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PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF STERICALLY HINDERED ARYLDIAZONIUM SALTS

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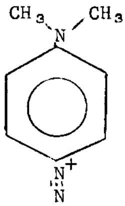
Aryldiazonium salts are unique chemical systems. The diazonium moiety, $-N{\equiv}N^+$, is the most electron withdrawing substitutent known.[1] This electron withdrawing power is reflected in the strong substitutent sensitivity of the electronic absorption spectrum,[2] the N-N stretching frequency[3-5] as well as chemical reactivity of substituted benzenediazonium cations.[3] Analyses of these structural effects on both electronic and vibrational spectra have lead to the conclusion[4-8] that the quinoid structure Ia plays a dominate role in the ground state of 4-dimethylaminobenzenediazonium cation. Although x-ray data on the corresponding dimethylaminonitrobenzene (DMN)[9] indicate some quinoid structure in the ground state the effect of sterically twisting the dimethylamino group is to produce a blue shift in the electronic absorption maxima of lowest singlet-singlet transition.[10,11] This is most easily interpreted from 1st order perturbation theory[12] by assuming that the C-N (aryl-amino) bond order is larger in the excited state than the ground state. In order to determine whether I is uniquely different than DMN the 3-methyl, 3-ethyl, 3-propyl, 3-t-butyl, and 3,5-dimethyl derivatives of I were prepared by standard methods[2] and the UV-Visible and IR spectra determined (see Table). As part of studies on the primary photochemical processes in aryldiazonium cations, as yet inadequately investigated,[13] we have determined the quantum yield-wavelength dependency of these materials. These yields (see Table) were unaffected by the presence or absence of O_2. The quantum yields of substances I, II, and VII were the same in aqueous 2 M NaBr as in water. Neither fluorescence or phosphorescence (ice, -196°) was observed for substances I-VII.[14]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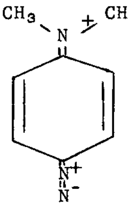
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Table

ABSORPTION SPECTRA AND QUANTUM YIELD DATA ON SUBSTANCES I-VII

Benzenediazonium Salt	λ_{max}[d]	ϵ_{max}	ν_{N-N} (cm^{-1})[e]	Quantum Yield,[f] 25°		
				365 mμ	405 mμ	435 mμ
I. 4-N-dimethylamino[a,b]	378	36,100	2171	0.57[g,h]	0.44	--[i]
II. 4-N,N-diethylamino[b]	378	40,200	--	0.50[g,h,j]	0.44	--
III. 3-methyl-4-N,N-dimethylamino[b]	393	34,000	2186	0.47	0.55	0.45
IV. 3-ethyl-4-N,N-dimethylamino-[c]	394	32,400	2187	0.51	0.48	0.42
V. 3-propyl-4-N,N-dimethylamino-[c]	397	29,600	2193	--	--	--
VI. 3-t-butyl-4-N,N-dimethylamino-[b]	406	17,600	2220	0.42	0.45	0.32
VII. 3,5-dimethyl-4-N,N-dimethylamino-[c]	425	26,900	2204	0.34	0.31	0.23[g]

a) ½$ZnCl_2$ salt; b) BF_4 salt; c) ½$SnCl_2$ salt; d) H_2O; e) dimethylsulfoxide; f) determined in water by the literature method (ref. 24) using ferrioxalate actinometry, extinction coefficients and narrow band pass (5 mμ , monochrometer-1 KW Xe-Hg arc) at each wavelength, values rechecked using thermopile and compounds II and VII as standards, estimated relative values across entire Table reproducible to ±0.02 units in water and 0.1 N H_2SO_4; g) values in 2M NaBr (aqueous) identical ±0.01 units; h) reported yields 0.58 (ref. 4, 380 mμ), ca. 0.5 (ref. 15, 365 mμ) and 1.00 (?) (ref. 16); i) yields at various wavelengths are 0.54 (350 mμ), 0.46 (380 mμ), and 0.24 (445 mμ), in water (ref. 17); j) 0.50 (380 mμ) water, (ref. 18).

As seen by inspecting the above Table steric distortion of structures VI and VII is reflected in the shift of the N-N stretching frequency from I. In contrast to the sterically hindered 4-dimethylaminonitrobenzenes, the corresponding diazonium cations exhibit a red shift in the lowest observed electronic transition. Although the IR data are inconclusive, the behavior of the electronic absorption maxima and intensities of substances I-VII supports the idea that the aryl-amino C-N bond order is higher in the ground state than the excited state.

The interpretation of the structural and wavelength dependency of the quantum yield is less clear. Although the latter phenomena has been mentioned for diazonium salts[17,19,20] no documentation has been published. Both the lack of luminescence and absence of bromide quenching or quantum yield enhancement indicate extremely rapid photochemical and other nonradiative processes. The quantum yield-wavelength dependency is interpretable within the context of the crossing of bonding and repulsive potential energy surfaces. The surface crossing of the pi-pi* electronic states[2] (singlet or triplet) by higher energy states can be argued from additional pieces of information and orbital symmetry analysis. It has been shown that the substituent effects on the ground state solvolysis of benzenediazonium cations are interpretable within the context that the final sigma aryl cation is biradial in nature[21] resulting from the demotion of one of the pi-electrons into the empty sp^2 orbital. Energetically this demotion is favored by the fact that the valence state ionization potential of the pure p-electron (11.16 ev) is considerably lower than the sigma orbital (15.62 ev) in the $trtrtr\pi$ configuration.[22] Thus, in the gas phase, the ground state of the aryl cation, C_6H_5+, should be biradical in character having nearly degenerate singlet and triplet states. If the N_2 moiety departs in a manner retaining the planar symmetry for the aryl-$\overset{+}{N_2}$ unit simple orbital symmetry arguments dictate that the ground state of the aryl cation (singlet or triplet) is adiabatically correlated with the corresponding sigma-pi* and pi-sigma* excited states (singlet or triplet) of the aryldiazonium cation (assuming that the released N_2 is in the ground electronic state). Conversely, the ground and excited singlet and triplet pi-pi* states of the aryldiazonium cation are correlated with the excited pi-states of the aryl cation. Involvement of water or departure of the N_2 in a non-planar fashion may generate non-crossing of these curves (of appropriate multiplicity). Thus, qualitatively, the potential energy surfaces for both thermal and photolytic decomposition of aryldiazonium cations should exhibit complex crossing patterns which could conceivably generate the effects observed. The non-unities of the quantum yields are indicative of return to the ground state of the diazonium salts by one or more non-radiative processes. How much of this return is due to partitioning along different directions of the potential energy surfaces of the type described above or through unspecified intermediates as proposed by Lewis and coworkers[23] cannot be stated at this time. Our results do indicate that for the materials investigated bromide ion is not kinetically involved with either the electronically excited diazonium cation or any possible intermediate which may return to the ground state of that ion. In analogous cases halide ion is involved in a competitive manner in determining product composition.[23] We are presently studying this and related problems connected with the surface hypothesis stated above.

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