UV–VIS–Near-IR, MO and EPR studies of five redox stages of an octaethyltetraoxa[26]porphyrin

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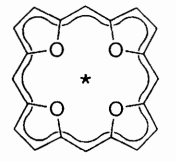
The radical cation ($3^{•+}$), the radical anion ($3^{•-}$) and the dianion (3^{2-}) of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin were generated from the neutral compound (3) and the dication (3^{2+}). The electronic spectra of these five redox stages resemble those in the tetraoxaporphyrin series, 1^{2+}, $1^{•+}$, 1, $1^{•-}$ and 1^{2-}, but are shifted to lower energies by 0.7–1.0 eV. Thus, the Soret and Q bands of the four charged species, 3^{2+}, $3^{•+}$, $3^{•-}$ and 3^{2-}, lie at 450–600 and 700–1300 nm, respectively. The spectrum of the neutral 3 is characteristic of $4n\pi$-systems. The absorption bands were assigned to electronic transitions with the use of PPP calculations. The diions 3^{2+} and 3^{2-} are predicted to preserve the symmetry D_{4h} of the π-system with cyclic delocalization along the 28-membered perimeter, whereas in the neutral 3 the symmetry is lowered to D_{2h} with localization of the double bonds. The four oxygen atoms in 3^{2+} should bear one positive charge which is only slightly decreased on consecutive reductions, so that the additional negative charges are taken up almost exclusively by the perimeter. Proton-coupling constants were determined for the radical cation $3^{•+}$ and the radical anion $3^{•-}$ by EPR spectroscopy. Within the limits of experimental resolution, they are the same for both radical ions and consistent with an effective D_{4h} symmetry. The large inherent width of the EPR lines—and their reluctance to saturation—point to a degenerate or nearly degenerate ground state of $3^{•+}$ and $3^{•-}$ undergoing a dynamic Jahn–Teller effect.

Some years ago, we reported on spectroscopic and theoretical studies of five redox stages derived from the tetraoxaporphyrin[1] and tetraoxaporphycene[2] dications (1^{2+} and 2^{2+}, respectively), in which the NH groups and N atoms of the parent molecules are formally replaced by O atoms and O^+ ions, respectively. In the meantime, an expanded analogue of 1^{2+}, the 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin dication (3^{2+}),† was prepared as a stable perchlorate salt;[3,4] it is iso-π-electronic with the previously synthesized 2,3,9,10,16,17,23,24-octaethyl-*N*,*N*′,*N*″,*N*‴-tetramethyl[26]porphyrin dication.[5] The synthesis of the parent [26]porphyrin has not yet been reported. Exhaustive reduction of 3^{2+} with potassium in tetrahydrofuran at 193 K yields the corresponding dianion 3^{2-} which could be gently reoxidized by dioxygen to the neutral molecule 3 isolated as a rather unstable compound.[4] Both diions, 3^{2+} and 3^{2-}, are highly diatropic ($4n + 2$)π-electron systems, while 3 with $4n\pi$-electrons is paratropic.

Starting from 3^{2+} and 3, we have generated the intermediate radical cation $3^{•+}$ and radical anion $3^{•-}$. All five redox stages, 3^{2+}, $3^{•+}$, 3, $3^{•-}$ and 3^{2-}, are characterized by their electronic spectra in the UV–VIS-near-IR region, the absorption bands being assigned to transitions between orbitals with the aid of Pariser-Parr-Pople (PPP)[6] calculations. EPR spectroscopy is used to specify the radical ions $3^{•+}$ and $3^{•-}$.



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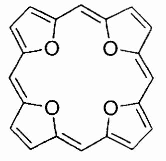

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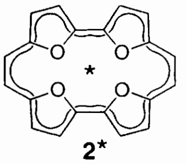

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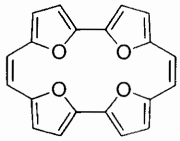

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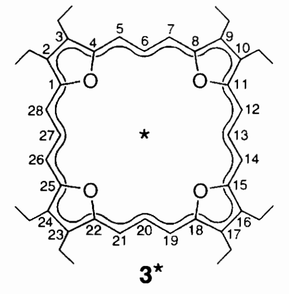

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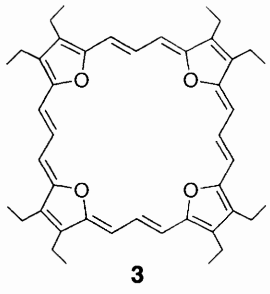

