

## 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.<sup>1,2</sup>

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<sup>3</sup> with other substituted aminoanthraquinones. By analogy with substituted benzophenones,<sup>4</sup> these longest wavelength bands appear to be

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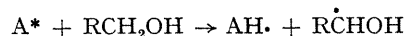
intramolecular charge-transfer (C-T) in type. The red band of 1-piperidinoanthraquinone is not observed in aqueous-alcoholic solutions of pH *ca.* 0.5 whereas, under the same conditions, the band of the 2-piperidinoanthraquinone remains unchanged. In propan-2-ol-water (3:2 by volume) we find a *pK* value of 3.1 for the equilibrium between unprotonated and protonated forms of 1-piperidinoanthraquinone. The longest wavelength band of the protonated form ( $\lambda_{\text{max}} = 405$  nm) has the typical features of an  $n \rightarrow \pi^*$  band found, for example, with the anthraquinone sulphonates.<sup>5</sup>

TABLE

Solvent	1-Piperidino-	2-Piperidino-
	anthraquinone	anthraquinone
	$\lambda_{\text{max}}$ (nm.)	$\lambda_{\text{max}}$ (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.<sup>6,7</sup> 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.<sup>8</sup> In aerobic aqueous-alcoholic solutions, oxygen absorption was detected only with the protonated form.<sup>7,9</sup> These experiments demonstrate that the hydrogen abstraction reaction,



which is well established for the anthraquinone 2-sulphonates,<sup>7,9</sup> 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.<sup>1</sup> 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<sup>2</sup> 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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<sup>1</sup> G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers and Colourists*, 1967, **83**, 409.

<sup>2</sup> S. M. Yeremenko, M. S. Ashkinazi, and B. Y. Dayin, *Ukrain. khim. Zhur.*, 1968, **34**, 694.

<sup>3</sup> Z. Yoshida and F. Takabayashi, *Tetrahedron*, 1968, **24**, 993.

<sup>4</sup> G. Porter and P. Suppan, *Pure Appl. Chem.*, 1964, **9**, 499; *Trans. Faraday Soc.*, 1965, **61**, 1664.

<sup>5</sup> G. O. Phillips, A. K. Davies, and J. F. McKellar, unpublished data.

<sup>6</sup> N. K. Bridge and M. Reed, *Trans. Faraday Soc.*, 1960, **56**, 1796; E. W. Abrahamson and I. Panik, "Advances in Molecular Spectroscopy," Proceedings IVth International Meeting on Molecular Spectroscopy, Vol. 1, Pergamon, London, 1962, p. 354.

<sup>7</sup> G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharpe, *J. Chem. Soc. (A)*, 1969, 767.

<sup>8</sup> H. R. Cooper, *Trans. Faraday Soc.*, 1966, **62**, 2865.

<sup>9</sup> J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.*, 1954, **A**, **225**, 405; C. F. Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719.