-ray crystallographic investigation of three compounds of type IV, 2-(2-propoxyphenyl)-8-azahypoxanthine (V), 2-(2-propoxy-5-(propylsulfonyl)phenyl)-8-azahypoxanthine (VI), and 2-(2-propoxy-5-(*N*-methyl-*N*-isopropylsulfamoyl)phenyl)-8-azahypoxanthine (VII), all of which show marked antiallergenic activity.[4] We also anticipated that this study would provide us with additional information on the relative basicities of the nitrogen atoms

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