3

	*
Dication	2^+
Radical cation	$•+$
Radical anion	$•-$
Dianion	2^-

Experimental

The syntheses of the dication 3^{2+} perchlorate and the neutral compound 3 are described elsewhere.[3,4] The radical cation $3^{•+}$ was generated by reduction of 3^{2+} with zinc in *N*,*N*-dimethylformamide (DMF) at 298 K, whereas oxidation of 3, even with mild reagents, failed to produce $3^{•+}$ because the reaction proceeded to 3^{2+}. The radical anion $3^{•-}$ was formed by a brief contact of 3 with potassium mirror in 1,2-dimethoxyethane (DME) at 193 K; further reduction led to 3^{2-}. Both $3^{•-}$ and 3^{2-} could be obtained directly by a prolonged reaction of 3^{2+} with potassium in DME (Scheme 1). Owing to disproportionation of the radical ions, $2 \times 3^{•+} \longrightarrow 3 + 3^{2+}$ and $2 \times 3^{•-} \longrightarrow 3 + 3^{2-}$, to the energetically close diamag-

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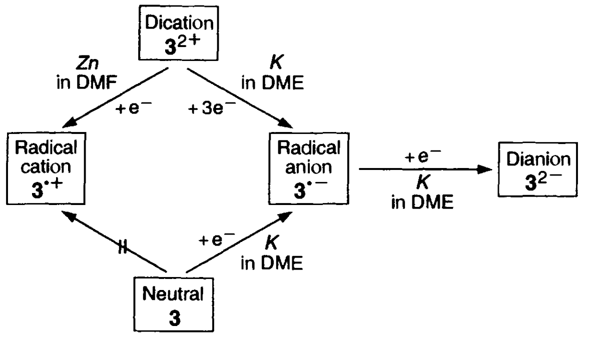
† 26 is the characteristic number of π-electrons in the dication 3^{2+}.[3,5] According to this nomenclature, 1^{2+} should be denoted the tetraoxa[18]porphyrin dication.



Scheme 1

Table 1 Maxima, λ/nm,[a] of electronic bands for the five redox stages of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin[b]

$\mathbf{3}^{2+}$	$\mathbf{3}^{\cdot+}$	$\mathbf{3}$	$\mathbf{3}^{\cdot-}$	$\mathbf{3}^{2-}$
495 (s)	480 (vs)	400 (vs)	459 (vs)	538 (s)
524 (vs)	888 (w)	417 (vs)	496 (vs)	570 (vs)
706 (w)	1005 (w)	426 (vs)	538 (vs)	818 (w)
771 (s)	1052 (s)	497 (w)	970 (w)	914 (s)
782 (s)	1084 (s)	535 (w)	1060 (w)	924 (s)
844 (w)		580 (w)	1252 (s)	
		638 (w)		
		650–850 (br, vw)		

[a] Experimental error: ±2 nm. [b] Conditions specified in the caption to Fig. 1. Abbreviations: s = strong, vs = very strong, w = weak, vw = very weak, br = broad.

netic redox stages, the solutions of $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$ also contained the neutral compound **3** and the diion $\mathbf{3}^{2+}$ or $\mathbf{3}^{2-}$ in concentrations depending on the progress of reaction.

Formic acid served as the solvent for the UV–VIS–near-IR studies of $\mathbf{3}^{2+}$. Those of $\mathbf{3}^{\cdot+}$, $\mathbf{3}^{\cdot-}$ and $\mathbf{3}^{2-}$ were performed on the reaction mixtures, in which these species were generated. The spectrum of **3** was registered prior to the contact of the compound with potassium metal in DME. The optical cell was attached to the evacuated reaction vessel together with an EPR tube, so that the progress of oxidation or reduction could be monitored by formation or decay of the paramagnetic stages $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$.

The electronic absorption spectra were taken on a Perkin-Elmer Lambda 9 UV–VIS–near-IR instrument at ambient temperature, while a Varian-E9-spectrometer served for EPR studies in the range 253–298 K ($\mathbf{3}^{\cdot+}$) and 193–243 K ($\mathbf{3}^{\cdot-}$).

