Electronic Absorption Spectroscopy of some Exceptionally Stable 1,4-Dialkyl-1,4-dihydro-1,4-diazinium Radical Cations: Assignment of Transitions, Vibrational Structure and Effects of π–π Dimerization

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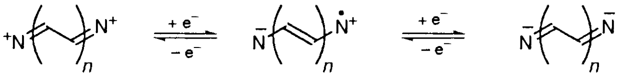
UV–VIS Absorption spectroscopy of the unusually stable and structurally characterized radical cations 1,4-diethyl-1,4-dihydropyrazinium ($\mathbf{1}^{\cdot+}$), 1,4-diethyl-1,4-dihydroquinoxalinium monomer ($\mathbf{2}^{\cdot+}$) and π–π dimer [$(\mathbf{2}^{\cdot+})_2$], 1,4,6,7-tetramethyl-1,4-dihydroquinoxalinium ($\mathbf{3}^{\cdot+}$) and 5,10-diethyl-5,10-dihydrophenazinium ($\mathbf{4}^{\cdot+}$) reveals low-energy π→π* transitions with different intensities and partial vibrational structuring. The spectra of the radical cations and of the corresponding dications ($\mathbf{1}^{2+}$–$\mathbf{4}^{2+}$) have been analysed with the help of INDO/S calculations; the resulting assignments could also be rationalized using Hückel MO theory. Both higher symmetric systems $\mathbf{1}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ exhibit vibrationally split long-wavelength bands. The additional long-wavelength absorption of the π–π dimer $(\mathbf{2}^{\cdot+})_2$ (K_D *ca.* 4×10^3) is assigned to a charge transfer transition, similar to that of methylviologen radical dimer.

Radical intermediates of two-step reversible redox systems of the Weitz type (Scheme 1)[1] often exhibit conspicuous colours because of low-energy π→π* transitions which involve the singly occupied molecular orbital (SOMO). The most prominent examples are the 1,1′-dialkyl-4,4′-bipyridinium or 'methylviologen' radical cations (Fig. 1) which display intense blue or purple colours[1-5] and can thus be used for electrochromic display devices[4,5] or for analysis of biochemical redox processes.[6]



Scheme 1

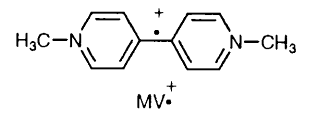


Fig. 1

We have recently synthesized several unusually stable 1,4-dihydropyrazinium ($\mathbf{1}^{\cdot+}$)[7] and 1,4-dihydroquinoxalinium radical cations ($\mathbf{2}^{\cdot+}$)[8] and characterized them structurally[7,9-11] and electrochemically.[8,12] The electrochemical stability ranges of these intermediates (Fig. 2) of novel Weitz type redox systems are quite large (> 750 mV) and the individual redox potentials have physiologically acceptable values between *ca.* −700 and +600 mV *vs.* SCE.[8,12,13] We now report the absorption spectra of the radical cations $\mathbf{1}^{\cdot+}$–$\mathbf{4}^{\cdot+}$, of the dimer $(\mathbf{2}^{\cdot+})_2$ and of the corresponding dications $\mathbf{1}^{2+}$–$\mathbf{4}^{2+}$. For assignment of the bands we have performed INDO/S calculations which are based on reported structures[7,9-11,14,15] of these unusually stable cation radicals (Fig. 2).

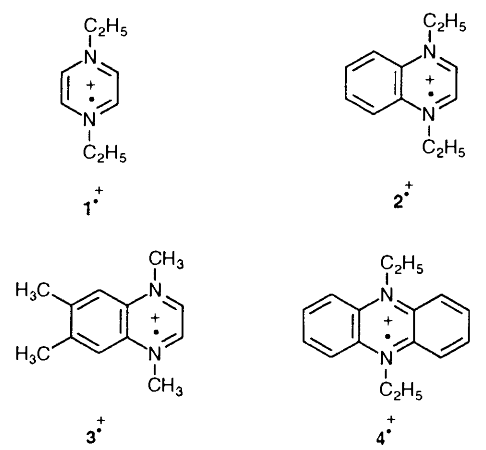


Fig. 2

Experimental

Materials and Instrumentation.—The syntheses of dications $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ (as bis-tetrafluoroborates) and of various radical cation salts have been described previously.[7-12,14-16] The diquaternary salt $\mathbf{4}^{2+}(PF_6)_2$ was obtained by treating phenazine (360 mg, 2 mmol) with triethyloxonium hexafluorophosphate (1.1 g, 4.5 mmol) in dry 1,2-dichloroethane (DCE; 5 cm^3) under reflux. The extremely sensitive red precipitate was isolated by filtration and washed with DCE. Sufficiently stable and concentrated solutions of $\mathbf{4}^{2+}$ for spectroscopy were only obtained in concentrated sulfuric acid. The dark-green radical cation $\mathbf{4}^{\cdot+}$ was prepared from a suspension of $\mathbf{4}^{2+}$ in acetonitrile using zinc as reductant.

