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Electronic Spectroscopy of *trans*-Styrylpyridines and Their Conjugate Acids[1]

Sir:

The electronic spectra of the three isomeric *trans*-styrylpyridines and their conjugate acids (referred to as *n*-StP and *n*-StPH$^+$, respectively, where $n = 2$, 3, or 4) show unusual and hitherto unexplained characteristics.[2-9] We report the results of a new theoretical investigation which support the hypothesis that the bases possess a low-lying $^1n\pi^*$ state.[5,6,8] Our results also indicate that the common assumption that only the $n\pi^*$ states of N heteroaromatics are strongly affected by protonation is not valid for these systems. In particular, protonation changes the lowest $^1\pi\pi^*$ state from an "ethylenic" state into a "charge-transfer" state.

The absorption spectra[2] of these systems appear to be characterized by a strong "ethylenic" band and one or two weaker bands in the same spectral region. Trans-cis isomerization follows excitation to the singlet and triplet manifolds.[3-9] The trans isomers fluoresce with a quantum yield that is strongly system and temperature dependent.[4-6,8] *trans*-3-StP is unusual in that its absorption and fluorescence excitation spectra are different and its isomerization quantum yield is wavelength dependent across the principal absorption band.[9] At least two electronic band systems overlap in this region and the corresponding states appear to be noncommunicating. 3-StPH$^+$ is exceptional in exhibiting fluorescence that is relatively long lived and nonethylenic.[7]

We calculated the spectra of these systems using the all-valence-electron CNDO/S MO model.[10] Pedersen et al.[11] and Distefano et al.[12] have reported CNDO/2 and CNDO/S calculations, respectively, for the bases. Unlike the latter authors, we used the Mataga-Nishimoto[13] formula instead of the Pariser-Parr formula[14] to evaluate the interatomic repulsion integrals because the former locates the singlet states more accurately.[10c] We extended the CNDO/S model to the StPH$^+$'s and performed a complete configuration interaction (CI) calculation between the (49) singly excited $^1\pi\pi^*$ states and a separate CI calculation between the 49 lowest $^1\sigma\pi$ singly excited states.

The calculated absorption spectra are depicted in Figure 1 as vibrationless line spectra superimposed on observed spectra. Observable transitions are indicated by full lines and transitions too weak to show by arrows. Broken arrows denote $^1\sigma\pi$ transitions which are forbidden in the CNDO approximation. Part of the observed spectrum for 3-StPH$^+$ corresponds to a weak, poorly resolved absorption band constructed with reference to the emission spectrum.[7] The lowest $^1\sigma\pi$ state of the StP's is $^1n\pi^*$ in character. The red shift predicted to accompany protonation is overestimated by ~0.4 eV. Similar results have been obtained for the cations of phenazine by Chalvet et al.,[15] who report improved agreement with experiment when the isolated species are replaced by cations hydrogen bonded to water molecules.

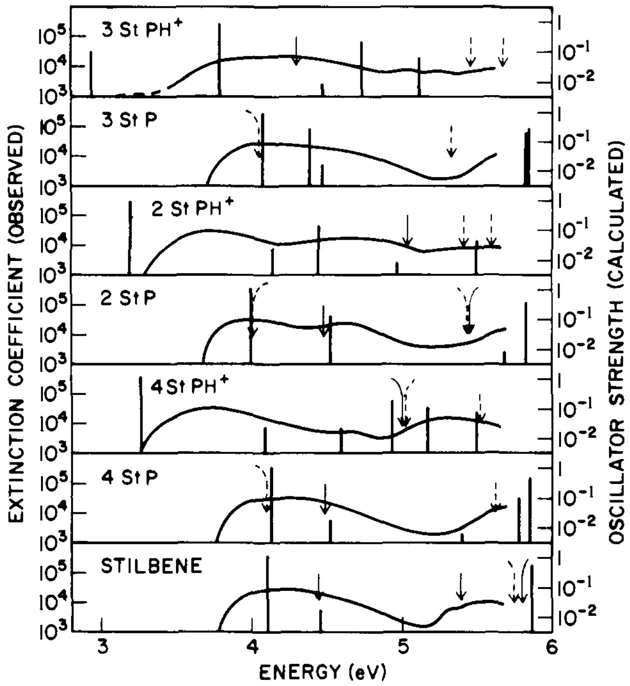

Figure 1. Calculated and observed absorption spectra of stilbene, the three isomeric styrylpyridines, and their conjugate acids. Vertical lines and arrows represent calculated vibrationless line spectra; arrows refer to weak or forbidden transitions. Full and broken arrows denote $^1\pi\pi^*$ and $^1\sigma\pi$ transitions, respectively. The observed spectra are low-resolution, room-temperature spectra taken from the literature.[2-9]

The present CNDO/S model supports the suggestion[5,6,8] that the StP's possess low-energy $^1n\pi^*$ states. These states are calculated to be almost degenerate with the lowest $^1\pi\pi^*$ state, but the accuracy of the model is such that their order in each isomer remains somewhat equivocal.[5,6,8,9,12] The model accounts for the close similarity between the spectra of 4-StP and stilbene, for the emergence of a second strong absorption band at ~4.4 eV in 2-StP, and for the observation[9] of another such band strongly overlapping the first band of 3-StP. It identifies the excited states associated with these transitions in 2- and 3-StP as $^1\pi\pi^*$ states and thus supports Bartocci and Mazzucato's contention that the 3-StP state which they designated S_3 is a $^1\pi\pi^*$ state.[9]