Results and discussion

UV–VIS–near-IR spectra

Fig. 1 shows the electronic absorption spectra of the five redox stages, $\mathbf{3}^{2+}$, $\mathbf{3}^{\cdot+}$, **3**, $\mathbf{3}^{\cdot-}$ and $\mathbf{3}^{2-}$, in the range 300–1400 nm, while Table 1 lists the wavelengths, λ, of the band maxima. A prominent feature of the charged species, $\mathbf{3}^{2+}$, $\mathbf{3}^{\cdot+}$, $\mathbf{3}^{\cdot-}$ and $\mathbf{3}^{2-}$, shared by them with all porphyrins, is the occurrence of two distinct absorption regions, the highly intense Soret bands at 450–600 nm ($\varepsilon = 10^5$–10^6 dm^3 mol^{-1} cm^{-1}) and the less strong Q bands at 700–1300 nm ($\varepsilon = 5 \times 10^4$ dm^3 mol^{-1} cm^{-1}). For the neutral **3**, a very intense Soret-like band at about 420 nm ($\varepsilon = 4 \times 10^5$ dm^3 mol^{-1} cm^{-1}) is flanked on the long-wave side by weak bands in the intermediate region at 500–650 nm ($\varepsilon \approx 5 \times 10^3$ dm^3 mol^{-1} cm^{-1}) which terminate in a still weaker absorption extending from 650 to 850 nm ($\varepsilon \approx 2 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The spectra of $\mathbf{3}^{2+}$, $\mathbf{3}^{\cdot+}$, **3**, $\mathbf{3}^{\cdot-}$ and $\mathbf{3}^{2-}$ resemble those of $\mathbf{1}^{2+}$, $\mathbf{1}^{\cdot+}$, **1**, $\mathbf{1}^{\cdot-}$ and $\mathbf{1}^{2-}$, respectively, but are shifted to lower energies by 0.7–1.0 eV. Such a shift of the intense Soret or Soret-like bands from the near UV into the visible region, on going from the latter to the former, gives rise to a considerably deeper colouring of the solutions. The similarities in the spectra of the neutral compounds **3** and **1**, particularly the appearance of the broad and weak terminal absorption, are noteworthy because they comply with the lowering of the symmetry from D_{4h} to D_{2h} (see below).

As in the spectra of the four charged species of **1**[1] and **2**,[2] the Q bands of the radical ions $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$ are displaced bathochromically relative to those of the diions $\mathbf{3}^{2+}$ and $\mathbf{3}^{2-}$, whereby the negatively charged species absorb at longer waves than the corresponding positively charged ones. Thus, the following sequence is observed with respect to λ: $\mathbf{3}^{2+}$ (771 nm) < $\mathbf{3}^{2-}$ (924) < $\mathbf{3}^{\cdot+}$ (1084) < $\mathbf{3}^{\cdot-}$ (1252).

Assignments of the electronic bands to transitions between orbitals

PPP calculations[‡,6] were carried out for the three species with an even number of electrons, $\mathbf{3}^{2+}$, **3** and $\mathbf{3}^{2-}$; they are based on the structural data for $\mathbf{3}^{2+}$ as determined by X-ray crystallography.[4] The effect of the octaethyl-substitution on the results of such calculations proved to be negligible and was, therefore, not taken into consideration. These results parallel those obtained for $\mathbf{1}^{2+}$, **1** and $\mathbf{1}^{2-}$ by the PPP method.[1] All three species, $\mathbf{3}^{2+}$, **3** and $\mathbf{3}^{2-}$, are predicted to be diamagnetic closed-shell systems. The symmetry D_{4h} of the π-system is preserved in the diions $\mathbf{3}^{2+}$ and $\mathbf{3}^{2-}$ which have a degenerate pair of frontier orbitals with an occupation number zero in the dication $\mathbf{3}^{2+}$ and four in the dianion $\mathbf{3}^{2-}$. The neutral **3** achieves the closed-shell configuration by lowering the symmetry from D_{4h} to D_{2h}, whereby e_g splits into the HOMO b_{2g} and the LUMO b_{3g}. Fig. 2 depicts the Self-Consistent-Field (SCF) energy levels of the highest bonding and the lowest antibonding π-orbitals. In the case of the two paramagnetic open-shell systems, $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$, with an odd number of electrons, the PPP calculations meet with serious problems due to degeneracy of their ground-state in the D_{4h} symmetry. Problems of this kind were addressed in a previous work[1] with respect to the analogous calculations for $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{\cdot-}$. In that work, the SCF-MO energy levels of the diions $\mathbf{1}^{2+}$ and $\mathbf{1}^{2-}$ were assumed to be adequate for a qualitative treatment of the corresponding radical ions. The same approach is adopted in the present work by considering the SCF-MO levels of $\mathbf{3}^{2+}$ and $\mathbf{3}^{2-}$ as being also appropriate for $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$, respectively (Fig. 2). This treatment is all the more justified, as EPR studies of $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$ (see below) indicate that both radical ions have an effective D_{4h} symmetry characteristic of the diions and that the π-spin distribution is consistent with the unpaired electron entering a pair of degenerate or nearly degenerate orbitals. The relevant pair is thus regarded as e_g with an occupation number one in $\mathbf{3}^{\cdot+}$ and three in $\mathbf{3}^{\cdot-}$, so that the radical cation $\mathbf{3}^{\cdot+}$ is related to the radical anion $\mathbf{3}^{\cdot-}$ in the same way as the dication $\mathbf{3}^{2+}$ to the dianion $\mathbf{3}^{2-}$. Occupancies of e_g, b_{2u} and b_{1u} in $\mathbf{3}^{2+}$ and $\mathbf{3}^{\cdot+}$ correspond to vacancies in e_g, a_{1u} and a_{2u} of $\mathbf{3}^{2-}$ and $\mathbf{3}^{\cdot-}$, respectively. These relations are reminiscent of the pairing properties of alternant hydrocarbons.[8]