Except for $\mathbf{4}^{2+}(PF_6)_2$ (96% H_2SO_4) all UV–VIS absorption measurements were carried out in acetonitrile solutions, using Shimadzu UV 160 and Bruins Instruments Omega 10 spectrometers.

Calculations.—The electronic structures of dications and radical cations were calculated using all-valence electron and INDO/S methods within RHF approximations for open-shell systems.[17,18] Limited configuration interaction (CI) was applied to calculate energies and oscillator strengths of individual electronic transitions. The discussion of experimental spectra is based on the main components of the doublet (radical cations) and singlet excited states (dications).

Calculations of the radical cations were based on the averaged experimental[7-10,14,15] bond lengths and angles in

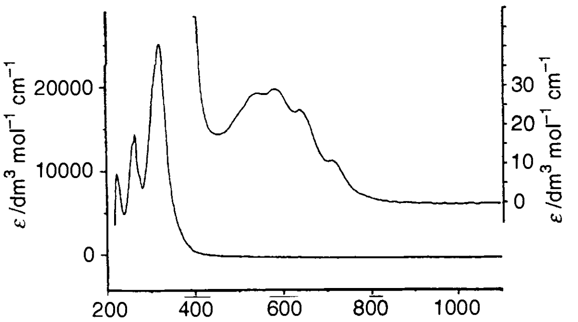


Fig. 3 Absorption spectrum of $1^{\cdot+}(BPh_4)$ in acetonitrile

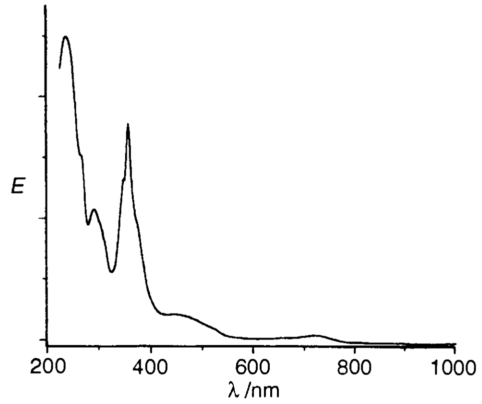


Fig. 4 Absorption spectrum of $2^{\cdot+}(I)$ in acetonitrile (0.15 mmol dm^{-3}), showing bands from $2^{\cdot+}$ and $(2^{\cdot+})_2$

order to maintain a relatively high symmetry of the systems (C_{2h} for 1^{n+} and 4^{n+}, C_2 for 2^{n+} and 3^{n+}). The calculated transition energies are slightly sensitive to small geometry variations, however, the qualitative features of calculated spectra remain unaffected. Because of unknown experimental structures we used AM1[19] optimized geometries for the calculations of the dications.

Results and Discussion

Representative spectra of radical cation species are shown in Figs. 3–5; the spectra of some quinoxalinium radical cations were reported previously.[12] Table 1 summarizes experimental absorption maxima and the results from INDO/S calculations together with assignments of transitions. Although available experimental geometries of the radical cations[7,9–11,14,15] with different conformations of the ethyl substituents were employed for the calculations, we have used the idealized, 'spectroscopically effective' D_{2h} (1^{n+}, 4^{n+}) and C_{2v} symmetries (2^{n+}) for the assignments of the transitions.

The Pyrazinium System.—Whereas solutions of the aromatic[13,16] dication 1^{2+} absorb only in the UV region, the radical cation $1^{\cdot+}$ (which forms green crystals with tetraphenylborate[7]) exhibits a very characteristic UV–VIS spectrum in acetonitrile solution (Fig. 3). Intense absorptions in the UV region are accompanied by a very weak ($\varepsilon < 30$ cm^3 mol^{-1} cm^{-1}) but distinctly structured band system in the visible. Whereas the intense UV band at 322 nm can be associated with the allowed HOMO→SOMO transition in $1^{\cdot+}$ (HOMO→LUMO in the precursor dication), the calculations suggest the occurrence of additional low-energy transitions originating from the singly occupied MO. In particular, the transition with the lowest energy should be a u→u process which is forbidden in either C_{2h} (cation structure[7]) or D_{2h} symmetry (idealized π system, Table 1). The four recognizable long-wavelength features of the long-wavelength band have a separation of about 1500 cm^{-1} which clearly points to a vibrational fine structure associated with ring vibrations.

