Five Redox Stages of Tetraoxaporphyrin: A UV/Visible/Near-IR, ESR, and MO-Theoretical Study[‖]

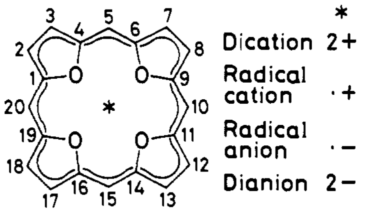
Rainer Bachmann,[†] Fabian Gerson,*[,†] Georg Gescheidt,[†] and Emanuel Vogel[‡]

Contribution from the Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, and the Institut für Organische Chemie der Universität zu Köln, Greinstrasse 4, D-5000 Köln 41, Germany. *Received August 1, 1991. Revised Manuscript Received August 27, 1992*

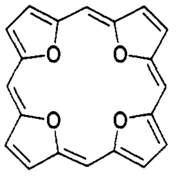
Abstract: Starting from the dication of tetraoxaporphyrin and the corresponding neutral compound, i.e., tetraoxaisophlorin, three further redox stages were generated: the radical cation, the radical anion, and the dianion. Electronic absorption spectra were registered for all five redox stages in the UV/visible/near-IR region (300–900 nm), together with the emission bands for the three fluorescent diamagnetic species (dication, neutral, dianion). The patterns of these spectra suggest differences in electronic structure and symmetry, particularly between the ions and the neutral molecule. Calculations by the PPP method performed on the three closed-shell systems and starting with D_{4h} symmetry indicate that this symmetry is retained in the two diions; a degenerate pair, e_g, of frontier MO's is vacant in the dication and fully occupied in the dianion. By contrast, in the neutral tetraoxaisophlorin, the symmetry is lowered to D_{2h} due to bond-length alternation along the 20-membered π-perimeter; the pair e_g splits into a HOMO b_{2g} and a LUMO b_{3g}. The observed electronic transitions in the diions and the neutral compound are satisfactorily reproduced by the PPP calculations with the participation of two further occupied and two unoccupied MO's, in addition to e_g or b_{2g} and b_{3g}. The MO schemes of the radical ions have been assumed to be similar to those of the corresponding diions with a single and triple occupancy of e_g or nearly degenerate e_g-like orbitals in the cation and anion, respectively. This assumption accounts qualitatively for the observed electronic transitions in the radical ions, and it is consistent with the hyperfine pattern of their ESR spectra which exhibit an effective D_{4h} symmetry. The width of the hyperfine lines and their behavior on saturation strongly suggest that both radical ions are subject to a dynamic Jahn–Teller effect. The π-charge distribution in the dication is adequately described by one unit of positive charge being shared by the four oxygen atoms. This charge is only slightly reduced on the taking up of additional electrons which thus are accommodated in the 20 carbon π-centers of the perimeter.

Introduction

Oxidized and reduced stages of porphyrins have been subject to numerous investigations.[1] The π-system of porphyrin in the free base or in some metal complexes can take up additional electrons to form radical anions, dianions, radical trianions, and tetraanions.[2] Recently the tetraoxaporphyrin dication, in which the NH groups and the N atoms of the free base porphyrin are formally replaced by O and O^+, respectively, has been synthesized and isolated as a stable perchlorate salt.[3] As will be described in detail in a forthcoming publication,[4] the neutral compound corresponding to the dication, the air-sensitive tetraoxaisophlorin, could now also be prepared.



Tetraoxaporphyrin

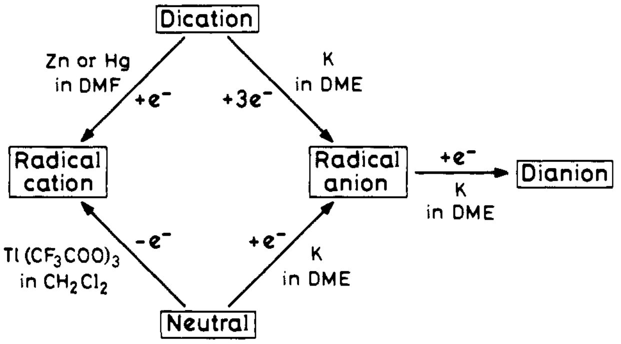


Tetraoxaisophlorin

The ^1H and ^{13}C NMR spectra of the tetraoxaisophlorin,[4] like those of the tetraoxaporphyrin dication[3a] and dianion,[4] exhibit sharp resonances, thus indicating that all three species are diamagnetic.