Only two E_u-transitions are allowed between the highest bonding and lowest antibonding orbitals of the diions $\mathbf{3}^{2+}$ and $\mathbf{3}^{2-}$ presented in Fig. 2. As indicated in Table 2, the interaction of these two transitions gives rise, in each diion, to an intense Soret band at higher energy and to a weaker Q band at lower energy. The four allowed transitions in the neutral **3** belong pairwise to B_{2u} and B_{3u} (Fig. 2) and their interaction accounts

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[‡] The two-centre repulsion integrals $\gamma_{\mu\nu}$ were calculated according to Mataga and Nishimoto.[7] Energy parameters in eV: $\Delta U(\mathrm{O}) = \mathrm{IP(C)} - \mathrm{IP(O)} = -21.48$; $\gamma_{\mu\mu}(\mathrm{C}) = \mathrm{IP(C)} - \mathrm{EA(C)} = +10.84$; $\gamma_{\mu\mu}(\mathrm{O}) = \mathrm{IP(O)} - \mathrm{EA(O)} = +22.90$; $\beta_0(\mathrm{C{-}C}) = \beta_0(\mathrm{C{-}O}) = -2.318$. Nuclear-charge number of O: 2. The parameter $\beta_{\mu\nu}$ was fitted iteratively to the bond orders $p_{\mu\nu}$ by means of the formula $\beta_{\mu\nu} = \beta_0 \exp[s(p_{\mu\nu} - \frac{2}{3})]$ where the scaling factor s amounted to 0.25 for $\mathbf{3}^{2+}$ and $\mathbf{3}^{2-}$ and to 0.1 for **3**.