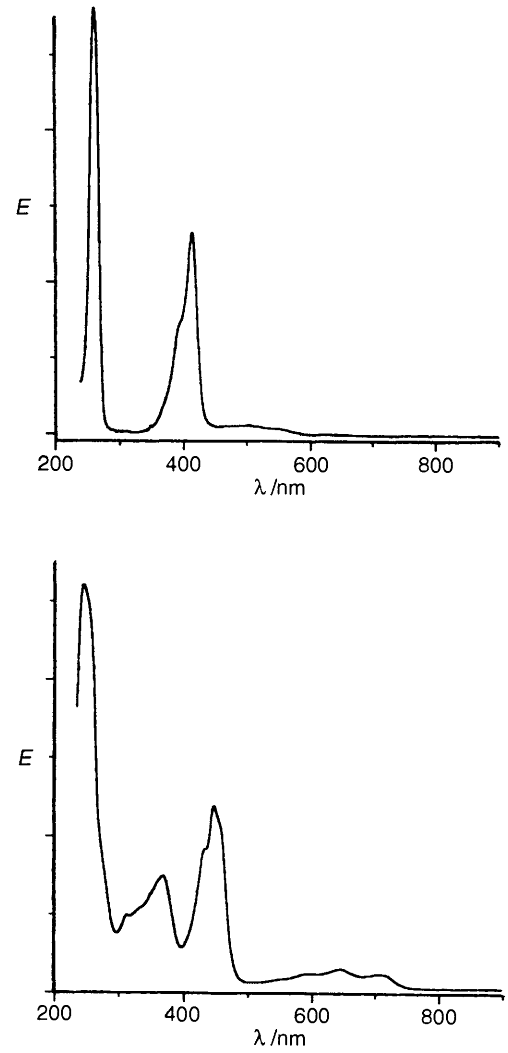


Fig. 5 Absorption spectra of $4^{2+}(PF_6)_2$ in 96% H_2SO_4 (top) and of $4^{\cdot+}$ in acetonitrile solution (bottom)

A negligible contribution from the nitrogen π centres to the lowest-lying completely unoccupied orbital a_u (Fig. 6) reduces the substituent effect from the rotationally and vibrationally flexible ethyl groups to the lowest-lying b_{1u}→a_u transition. The rather high symmetry and the particular type of transition thus contribute to the rather well resolved vibrational fine structure in Fig. 3.

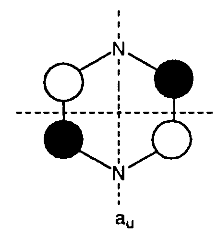


Fig. 6

The Monomeric Quinoxalinium Systems.—1,4-Dialkyl-1,4-dihydroquinoxalinium radical cations such as $2^{\cdot+}$ or $3^{\cdot+}$ generally show a narrow intense band around 360 nm, a weaker

Table 1 Calculated and spectroscopically observed transitions of dications and radical cations

