

A Study of the Reduced States of Four Isomeric Bidiazines (Diaza-2,2'-bipyridines) by UV-VIS/NIR-Spectroelectrochemistry

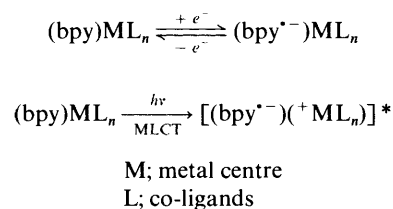
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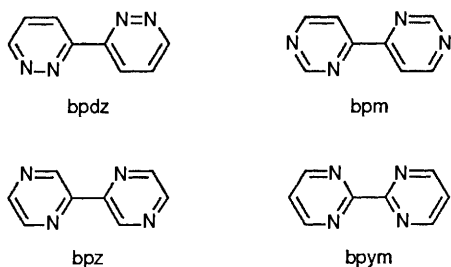
Singly and doubly reduced forms of the four isomeric bidiazines 2,2'-bipyrazine, 3,3'-bipyridazine, 2,2'- and 4,4'-bipyrimidine have been generated in a spectroelectrochemical cell and studied by UV-VIS/NIR spectroscopy. As derivatives of 2,2'-bipyridine the compounds exhibit several groups of vibrationally structured long-wavelength bands in the paramagnetic anion radical state. The assignments and variations of transition energies depending on the diaza perturbation may be rationalized using CNDO/S configuration interaction calculations.

2,2'-Bipyridine (bpy) is a ubiquitous chelate ligand¹⁻³ which can act as π acceptor towards formally low-valent metal centres in the ground state (reversible reduction) or in photochemically useful³ metal-to-ligand charge transfer (MLCT) excited states.



Considering the necessity to assign correct oxidation states within metal complexes, the optical spectra of singly and doubly reduced bpy were determined and interpreted in 1970 by König and Kremer within a Hückel MO and configuration interaction (CI) π orbital approach.⁴

The introduction of the set of four isomeric bidiazines (bdz) as systematically constructed symmetric diaza-2,2'-bipyridines with rather individual molecular properties^{5,6} has allowed a better understanding of the electronic structure in complexes of such aromatic α -diimine ligands.⁵⁻⁷ The occurrence of highly coloured catalytic intermediates (α -diimine)Rh(C₅Me₅) which seem to contain spin-paired α -diimine anion radicals and Rh^{II} in the ground state^{6,7e} has prompted us to investigate the UV-VIS/NIR (near infrared) spectroelectrochemistry of these isomers and to interpret these data within a specially parametrized CNDO/S-CI method.



Experimental

Materials.—The bidiazines (bdz) were commercially available (bpz, bpym) or synthesized according to published procedures (bpdz, bpm).^{5,7a} *N,N*-Dimethylformamide (DMF) was purified and dried as described previously.^{8a} Tetrabutylammonium

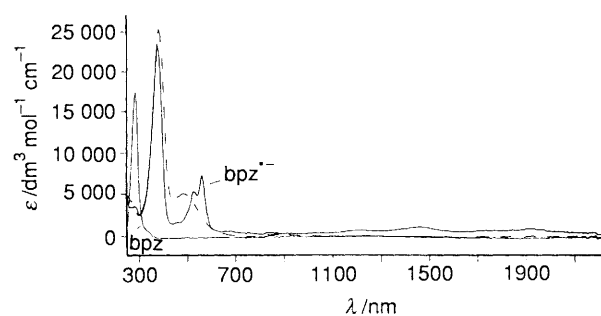


Fig. 1 Absorption spectra of bpz (—), bpz^{·-} (---) and bpz²⁻ (····) in DMF/0.1 mol dm⁻³ Bu₄NBF₄

