Factors affecting the Photochemistry of Piperidinoanthraquinones

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Summary The longest-wavelength absorption bands of unprotonated piperidinoanthraquinones are charge-transfer in type, but on protonation of 1-piperidinoanthraquinone the band becomes $n \rightarrow \pi^*$, accompanied by marked differences in photosensitizing behaviour between unprotonated and protonated forms.

WE describe experiments with 1- and 2-piperidinoanthraquinones which show that the nature of the lowest-lying excited-state can be an important factor in determining differences in the photosensitizing properties of these compounds.[1,2]

The Table gives the maxima of the longest-wavelength bands observed with solvents of differing polarity. Similar red shifts with increasing solvent polarity were observed by Yoshida and Takabayashi[3] with other substituted aminoanthraquinones. By analogy with substituted benzophenones,[4] these longest wavelength bands appear to be

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intramolecular charge-transfer (C-T) in type. The red band of 1-piperidinoanthraquinone is not observed in aqueous–alcoholic solutions of pH *ca.* 0·5 whereas, under the same conditions, the band of the 2-piperidinoanthraquinone remains unchanged. In propan-2-ol–water (3 : 2 by volume) we find a pK value of 3·1 for the equilibrium between unprotonated and protonated forms of 1-piperidinoanthraquinone. The longest wavelength band of the protonated form (λ_{max} = 405 nm) has the typical features of an $n \rightarrow \pi^*$ band found, for example, with the anthraquinone sulphonates.[5]

TABLE

Solvent	1-Piperidino-anthraquinone λ_{max} (nm.)	2-Piperidino-anthraquinone λ_{max} (nm.)
Carbon tetrachloride ..	506	446
Propan-2-ol	515	468
4 : 1 Propan-2-ol–water ..	523	478
3 : 2 Propan-2-ol–water ..	527	484

This difference in the character of the longest-wavelength bands was paralleled by a substantial increase in the photosensitizing behaviour of 1-piperidinoanthraquinone in its protonated form. In anaerobic aqueous–alcoholic solutions, transients were observed in flash photolysis of the protonated form which were similar to those observed with the anthraquinone 2-sulphonates.[6,7] No transients, however, were observed under similar conditions with the unprotonated form. On continuous photolysis, photoreduction of the quinone to the hydroquinone in aqueous–alcoholic solution occurred much more readily with the protonated than with the unprotonated form. At pH values < 1 the kinetics of photoreduction were similar to those already reported for the anthraquinone 2-sulphonates.[8] In aerobic aqueous–alcoholic solutions, oxygen absorption was detected only with the protonated form.[7,9] These experiments demonstrate that the hydrogen abstraction reaction,

$$A^* + RCH_2OH \rightarrow AH\cdot + R\dot{C}HOH$$

which is well established for the anthraquinone 2-sulphonates,[7,9] is readily achieved by the excited protonated form. We suggest that the much greater photosensitizing power of protonated as compared to unprotonated 1-piperidinoanthraquinone is due to the observed change in the nature of the lowest-lying excited-state from C-T to $n \rightarrow \pi^*$. It is our view that this phenomenon is general for aminoanthraquinones and we are now proceeding to verify this.

At neutral and moderately alkaline conditions, where the lowest-lying excited-state for both the 1- and 2-piperidino derivatives is probably C-T, we have observed similar differences in the photosensitizing properties of the 1- and 2-piperidinoanthraquinones to those described by Egerton.[1] In anaerobic 4 : 1 propan-2-ol–water at very high pH (>12) we observed free-radical production from the 2-piperidinoanthraquinone, using e.s.r., which was not found with the 1-piperidinoanthraquinone. Evidently additional factors such as intramolecular hydrogen-bonding[2] influence the photochemical reactions of the piperidino-derivatives in their C-T state. Our results emphasize the importance of controlling the pH of dyed textile systems when investigating the phototendering properties of anthraquinonoid vat dyes.

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