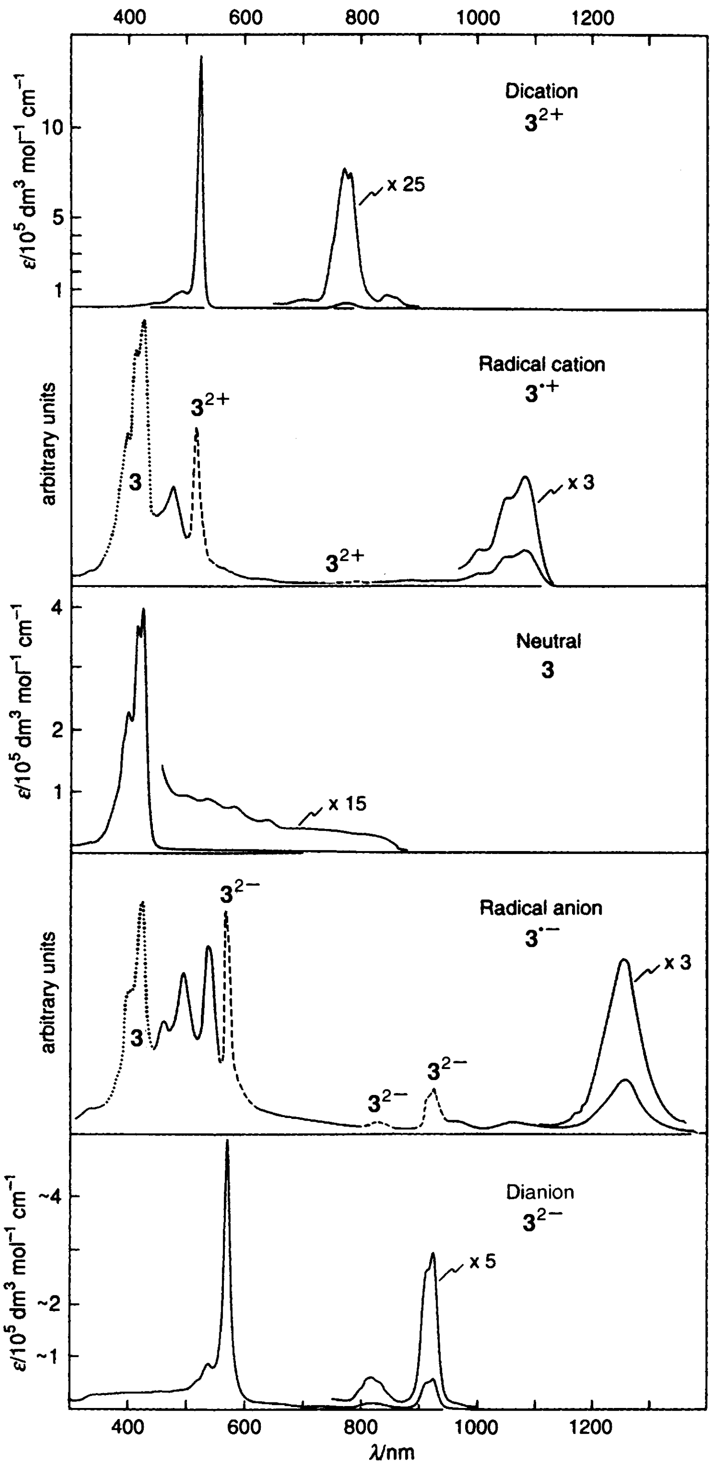

Fig. 1 Electronic spectra of the five redox stages of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin in the range 300–1400 nm. Dication 3^{2+}: solvent H_2CO_2, counterion ClO_4^-. Radical cation $3^{\cdot+}$: solvent DMF, counterion ClO_4^-. Neutral 3: solvent DME. Radical anion $3^{\cdot-}$ and dianion 3^{2-}: solvent DME, counterion K^+. Temperature 298 K throughout. In the spectra of $3^{\cdot+}$ and $3^{\cdot-}$, bands arising from 3 and 3^{2+} or 3^{2-} are drawn by dotted and dashed lines, respectively.

for the strong Soret-like band at higher energy and the adjacent less intense bands at the long-wave side, while the broad and weak absorption at the lowest energy is assigned to the forbidden B_{1g}-transition (LUMO←HOMO) which is diagnostic of $4n\pi$-electron systems[9] (Table 2). Such a transition was also observed for the neutral **1**,[1] albeit with a very low intensity ($\varepsilon \approx 500$ dm³ mol⁻¹ cm⁻¹) which required the use of highly concentrated solutions for its detection.

For $3^{\cdot+}$ and $3^{\cdot-}$ in the D_{4h} symmetry, two allowed E_u-transitions, which have no counterparts in 3^{2+} and 3^{2-}, add to the two already present in the diions. The interaction of the former with the latter shifts the Q bands of the radical ions to lower energies relative to those of the corresponding diions.

Double-bond localization and charge distribution

As stated above, the PPP calculations predict that the D_{4h} symmetry of the π-system should be preserved in the diions 3^{2+} and 3^{2-} but lowered in the neutral **3**. This change in the symmetry is reflected by the π-bond orders and π-charge populations obtained by these calculations when all occupied orbitals are taken into account. It is evident from Fig. 3 that the bond orders along the 28-membered perimeter of 3^{2+} and 3^{2-},