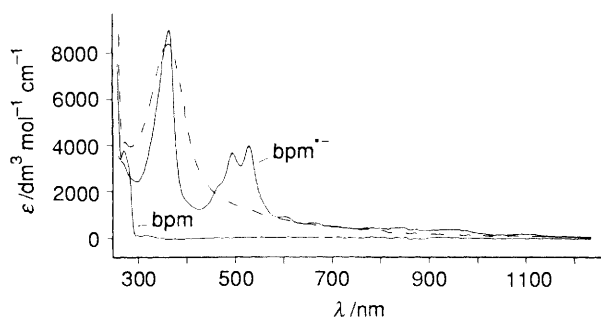


Fig. 2 Absorption spectra of bpm (—), bpm^{·-} (---) and bpm²⁻ (····) in DMF/0.1 mol dm⁻³ Bu₄NBF₄

tetrafluoroborate (Bu₄NBF₄) was purchased from Fluka and used after drying.

Instrumentation.—The optically transparent thin-layer electrolyte (OTTLE) cell and its use for spectroelectrochemistry was described previously.⁸ Spectra were recorded on a Bruins Instruments Omega 10 spectrometer.

Calculations.—Because of the unknown geometry of the bidiazine ligands the Austin model (AM1) method⁹ was used for geometry optimization. The dependence of the potential energy on the interplanar angle showed that the *trans* conformation is more stable than the *cis* arrangement for neutral, and singly and doubly reduced compounds, the energy minima lying close to coplanar geometry. Thus optimized planar *trans* configurations were utilized in the calculations of spectra which were based on the parametrized CNDO/S method^{10,11} followed by limited configuration interaction. Open shell systems

Table 1 Absorption maxima of the bidiazines (bdz) and of their reduced forms from spectroelectrochemistry in DMF/0.1 mol dm⁻³ Bu₄NBF₄^a

Compound	bdz		bdz ^{•-}		bdz ²⁻
	$\lambda_{\max}(\epsilon \times 10^{-3})$	λ_{\max}	$\bar{\nu}_{\max}$	$(\epsilon \times 10^{-3})$	$\lambda_{\max}(\epsilon \times 10^{-3})$
bpdz	255(sh)	350(sh)	28 570(sh)	(10)	not obtained
	316(br)	<u>367</u>	<u>27 250</u>		
		435(sh)	23 000(sh)		
		528(sh)	18 940(sh)		
		<u>563</u>	17 760		
		<u>606</u>	<u>16 500</u>		
	1 050(br)	9 520(br)	(6.5)	(6.5)	
		($\Delta\bar{\nu}_{\frac{1}{2}}$ 2 200 cm ⁻¹)			
bpm	<u>272</u> (3.6)	350(sh)	28 570(sh)	(8.5)	<u>363</u> (8) ($\Delta\bar{\nu}_{\frac{1}{2}}$ 7500 cm ⁻¹)
	318(br)	<u>362</u>	<u>27 620</u>		
		445(sh)	22 470(sh)		
		468(sh)	21 370(sh)		
		496	20 160		
		<u>530</u>	<u>18 870</u>		
		603	16 580		
		660	15 150		
		840	11 900		
		950	10 530		
		1 100	9 090		
			(0.2)		
			(0.2)		
bpz	<u>290</u> (18)	381	26 250	(23)	<u>386</u> (25)
	339(sh)	<u>462</u>	<u>21 650</u>	(0.4)	487 (5)
		500(sh)	20 000(sh)		
		<u>531</u>	<u>18 830</u>	(5)	
		<u>566</u>	<u>17 670</u>	(7)	
		<u>670</u>	<u>14 930</u>	(0.4)	
		1 205	8 300	(0.6)	
		1 470	6 810	(1.1)	
		1 915	5 220	(1.0)	
bpym	<u>255</u>	350(sh)	28 570(sh)	(19)	<u>426</u> (24) ($\Delta\bar{\nu}_{\frac{1}{2}}$ 2 800 cm ⁻¹)
	292(br)	<u>369</u>	<u>27 100</u>		
		427	23 420		
		487(sh)	20 530(sh)		
		<u>517</u>	<u>19 340</u>		
		<u>548</u>	<u>18 250</u>		
		820	12 200		
		930	10 750		
			(0.2)		

^a λ (nm), $\bar{\nu}$ (cm⁻¹), ϵ (dm³ mol⁻¹ cm⁻¹). Most intense components are underlined.

were calculated by the restricted Hartree–Fock method within the Longuet–Higgins and Pople approximations. All π and higher lying non-bonding molecular orbitals were included in the configuration interaction. The consistency of the MO basis was preserved throughout neutral, singly and doubly reduced species.