Here, we report on the electronic structures of these novel porphyrinoid species, along with those of the radical cation and the radical anion generated from them by oxidation or reduction. All five redox stages of tetraoxaporphyrin have been studied by UV/visible/near-IR spectroscopy with the use of MO-theoretical models for the interpretation of the experimental results. ESR spectroscopy has been applied to the two radical ions. As the tetraoxaporphyrin dication is isoelectronic with the free base porphyrin, the radical cation, neutral molecule, radical anion, and dianion, derived from this dication, are isoelectronic with the porphyrin radical anion, dianion, radical trianion, and tetraanion, respectively.

Scheme I



Experimental Section

The synthesis of the tetraoxaporphyrin dication (as the perchlorate) was carried out as described in the literature,[3] while that of the previously

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[‖] Dedicated to Professor Edgar Heilbronner on the occasion of his 70th anniversary.

[†] Universität Basel.

[‡] Universität zu Köln.

(1) *The Porphyrins*: Dolphin, D. J., Ed.; Academic Press: New York, 1978/1979; Vols. I–VII.

(2) (a) Reference 1, Vols. III–V. (b) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 818. (c) Dodd, J. W.; Hush, N. S. *J. Chem. Soc.* **1964**, 4607. (d) Clack, D. W.; Hush, N. S. *J. Am. Chem. Soc.* **1965**, *87*, 4238. (e) Hush, N. S. *Theor. Chim. Acta* **1966**, *4*, 108. (f) Hush, N. S.; Rowlands, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2976. (g) Shul'ga, A. M.; Sinyakov, G. N.; Gurinovich, G. P. *Biofizika* **1978**, *23*, 5; *Chem. Abstr.* **1978**, *88*, 202315j. (h) Gurinovich, G. P.; Gurinovich, I. F.; Ivashin, N. V.; Sinyakov, G. N.; Shulga, A. M.; Terekhov, S. N.; Filatov, I. V. *J. Mol. Struct.* **1988**, *172*, 317. (i) Cosmo, R.; Kautz, C.; Meerholz, K.; Heinze, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 604.

(3) (a) Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406. (b) Haas, W.; Knipp, B.; Sicken, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 409.

(4) Vogel, E.; Röhrig, P.; Knipp, B.; Schmickler, H.; Lex, J. Manuscript in preparation. The following data are taken from the Ph.D. thesis of P. Röhrig, Universität zu Köln, 1991. Tetraoxaisophlorin: black crystals (air-sensitive) that decompose on slight heating: ^1H NMR (300 MHz, THF-d_8) δ 2.47 (s, $J_{2,3}$ = 4.69 Hz, 8 H, H-2,3,7,8,12,13,17,18), −0.15 (s, 4 H, H-5,10,15,20); ^{13}C NMR (75.5 MHz, THF-d_8) δ 164.54 (C-1,4,6,9,11,14,16,19), 122.34 (C-2,3,7,8,12,13,17,18), 97.47 (C-5,10,15,20); EIMS *m/z* (relative intensity) 316 (M^+, 100), 158 (M^{2+}, 22); IR (KBr) $\bar{\nu}$ 3120, 1624, 1346, 1285, 1123, 1020, 978, 937, 820, 784 cm^{-1}. UV–visible (THF) data correspond to those in Table 1 with DME as the solvent (Figure 1).