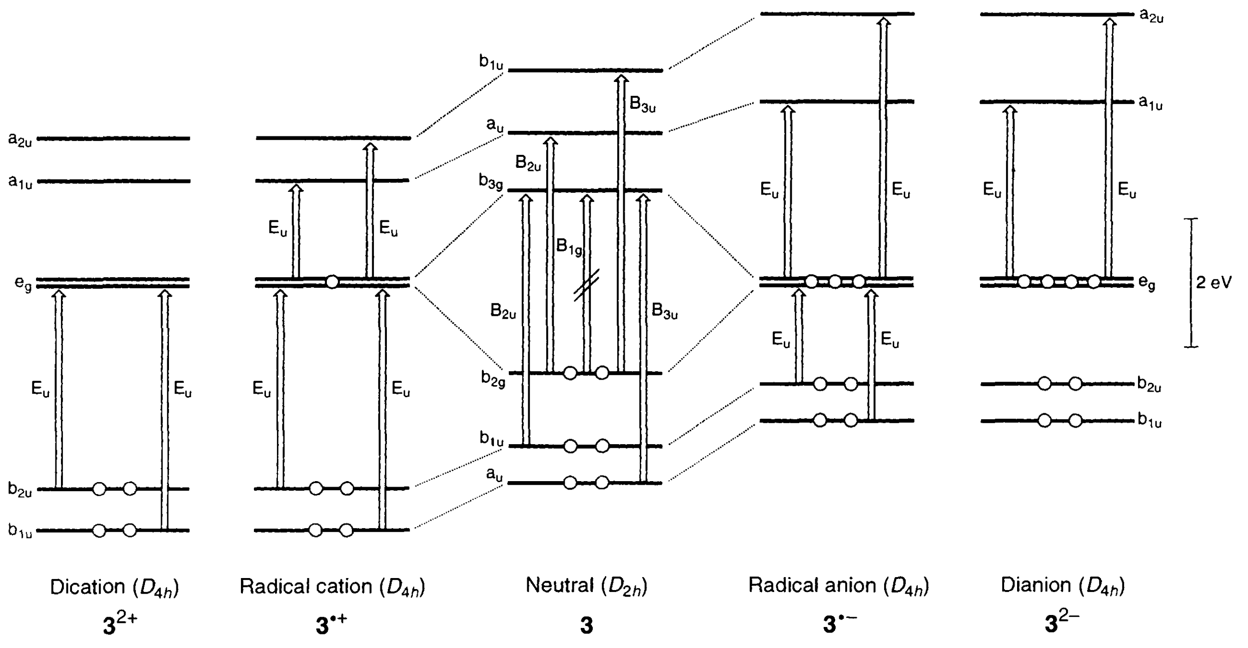

Fig. 2 Transitions between SCF-MO energy levels of several highest bonding and lowest antibonding π-orbitals in the five redox stages of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin. For the closed-shell systems, the dication $\mathbf{3}^{2+}$, the neutral **3** and the dianion $\mathbf{3}^{2-}$, these levels were calculated by the PPP method. Those for the open-shell systems, the radical cation $\mathbf{3}^{\bullet+}$ and the radical anion $\mathbf{3}^{\bullet-}$, were taken over from the corresponding diions. Instead of using the absolute energy scale, the levels are drawn relative to that of the degenerate pair e_g. The choice of mirror planes in the symmetry groups D_{4h} and D_{2h} is specified in Fig. 3.

Table 2 Energies, intensities and compositions of electronic transitions for the three closed-shell redox stages of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin as calculated by the PPP method [SCF CI (Configuration Interaction)]

	Transition	ΔE/eV	ε/dm^3 mol^{-1} cm^{-1}	Substantial contribution (%)		Observed band
Dication $\mathbf{3}^{2+}$	$^1E_u \leftarrow {}^1A_{1g}$ [a]			$e_g \leftarrow b_{2u}$	$e_g \leftarrow b_{1u}$	
		2.9	3×10^5	41	55	Soret
		1.2	4×10^3	55	40	Q
Neutral **3**	$^1B_{2u} \leftarrow {}^1A_g$			$a_u \leftarrow b_{2g}$	$b_{3g} \leftarrow b_{1u}$	
		2.7	3×10^5	34	64	Soret-like
		2.1	7×10^3	63	34	interm. reg. [b]
	$^1B_{3u} \leftarrow {}^1A_g$			$b_{1u} \leftarrow b_{2g}$	$b_{3g} \leftarrow a_u$	
		3.0	2×10^5	69	29	Soret-like
		2.5	9×10^3	27	67	interm. reg. [b]
	$^1B_{1g} \leftarrow {}^1A_g$ [c]			$b_{3g} \leftarrow b_{2g}$		
		0.7	0	96		LUMO←HOMO
Dianion $\mathbf{3}^{2-}$	$^1E_u \leftarrow {}^1A_{1g}$ [a]			$a_{1u} \leftarrow e_g$	$a_{2u} \leftarrow e_g$	
		2.9	3×10^5	30	69	Soret
		1.2	2×10^4	68	28	Q

[a] Pairs of degenerate transitions. [b] Intermediate region at 500–650 nm. [c] Forbidden transition.

like those along the 20-membered perimeter of $\mathbf{1}^{2+}$ and $\mathbf{1}^{2-}$, are compatible with cyclic π-delocalization, whereas nearly all of the corresponding values for **3** alternate between the orders appropriate for essential single and double bonds. Such a localization of the double bonds along the perimeter is also characteristic of the neutral **1** but it is less pronounced in **3** than in **1**.[1] Fig. 3 also shows that the sum of π-charge populations at the four oxygen atoms in $\mathbf{3}^{2+}$ amounts to $+1.04$. On going from $\mathbf{3}^{2+}$ to **3** and to $\mathbf{3}^{2-}$, this positive unit charge is only marginally decreased, so that additional electrons introduced by successive reduction steps are almost exclusively accommodated by the 28-membered perimeter. The structure of the dication $\mathbf{3}^{2+}$ can adequately be represented by the mesomeric formulae drawn in Fig. 4.

EPR spectra

Fig. 5(*a*) shows the EPR spectrum of the radical cation $\mathbf{3}^{\bullet+}$ observed upon mild reduction of the dication $\mathbf{3}^{2+}$ with zinc in DMF at 298 K ($g = 2.0027 \pm 0.0001$), while that of the corresponding radical anion $\mathbf{3}^{\bullet-}$, generated by a brief contact of the neutral **3** with potassium in DME at 193 K ($g = 2.0029 \pm 0.0001$), is presented in Fig. 6(*a*). The spectra do not markedly depend on the temperature in the range of investigation (see Experimental section). Their intensity increases when the microwave power is raised from 2 to 200 mW. The reluctance to saturation, precluding the use of the ENDOR technique, is characteristic of radicals in a degenerate or nearly degenerate ground state undergoing a dynamic Jahn-Teller effect.[10] This phenomenon is also responsible for the inherently large width of the hyperfine lines. The better spectral resolution for $\mathbf{3}^{\bullet-}$ relative to that for $\mathbf{3}^{\bullet+}$ enables one to carry out a computer-assisted analysis which yields three proton-coupling constants, a_{H_μ}, of 0.126 (8 H), 0.079 (4 H) and 0.033 mT (16 H). Agreement with experiment is demonstrated by the simulated spectrum of $\mathbf{3}^{\bullet-}$ [Fig. 6(*b*)]. Despite an experimental uncertainty of ± 0.003 mT, the analysis can be considered as reliable, because the simulation is distinctly affected by slight deviations from the coupling constants a_{H_μ} used in it. The same set of a_{H_μ}