Results

While data on singly reduced 2,2'-bipyrimidine (bpym) have been reported,¹² the absorption spectra of the other compounds in their reduced forms are not known. The 3,3'-bipyridazine system could not be reduced reversibly beyond the first reduction step even in very dry *N,N*-dimethylformamide/0.1 mol dm⁻³ Bu₄NBF₄; however, the other three isomers were studied in both mono- and di-anionic forms, using a previously described optically transparent thin-layer electrolytic (OTTLE) cell.⁸ Two representative series of spectra are shown in Figs. 1 and 2, the absorption maxima and extinction coefficients are summarized in Table 1.

Calculations of transition energies and oscillator strengths were performed for optimized planar *trans* conformations of the compounds. The calculations were based on the parametrized CNDO/S method^{10,11} followed by limited configuration interaction; open shell systems were calculated by the restricted

Hartree–Fock method. All π and higher lying non-bonding molecular orbitals were included in the configuration interaction. The results are summarized in Table 2.

Discussion

The neutral 12-centre π systems show weak $n \rightarrow \pi^*$ transitions at about 320 nm and a first intense $\pi \rightarrow \pi^*$ ($\pi_6 \rightarrow \pi_7$) transition at shorter wavelength. Characteristically, the bpz isomer exhibits the lowest transition energies. Here the MO approach correctly describes the variation of these transitions within the series of the three isomers bpm, bpz and bpym which do not contain a N–N bond, *i.e.* excluding bpdz. The anion radicals, on the other hand, are distinguished by several typical groups of bands with very different intensities in the UV/VIS/NIR region. Such groups were observed and identified previously for bpy and related species.^{4,12–14}

Beginning in the near UV region, the anion radicals bdz^{•-} exhibit one very intense and fairly narrow band around 370 nm which often displays a shoulder to higher energy (vibrational structuring). In agreement with the calculations (Table 2) these bands are attributed^{4,12,14} to allowed transitions from the filled π_6 MO to the now singly occupied π_7 orbital; the transitions are shifted to lower energies in comparison to those of the corresponding neutral α -diimines. The transition energy is lowest for

Table 2 CNDO/S-calculated low-lying electronic transitions of the bidiazines and of their reduced forms^a

Transition	bpdz	bpm	bpz	bpym
Neutral molecules				
$n \longrightarrow \pi (^1A_u)$	344(0.015)	289(0.007)	330(0.007)	265(0.008)
$n \longrightarrow \pi (^1B_g)$	341(0.000)	270(0.000)	321(0.000)	266(0.000)
$\pi_6 \longrightarrow \pi_7 (^1B_u)$	282(0.518)	277(0.482)	315(0.649)	257(0.785)
Anion radicals				
$\pi_7 \longrightarrow \pi_8 (^2B_u)$	1286(0.003)	775(0.068)	1155(0.075)	778(0.007)
$\pi_7 \longrightarrow \pi_9 (^2A_g)$	1231(0.000)	718(0.000)	884(0.000)	808(0.000)
$\pi_7 \longrightarrow \pi_{10} (^2B_u)$	779(0.198)	611(0.184)	680(0.063)	596(0.197)
$\pi_7 \longrightarrow \pi_{11} (^2A_g)$	468(0.000)	412(0.000)	453(0.000)	397(0.000)
$\pi_6 \longrightarrow \pi_7 (^2B_u)$	415(0.297)	336(0.400)	418(0.363)	355(0.563)
$n \longrightarrow \pi (^2A_u)$	376(0.109)	298(0.003)	349(0.104)	282(0.005)
Dianions				
$\pi_7 \longrightarrow \pi_8 (^1B_u)$	681(0.032)	519(0.020)	668(0.126)	618(0.029)
$\pi_7 \longrightarrow \pi_{10} (^1B_u)$	401(1.267)	366(1.340)	393(1.203)	369(1.229)
$n \longrightarrow \pi (^1A_u)$	370(0.011)	268(0.001)	306(0.003)	302(0.006)

^a Wavelengths (nm) and oscillator strengths (in brackets). For details see Experimental section.