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Table I. Colors and Band Maxima (λ in nm) of the Five Redox Stages of Tetraoxaporphyrin[a]

	dication	radical cation	neutral	radical anion	dianion
abs	violet	green	yellow	orange	green-blue
	370 (vs)	336 (vs)	315 (vs)	364 (s)	412 (vs)
	486 (w)	366 (vs)	343 (vs)	381 (vs)	585 (w)
	500 (w)	374 (vs)	422 (s)	394 (vs)	608 (w)
	524 (s)	410 (s)	452 (s)	510 (w)	644 (s)
	569 (w)	609 (w)	487 (s)	535 (w)	
		642 (w)	680 (w)	550 (w)	
		681 (s)	770 (w)	780 (w)	
		723 (w)		810 (w)	
				888 (s)	
em	orange-red		green		red
	574 (w)		495 (s)		655 (s)
	594 (w)		530 (s)		736 (w)
	630 (s)				

[a] Abbreviations: vs = very strong; s = strong; w = weak; abs = absorption; em = emission. For the experimental conditions, see legend to Figure 1.

unknown neutral tetraoxaisophlorin (to be published in a different context)[4] was achieved by exhaustive reduction of the dication to the dianion with potassium in tetrahydrofuran (THF) at 193 K, followed by partial oxidation of the dianion in THF at the same temperature employing carefully dosed, dry dioxygen as the oxidant. Samples of tetraoxaisophlorin[4] thus obtained from several experiments gave rise to identical spectroscopic data so that occurrence of impurities was unlikely. The radical ions were prepared from the dication or the neutral compound according to Scheme 1.

The radical cation was generated at ambient temperature by reduction of the dication with zinc or mercury in *N,N*-dimethylformamide (DMF) and by oxidation of the neutral tetraoxaisophlorin with thallium(III) trifluoroacetate in dichloromethane. The radical anion was produced by reduction of the neutral compound with potassium in 1,2-dimethoxyethane (DME) at 193 K. Further contact of the solution with the metallic mirror at this temperature yielded the dianion. The radical anion and, subsequently, the dianion could likewise be obtained from the dication by prolonged reaction with potassium in DME at 193 K.

Concentrated sulfuric acid served as the solvent for the UV/visible/near-IR studies of the dication. As for the radical cation, the radical anion, and the dianion, such studies had to be performed on the reaction mixtures in which these species were generated (see above). The optical cell was attached to the evacuated reaction vessel together with an ESR tube, so that the progress of oxidation or reduction could be monitored by formation and decay of the paramagnetic stages. The UV/visible/near-IR spectrum of the neutral compound was registered prior to contact with oxidizing or reducing agent, i.e., in a DME or a CH_2Cl_2 solution. All electronic absorption and (uncorrected) emission spectra were taken at ambient temperature on a Perkin-Elmer-Lambda 9 UV-vis-NIR instrument and Spex-Fluorolog/Spex-Datamate, respectively. A Varian-E 9-spectrometer served for the ESR studies.

Results and Discussion

UV/Visible/Near-IR Spectra. Figure 1 shows the electronic absorption spectra of the five redox stages of tetraoxaporphyrin in the range 300–900 nm,[5] along with the emission spectra of the three fluorescent diamagnetic species (dication, neutral, and dianion). The colors of the solutions and the wavelengths of the band maxima are given in Table I.[5]

Prior to a more detailed discussion, a few comments on the prominent features of these spectra are in place.

(i) The absorption spectra of the dication and the dianion are relatively simple compared to those of the three remaining species. They essentially consist of two rather sharp bands ca. 1 eV apart (dication, 370 and 524 nm; dianion, 412 and 644 nm). The long-wave bands are reflected by their fluorescence mirror images (dication, 630 nm; dianion, 655 nm).

(ii) The absorption spectra of the radical cation and the radical anion are more complex than those of the dication and dianion, as each of them exhibits more than two bands. Noteworthy is the large red shift of the prominent long-wave bands by ca. 0.5 eV on going from the diion to the corresponding radical ion (dication, 524 nm → radical cation, 681 nm; dianion, 644 nm → radical anion, 888 nm).