The model is particularly successful in explaining the differences between the spectra of the StPH$^+$'s. The moderate red shift of the principal absorption band, which apparently accompanies protonation of 2- and 4-StP, is replaced in 3-StP by the emergence of a new, much weaker band near 3.3 eV.[7] Protonation of the pyridine ring shifts its MO's to much lower energies. All the π MO's of the StPH$^+$'s, unlike those of stilbene and the StP's, are therefore (1) almost entirely localized on one ring or (2) mainly localized on one ring and one or both of the carbon atoms of the central bond. The wave functions of the lower excited states are dominated by a single configuration. Transitions to these states correspond to a transfer of an electron from the benzene to the pyridinium moiety that is modulated to a greater or lesser degree by the central bond. The final orbital in the lowest energy transition can be de-

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scribed in a first approximation as the lowest unoccupied (LU) MO of the pyridinium ion. However, the replacement of a CH group by an NH^+ group is such a strong perturbation that it imposes local "C_{2v}" symmetry on the levels of the substituted ring. Since there is a near node at the meta position in the LUMO of the pyridinium ion, only the 2 and 4 isomers are able to mix a significant contribution from the π orbitals of the central bond into their LUMO's. The lowest energy transition is therefore strong in both 2- and 4-$StPH^+$, but weak in 3-$StPH^+$.

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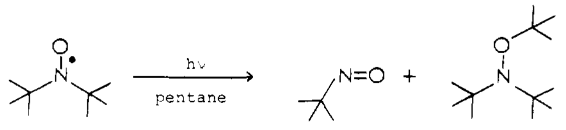
Electron-Transfer Photochemistry of Di-*tert*-butyl Nitroxide

Sir:

Although nitroxides, especially di-*tert*-butyl nitroxide (DTBN), have been extensively investigated as quenchers of electronically excited species, little is known about their photochemical reactivity. We have previously shown that DTBN is inert in its n,π^* doublet state and is reactive in its π,π^* doublet state.[1] When the π,π^* doublet state is populated by irradiation at 254 nm in pentane solvent, DTBN cleaves to *tert*-butyl radical and 2-methyl-2-nitrosopropane ($\phi_{\text{destruction}} = 0.21$). The *tert*-butyl radical is scavenged by DTBN to give



di-*tert*-butyl-*tert*-butoxyamine. Two modes of photochemical reactivity of some cyclic nitroxides, hydrogen atom abstraction[2-4] and fragmentation[5] with loss of nitric oxide, have also been reported.

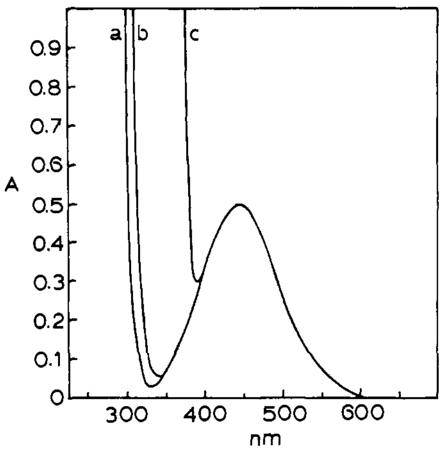
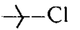


Figure 1. UV-visible absorption spectra of 0.05 M di-*tert*-butyl nitroxide in (a) pentane or methylene chloride, (b) chloroform, and (c) carbon tetrachloride solvents.

Table I. Observed and Calculated Quantum Yields

product	observed quantum yield[a]	quantum yield expression[b]	calculated quantum yield
	0.30	$\beta(1-\alpha)$	
	0.85	$\beta(1+\alpha)$	0.85
1	0.56	β	0.58
2	0.27	$\alpha\beta$	0.27
isobutylene	0.55	$2\alpha\beta$	0.54

[a] Quantum yields were measured at 366 nm with a 0.10 M solution of DTBN in argon degassed carbon tetrachloride. [b] The symbol α = 0.47 represents the fraction of di-*tert*-butyloxoammonium chloride which decomposes to isobutylene and hydrogen chloride. The symbol β = 0.58 represents the quantum yield of reaction of the charge transfer excited state (see Scheme I).

We now report that di-*tert*-butyl nitroxide weakly interacts by contact charge transfer[6] with carbon tetrachloride and that irradiation of the DTBN-CCl_4 charge-transfer band results in very efficient one-electron transfer to carbon tetrachloride.

The UV-visible spectrum of di-*tert*-butyl nitroxide in pentane solvent shows an n-π^* band at 460 nm (ϵ 8.9) and a π-π^* band at 238 nm (ϵ 2580).[7] A 0.05 M solution of DTBN in pentane solvent is almost transparent in the region between 310 and 370 nm. A 0.05 M solution of DTBN in carbon tetrachloride solvent, however, shows appreciable absorption in the 310–370 nm region in addition to the n-π^* band at 460 nm (see Figure 1). In methylene chloride solvent there is no additional absorption in the 310–370 nm region relative to pentane solvent, and in chloroform solvent there is an intermediate level of absorption in this region. We attribute the additional absorption in the region 310–370 nm to a contact charge-transfer interaction.[6] Contact charge transfer between nitroxides and halocarbons has also been observed by ^{13}C NMR spectroscopy.[8]

Irradiation of the n-π^* band of a 0.10 M solution of DTBN in carbon tetrachloride solvent results in no destruction; however, irradiation at 313 or 366 nm in the contact charge-transfer region results in efficient destruction of DTBN ($\phi_{\text{destruction}} = 1.7$). The products of the photoreaction are 2-methyl-2-nitrosopropane, isobutylene, *tert*-butyl chloride, di-*tert*-butyltrichloromethoxyamine (**1**), and di-*tert*-butylhydroxylammonium chloride (**2**). Hexachloroethane is not formed, and the solution is not significantly paramagnetic upon completion of the reaction. The products together with their quantum yields of formation are summarized in Table

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