$\text{bpy}^{\cdot-}$ ($\lambda_{\text{max}} \approx 390 \text{ nm}$)^{4,11,13} and $\text{bpz}^{\cdot-}$ (Table 1) in general agreement with calculations (Table 2); again, the largest discrepancy occurs for the bpdz system which is distinguished by N–N bonds.

At lower energies, *i.e.* in the visible and near-infrared regions, the radical intermediates display transitions originating from the singly occupied MO π_7 .^{4,12} All anion radicals show a very weak band around 450 nm (Figs. 1, 2) which we tentatively attribute to the symmetry-forbidden $\pi_7 \longrightarrow \pi_{11}$ transition. The coplanar *trans*-configuration (C_{2h}) derived from geometry optimization and used for the calculation may undergo distortion *e.g.* through ion pairing in solution and thus allow the observation of symmetry-forbidden transitions.

The main band of $\text{bdz}^{\cdot-}$ in the visible region has a very characteristic appearance (Figs. 1, 2), showing three discernible components from vibrational structuring with a typical progression $\Delta\bar{\nu}$ of about 1200 cm^{-1} . The visible component at highest energy appears as a shoulder in most instances. This very typical band is attributed to the allowed transition $\pi_7 \longrightarrow \pi_{10}$ which was calculated⁴ to be quite intense for $\text{bpy}^{\cdot-}$ where the experiments show λ_{max} at 562 nm¹² or 588 nm¹³ for the $0 \longrightarrow 0$ transition. The $\pi_7 \longrightarrow \pi_{10}$ transition appears at lower energies for the *ortho*-($\text{bpdz}^{\cdot-}$) and *para*-perturbed isomers ($\text{bpz}^{\cdot-}$) whereas the two bipyrimidine anion radicals $\text{bpm}^{\cdot-}$ and $\text{bpym}^{\cdot-}$ exhibit higher absorption energies. Although the variations in energy and intensity are correctly reproduced by the calculations for all isomeric anion radicals, the wavelengths are calculated at somewhat too large values (Table 2).

The isomers with the lowest-lying π_7 orbitals,⁵ bpz and bpm , show one or two ($\Delta\bar{\nu} = 1430 \text{ cm}^{-1}$) very weak bands between 600 and 700 nm (Figs. 1, 2). They could be tentatively assigned to the symmetry-forbidden transition $\pi_7 \longrightarrow \pi_9$ which is calculated at 884 nm ($\text{bpz}^{\cdot-}$) and 718 nm ($\text{bpm}^{\cdot-}$). Measured in 2-methyltetrahydrofuran (MTHF), the radical anion $\text{bpy}^{\cdot-}$ shows a corresponding band system with a maximum at 760 nm.¹³

The weak bands at very low energies, in the near infrared region ($\lambda > 750 \text{ nm}$), are due to forbidden⁴ transitions $\pi_7 \longrightarrow \pi_8$. In some cases, the vibrational structuring of these bands ($\Delta\bar{\nu} \approx 1500 \text{ cm}^{-1}$) is very obvious (Fig. 1); $\text{bpy}^{\cdot-}$ in MTHF exhibits a similar structure with a maximum at 1240 nm¹³ (calculated at $7750 \text{ cm}^{-1} = 1290 \text{ nm}^4$). The structure and energy maxima of this SOMO \longrightarrow LUMO transition vary quite remarkably; $\text{bpym}^{\cdot-}$ seems to exhibit the largest transition energy whereas $\text{bpz}^{\cdot-}$ reveals bands at very long wavelengths (Fig. 1). The low intensity of these broad bands and their

occurrence in the NIR region may not have allowed us to detect all components, especially in the case of $\text{bpdz}^{\cdot-}$; absorptions beyond 2000 nm were not accessible experimentally. Calculated transition energies are generally too high but the variation is reproduced well, except for the $\text{bpdz}^{\cdot-}$ ion. The presence of N–N bonds in this compound seems to be responsible for the poor reproduction of spectral properties by the calculations.