Table 3 Calculated π-spin populations ρ_μ as compared with the observed coupling constants, a_{H_μ} in mT,[a] for the radical ions, $3^{•+}$ and $3^{•-}$, of 2,3,9,10,16,17,23,24-octaethyltetraoxa[26]porphyrin

Position μ	ρ_μ Hückel[b]	ρ_μ McLachlan[c]	a_{H_μ}
5, 7, 12, 14, 19, 21, 26, 28	0.047	0.055	(−) 0.126 (8 α-H)
6, 13, 20, 27	0.030	0.025	(−) 0.079 (4 α-H)
2, 3, 9, 10, 16, 17, 23, 24	0.029	0.029	(+) 0.033 (16 β-H)[d]

[a] Experimental error: ±0.003 mT. [b] Heterocentre parameters: $\alpha_O = \alpha + 2.0\beta$; $\beta_{C-O} = 0.8\beta$. [c] Parameter $\lambda = 1$. [d] Methylene protons of the ethyl substituents.

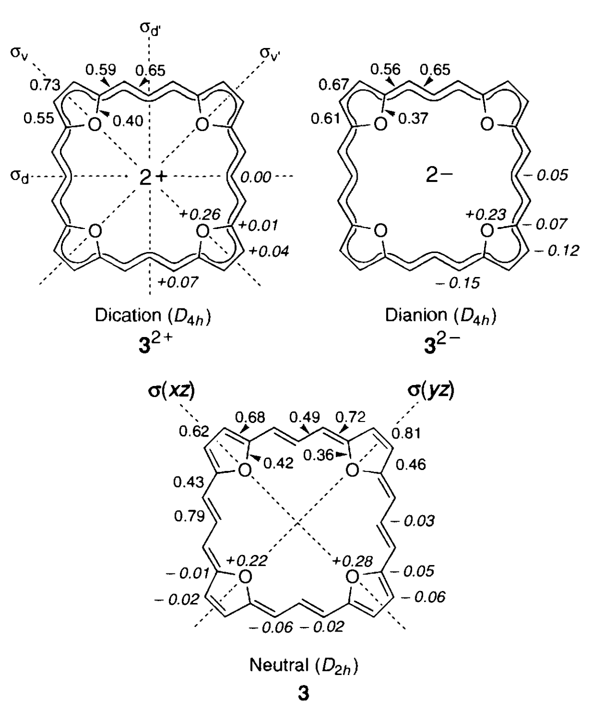

Fig. 3 π-Bond orders (upper halves of the formulae) and π-charge populations (lower halves, in italics) of the dication 3^{2+}, the dianion 3^{2-} and the neutral **3**, as calculated by the PPP method. The traces of the vertical mirror planes in the symmetry group D_{4h} and D_{2h} are indicated by dashed lines.

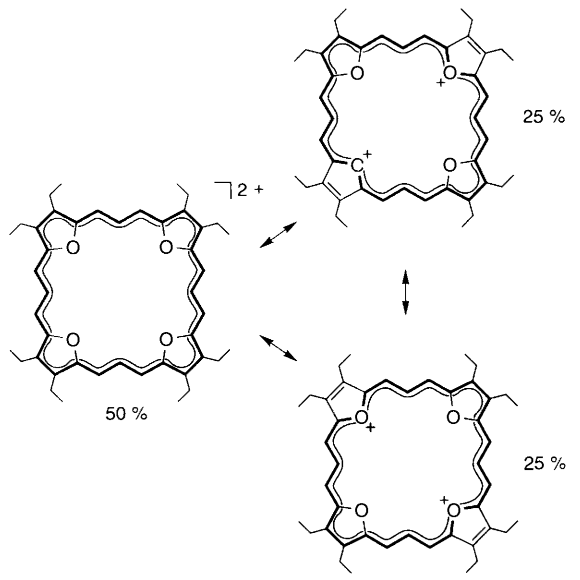

Fig. 4 Mesomeric formulae of the dication 3^{2+}

values, albeit with an increased line-width, also reproduces satisfactorily the spectrum of $3^{•+}$ [Fig. 5(*b*)]. This finding is by no means unprecedented, as almost equal proton-coupling constants were previously observed for the radical ions $1^{•+}$ and $1^{•-}$ [1]