	Calculated[a]			Experimental[b]
Compound	Transition wavelength[c]	Oscillator strength	Assignment[d] (main component)	Absorption maximum[c] (log ε)
$\mathbf{1}^{2+}$	312	0.286	$b_{3g}\rightarrow b_{1u}$, HOMO→LUMO	290
	213	0.075	$b_{2g}\rightarrow b_{1u}$, HOMO − 1→LUMO	235
$\mathbf{1}^{\cdot+}$	657	0.000	$b_{1u}\rightarrow a_u$, SOMO→LUMO	714(1.08)[e,f]
	485	0.037	$b_{1u}\rightarrow b_{2g}$, SOMO→LUMO + 1	500sh
	338	0.166	$b_{3g}\rightarrow b_{1u}$, HOMO→SOMO	320(4.41)
	267	0.121	$b_{2g}\rightarrow b_{1u}$, HOMO − 1→SOMO	265(4.16)
	228	0.033	$b_{1u}\rightarrow b_{2g}$, SOMO→LUMO + 4	224(3.98)
$\mathbf{2}^{2+}$	483	0.028	$a_2\rightarrow b_2$, HOMO→LUMO	400sh
	385	0.379	$b_2\rightarrow b_2$, HOMO − 1→LUMO	359
$\mathbf{2}^{\cdot+}$	550	0.0001	$b_2\rightarrow a_2$, SOMO→LUMO	(600)
	467	0.031	$a_2\rightarrow b_2$, HOMO→SOMO	456br
	427	0.027	$b_2\rightarrow a_2$, SOMO→LUMO + 2	456br
	402	0.112	$b_2\rightarrow b_2$, HOMO − 1→SOMO	382sh
	324	0.107	$b_2\rightarrow b_2$, SOMO→LUMO + 1	358
$\mathbf{3}^{2+}$	502	0.019	$a_2\rightarrow b_2$, HOMO→LUMO	430sh
	417	0.528	$b_2\rightarrow b_2$, HOMO − 1→LUMO	386
$\mathbf{3}^{\cdot+}$	516	0.039	$a_2\rightarrow b_2$, HOMO→SOMO	450br sh
	470	0.162	$b_2\rightarrow b_2$, HOMO − 1→SOMO	414
	356	0.101	$b_2\rightarrow b_2$, SOMO→LUMO + 1	366
$\mathbf{4}^{2+}$	678	0.056	$b_{2g}\rightarrow b_{1u}$, HOMO→LUMO	550sh[e,g]
	437	0.792	$b_{3g}\rightarrow b_{1u}$, HOMO − 1→LUMO	413
	268	1.107	$b_{2g}\rightarrow a_u$, HOMO→LUMO + 1	260
$\mathbf{4}^{\cdot+}$	736	0.030	$b_{2g}\rightarrow b_{1u}$, HOMO→SOMO	706[e,h]
	517	0.000	$a_u\rightarrow b_{1u}$, HOMO − 1→SOMO	460sh
	480	0.270	$b_3\rightarrow {}_u b_{1u}$, HOMO − 2→SOMO	446
	432	0.000	$b_{1u}\rightarrow a_u$, SOMO→LUMO	
	387	0.026	$b_{1u}\rightarrow b_{2g}$, SOMO→LUMO + 3	430sh
	340	0.122	$b_{1u}\rightarrow b_{3g}$, SOMO→LUMO + 1	368
	252	0.436	$b_{2g}\rightarrow a_u$, HOMO→LUMO	244

[a] From INDO/S calculations with CI. [b] In acetonitrile solution, except for $\mathbf{4}^{2+}$ (H_2SO_4). [c] Measured in nm. [d] D_{2h} symmetry for $\mathbf{1}^{n+}$ and $\mathbf{4}^{n+}$ (z axis perpendicular to the molecular plane, N atoms lying on x axis), C_{2v} symmetry for $\mathbf{2}^{n+}$ (y axis perpendicular to the molecular plane). [e] Long-wavelength feature of vibrationally structured band. [f] Other components: 640 (log ε 1.40), 587 (1.48), 540sh nm; see Fig. 5. [g] Other components: 503, 472sh nm. [h] Other components: 643, 592 nm.

transition between 380 and 420 nm, and a relatively broad band at *ca.* 450 nm (Table 1).[12] A very weak absorption can be detected in some instances at about 600 nm. According to the calculations, the latter is assigned to the SOMO→LUMO transition, the more intense HOMO→SOMO and SOMO→LUMO + 2 transitions at slightly higher energies may obscure this lowest-energy transition. The most intense bands lie in the near UV region and are assigned to the HOMO − 1→SOMO and SOMO→LUMO + 1 transitions. In the dications there is a weak HOMO→LUMO transition around 400 nm, usually observed as a shoulder, and a strong band around 360 nm which is attributed to the HOMO − 1→LUMO process.

The Dimeric Quinoxalinium System.—Using very weakly basic iodide as a counter anion we were recently able to observe and isolate the π–π dimer $(\mathbf{2}^{\cdot+})_2$ (Fig. 7) of cation radical $\mathbf{2}^{\cdot+}$.[11] It is distinguished by a rather short π–π distance of about 315 pm in the crystal, by considerable spin–spin interaction which lowers the effective magnetic moment, and by a long-wavelength band in solution.[11] The occurrence of additional long-wavelength absorption bands is typical for π–π dimers such as $(MV^{\cdot+})_2$ ($MV^{\cdot+}$: methylviologen cation radical)[2,5] or other extended π systems.[21] The phenomenon has been attributed to the interaction of π frontier MOs which results in orbital splitting and hence additional low-energy transitions of the charge transfer type.[2,20]

The presence of a monomer–dimer equilibrium [eqn. (1)]

$$2\,\mathbf{2}^{\cdot+} \rightleftharpoons (\mathbf{2}^{\cdot+})_2 \qquad (1)$$

not only in the solid state[11] but also in solution is evident from the concentration-dependent relative growth of a distinct additional long-wavelength band at 722 nm (Fig. 4). Analysis according to standard procedures[21] of absorbance data taken at 720 and 357 nm in the concentration range 1.5–5.5 mmol dm^{-3} yields an equilibrium constant K_D of *ca.* 4000.