All three dianions observed (Figs. 1, 2, Table 1) exhibit one intense band above 300 nm, bpm^{2-} at rather high energy (corresponding to the low-lying,⁵ now doubly occupied orbital π_7) and bpym^{2-} at about 4000 cm^{-1} lower energy. The band of bpm^{2-} is significantly broader ($\Delta\bar{\nu}_{\frac{1}{2}} = 7500 \text{ cm}^{-1}$) than that of the potentially more symmetrical (D_{2h}) bpym^{2-} ($\Delta\bar{\nu}_{\frac{1}{2}} = 2800 \text{ cm}^{-1}$). The assignment $\pi_7 \longrightarrow \pi_{10}$ for this most intense transition is supported by the calculations (Table 2), the values are close to the experiment for bpm^{2-} and bpym^{2-} but too high in energy for bpym^{2-} . bpz^{2-} shows a second, smaller band in addition to the intense absorption in the near UV (Fig. 1); this long-wavelength absorption is assigned to an unusually intense transition $\pi_7 \longrightarrow \pi_8$, in agreement with a calculated high oscillator strength for this transition in the case of bpz^{2-} (Table 1).

Summarizing, the distinct differences between the bidiazines, their metal complexes^{5–7} and reduction products¹⁵ are reflected by the electronic transitions of the mono- and dianionic ions. The suitability of individual compounds for certain applications^{3,6,16} in catalysis may thus be related to the electronic structures as determined in this work.

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References

- W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
- E. C. Constable, *Adv. Inorg. Chem.*, 1989, **34**, 1.
- A. Juris, F. Barigelletti, S. Campagna, V. Balzani, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
- E. König and S. Cremer, *Chem. Phys. Lett.*, 1970, **5**, 87.
- S. Ernst and W. Kaim, *J. Am. Chem. Soc.*, 1986, **108**, 3578.
- M. Ladwig and W. Kaim, *J. Organomet. Chem.*, 1991, **419**, 233.
- (a) S. D. Ernst and W. Kaim, *Inorg. Chem.*, 1989, **28**, 1520; (b) W.

- Kaim, H. E. A. Kramer, C. Vogler and J. Rieker, *J. Organomet. Chem.*, 1989, **367**, 107; (c) B. Olbrich-Deussner and W. Kaim, *J. Organomet. Chem.*, 1988, **340**, 71; (d) S. Ernst, S. Kohlmann and W. Kaim, *J. Organomet. Chem.*, 1988, **354**, 177; (e) M. Ladwig and W. Kaim, *J. Organomet. Chem.*, in the press.
- 8 (a) M. Krejčík and A. A. Vlček, *J. Electroanal. Chem. Interfacial Electrochem.*, 1991, **313**, 243; (b) M. Krejčík, M. Danek and F. Hartl, *J. Electroanal. Chem. Interfacial Electrochem.*, 1991, **317**, 179.
- 9 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- 10 J. DelBene and H. H. Jaffe, *J. Chem. Phys.*, 1968, **48**, 1807.
- 11 H. M. Chang, H. H. Jaffe and C. A. Masmanidis, *J. Phys. Chem.*, 1975, **79**, 1109.
- 12 P. S. Braterman, J.-I. Song, S. Kohlmann, C. Vogler and W. Kaim, *J. Organomet. Chem.*, 1991, **411**, 207.
- 13 T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988, p. 197.
- 14 P. S. Braterman and J.-I. Song, *J. Org. Chem.*, 1991, **56**, 4678.
- 15 W. Kaim and S. Ernst, *J. Phys. Chem.*, 1986, **90**, 5010.
- 16 R. J. Crutchley and A. B. P. Lever, *J. Am. Chem. Soc.*, 1980, **102**, 7128; S. Tazuke and N. Kitamura, *Pure Appl. Chem.*, 1984, **56**, 1269.

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