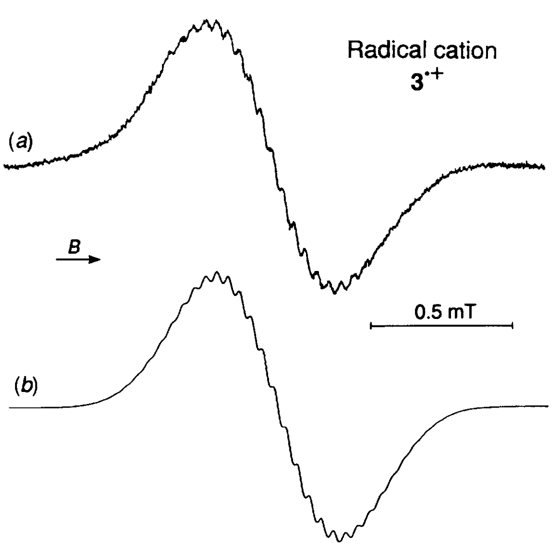

Fig. 5 (*a*) EPR spectrum of the radical cation $3^{•+}$: solvent DMF, counterion ClO_4^-, temperature 293 K. (*b*) Simulation: proton-coupling constants given in Table 3, line-shape Gaussian, line-width 0.045 mT.

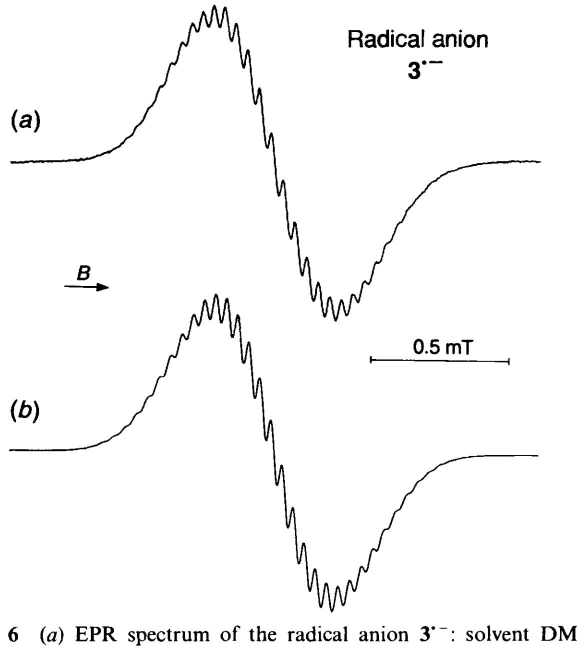

Fig. 6 (*a*) EPR spectrum of the radical anion $3^{•-}$: solvent DME, counterion K^+, temperature 198 K. (*b*) Simulation: proton-coupling constants given in Table 3, line-shape Gaussian, line-width 0.040 mT.

The differing numbers of equivalent nuclei in each of the three sets allow unequivocal assignments of the coupling constants a_{H_μ} to protons in individual positions μ. These assignments are indicated in Table 3 which also lists calculated π-spin populations ρ_μ common to both radical ions $3^{•+}$ and $3^{•-}$. In the Hückel model, these values were obtained by averaging the squared LCAO coefficients over two orbitals belonging to the degenerate pair e_g; they are only slightly modified by the McLachlan procedure[11] (Table 3). Correlation with the observed coupling constants a_{H_μ} makes use of the well-known equations $a_{H_\mu} = Q\rho_\mu$ for the ring protons (α)[12] and $a_{H_\mu} = B\rho_\mu \cos^2 \theta$ for the methylene protons (β) of the ethyl substituents.[13] The proportionality factor $|Q|$ has here an acceptable value of *ca.* 2.5 mT, while the product $|B| \cos^2 \theta$ amounts to 1.14 mT. Because $|B|$ is, in general, about twice as large as $|Q|$, the dihedral angle θ between the *p*-axis at the substituted carbon π-centre and the C–H(β) bond must be *ca.* 60°, in line with similar findings for such methylene protons.[14] The negative sign of Q and the positive one of B require that 0.126 and 0.079 mT should be negative, whereas 0.033 mT ought to be positive. The hyperfine splitting from the 24 methyl protons (γ) of the ethyl substituents is too small to be resolved.

Conclusions

Despite the large changes in the ring size, the basic π-electron structure is essentially preserved on passing from the five redox stages of tetraoxaporphyrin **1** to those of its expanded analogue **3**. Such a conclusion can be drawn from the comparison of the spectroscopic and other physical and chemical properties of the corresponding stages in the two series. These properties are primarily determined by the similar shape of the π-perimeter and the electron distribution over it.

Acknowledgements

This work was supported by the Swiss National Science Foundation. We thank Professor J. Wirz, Basel, for the permission to use his optical spectrometer.

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Paper 5/06328K
Received 26*th September* 1995
Accepted 17*th November* 1995