Calculations of the dimer were performed using a C_{2h} coplanar arrangement of monomer cations and the experimental interdimer separation (Fig. 7).[11] However, the calculated charge transfer transition energy was far too high in comparison with the experimental value due to the size inconsistency of limited CI for the description of aggregates which are composed of weakly interacting π subsystems.

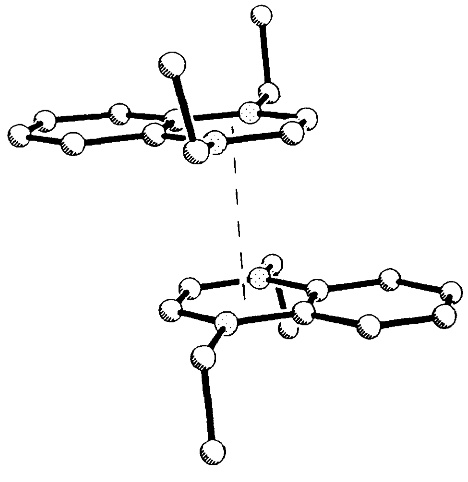


Fig. 7

The Phenazinium System.—*N*,*N*′-Disubstituted phenazinium radical compounds have been extensively studied[14,15,21] and the absorption data of radical cations and dications were reported as a result of spectroelectrochemical techniques.[22] For comparative purposes we have now investigated the 5,10-diethyl substituted system $\mathbf{4}^{\bullet +}$, confirming essentially previous experimental results for the 5,10-dimethyl species[22] and assigning the low-energy transitions (Table 1).

The extremely electrophilic dication $\mathbf{4}^{2+}$ exhibits three distinct bands in sulfuric acid solution. In contrast to the very intense feature at 260 nm the weak long-wavelength HOMO→LUMO transition and the more intense HOMO − 1→LUMO transition at 413 nm show slight vibrational structuring (Fig. 5).

The observed long-wavelength band of $\mathbf{4}^{\bullet +}$ in the visible region is vibrationally well structured with a slightly smaller spacing of 1300 cm^{-1} as compared to $\mathbf{1}^{\bullet +}$ (Fig. 5). However, this band is much more intense (ε *ca.* 3000 $dm^3\ mol^{-1}\ cm^{-1}$) than the similar band shown in Fig. 3. The reason for the higher intensity lies in the allowed u→g type of that transition (HOMO→SOMO); the other transitions are assigned according to the calculations (Table 1).

In general, the calculated wavelengths and oscillator strengths correlate quite well with the experimental data, thus supporting the assignments made in Table 1. Some uncertainty occurs for the 1,4-dihydroquinoxalinium radical cations because low-energy transitions to and from the SOMO have similar energies. In contrast to that ambivalent situation, the pyrazinium radical cation shows a larger HOMO–SOMO than SOMO–LUMO energy gap whereas the phenazinium systems are distinguished by small HOMO–SOMO and large SOMO–LUMO energy differences (Fig. 8).

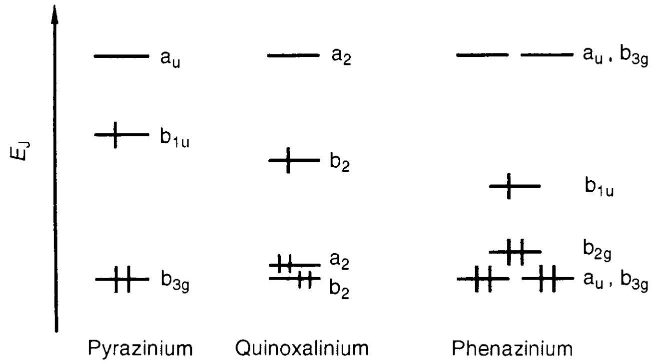


Fig. 8

The existence of crystal structure data as basis for MO calculations and the exceptional stabilities of the 1,4-dialkyl-1,4-dihydro-1,4-diazine radical cations (Fig. 2) have thus allowed us to carry out a complete spectral study of these open-shell systems, including the assignment of electronic transitions with very different intensities. Such results may be valuable to assign and further investigate other related π radical ions[23] most of which are less persistent to be studied under conventional conditions.

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