

ELECTRONIC ABSORPTION SPECTRA OF RADICAL IONS
AND DIANIONS OF AZOBENZENE DERIVATIVES

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There has been increasing interest in recent years in the study of the electronic absorption spectra of radical anions and dianions of aromatic hydrocarbons and related systems⁽¹⁾. Azobenzene derivatives can be readily reduced to radical anions and dianions⁽²⁾ and in this communication we report some important results obtained in the preliminary investigation of the electronic absorption spectra of the radical anions and dianions of a series of azobenzenes produced by metal reduction.

Most of the radical anions of azobenzene derivatives are green in colour and show three characteristic absorption bands, I, II and III, in the regions 300-350 m μ , 400-460 m μ and 600-650 m μ respectively, in the order of decreasing intensity. The λ_{\max} values for several radical anions are listed in Table 1. The I band of the radical anions corresponds to the lowest energy $\pi \rightarrow \pi^*$ transition of the neutral molecule, while the II and III bands can be ascribed to the additional transitions expected due to the presence of the electron in the lowest anti-bonding orbital^(1b). The dianions are yellow in colour and show only one band at ~ 580 m μ (Table 1). The number and positions of the observed bands of the mono and di-anions as well as their relative band intensities agree with the expected behaviour^(1b).

The spectra of many of the anions showed evidence for the presence of dianions and vice versa due to the disproportionation equilibrium, $2M^{\cdot-} \rightleftharpoons M^{2-} + M$. Such disproportionations of the radical ions are known in some other conjugated systems⁽¹⁾. The II band of the anions appears to be sensitive to substituent effects, electron withdrawing groups causing bathochromic shifts. Thus, the λ_{\max} values in 4,4'-dicarbethoxy, 4,4'-dichloro and 4,4'-dimethoxy derivatives are found at 515, 460 and 401 m μ respectively. The dianion band at ~ 580 m μ does not appear to be very sensitive to substitution.

TABLE I
Electronic Absorption Spectra of Radical Anions and Dianions of Azobenzene
Derivatives, $R-C_6H_4-N=N-C_6H_4-R$

(Counter ion, Li^+ ; Solvent, Tetrahydrofuran)

R	λ_{max} values (m μ)			
	Radical anions (a)		Dianions (a)	
H	315	420	605	579
4,4'-di-t-C ₄ H ₉	325	434 (b)	640	578
4,4'-di-i-C ₃ H ₇	330	415 (b)	610 (b)	580
4,0GH ₃	302	427 (b)	605	578
4,4'-di-OGH ₃	523	401 (b)	610 (c)	581
4,4'-di-Cl	303	460 (b)	620	578
4,4'-di-Br	303	460 (b)	608	572
4,4'-di-CO ₂ Et	304	515 (b)	624	561 (c) 400 (c)
4,4'-di-C ₆ H ₅	319	485	640 (c)	588 (c) 463
3,5'-di-CH ₃	312	424 (b)	612	580
3,5'-di-OGH ₃	312	395	610	573

(a) The spectra of the radical anions in some cases showed the presence of the dianions and *vice versa*; (b) broad; (c) shoulder

The II band of the radical anions were generally found to be very broad, the half-intensity band width in some cases being as large as 100 m μ . The bands were, however, sharper when the counter ion was Li^+ or when the solvents were polar, indicating that the large width of these bands was mainly due to the presence of intimate ion pairs (M^+C^+) and solvent separated species (M^+/C^+). This conclusion is supported by the observation of a sharp II band in the anion of 4,4'-di-methoxy azobenzene with Li^+ , where ESR evidence has also shown the absence of metal coupling⁽⁵⁾. The presence of intimate and solvent separated ion pairs is also likely to be responsible for the broad III band of some radical anions to appear as a doublet.

Both bands II and III show the expected variation in λ_{max} with the cation. Some data on the dibenzopyridazine radical anion are given below:

Cation	Cationic radius (r_0) in Å	λ_{max} of II and II bands in m μ (in THF)	
Li ⁺	0.68	415	615
Na ⁺	0.95	455	628
K ⁺	1.53	445	643
Free ion	-	481	680

The bathochromic shift with increase in r_0 arises from perturbation of the molecular levels by the cationic charge; increasing the r_0 is likely to destabilise the ground state more than the excited state. By extrapolating the r_0 to infinity, the λ_{max} values of the solvated free ion were estimated. Examination of the relative intensities of the two peaks in the doublet of band III of dibenzopyridazine anion with K⁺, Na⁺ and Li⁺ gave the proportion of M⁻//C⁺ to be approximately ~ 0.6 , ~ 0.8 and ~ 0.9 respectively in tetrahydrofuran. The band separation between the two peaks is ~ 4 K cal/mole. The relative intensities of the two peaks of the III band also showed variation with solvent dielectric constant, the proportion of M⁻//C⁺ increasing with increasing dielectric constant.

The spectra of the dianions also bear some evidence for the presence of more than one species possibly arising from intimate ion pairs and solvent separated ion pairs. Thus, the dianion bands which are normally broad become sharper when Li⁺ is the counter ion as well as when the solvents are more polar.

Studies on the disproportionation equilibrium as well as on the $M^{\cdot-}C^+ \rightleftharpoons M^-//C^+$ equilibrium in the azobenzene radical ions are presently in progress. The present studies clearly show that the recent preliminary report of Aylward and coworkers⁽⁵⁾ on the absorption spectra of the azobenzene radical anion and dianions are likely to be erroneous. The colours of the species reported by these workers are sufficient to indicate that they are dealing with species different from the mono- and di-anions, probably produced by protonation of these species. In the present study, we have also encountered spectra and colours similar to those reported by Aylward and coworkers⁽⁵⁾, but it appears that these arise from species produced by subsequent reactions of the anions. It may be mentioned that the mono- and di-anions are extremely sensitive to oxygen, moisture and other protonating solvents. All the spectra reported here were carefully determined in dry nitrogen atmosphere in

specially devised cells in a Cary 14-R spectrophotometer. A detailed report of this investigation will be published in the near future.

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