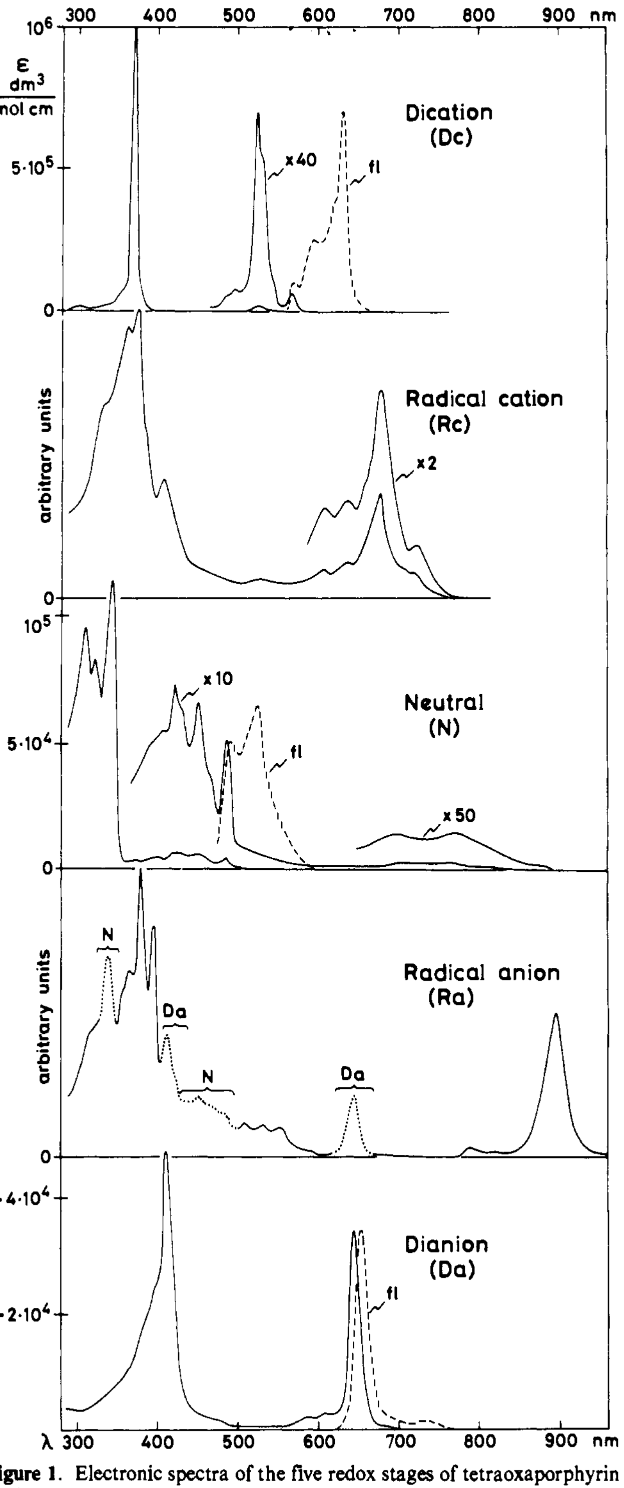

Figure 1. Electronic spectra of the five redox stages of tetraoxaporphyrin in the range 300–900 nm. Dication: solvent, conc H_2SO_4; counterion, ClO_4^- (HSO_4^-). Radical cation: solvent, DMF; counterion, ClO_4^-. Radical anion and dianion: solvent, DME; counterion, K^+. Neutral compound (tetraoxaisophlorin): solvent, DME. Temperature, 298 K throughout. In the spectrum of the radical anion, the bands drawn by dotted line stem from the neutral compound (N) or the dianion (Da). Fluorescence bands (fl) are drawn by dashed lines.

(iii) The absorption spectrum of the neutral compound contains at least two bands at shorter wavelengths (315 and 343 nm), several maxima in the intermediate region (422, 452, and 487 nm), and a broad weak absorption at longer wavelengths (600–900 nm). Despite its relative weakness (ϵ = 300 $dm^3/(mol\ cm)$), this absorption is reproducible and can hardly arise from species other

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[5] The absorption spectra and band maxima of the dication have been previously reported in ref 3a.

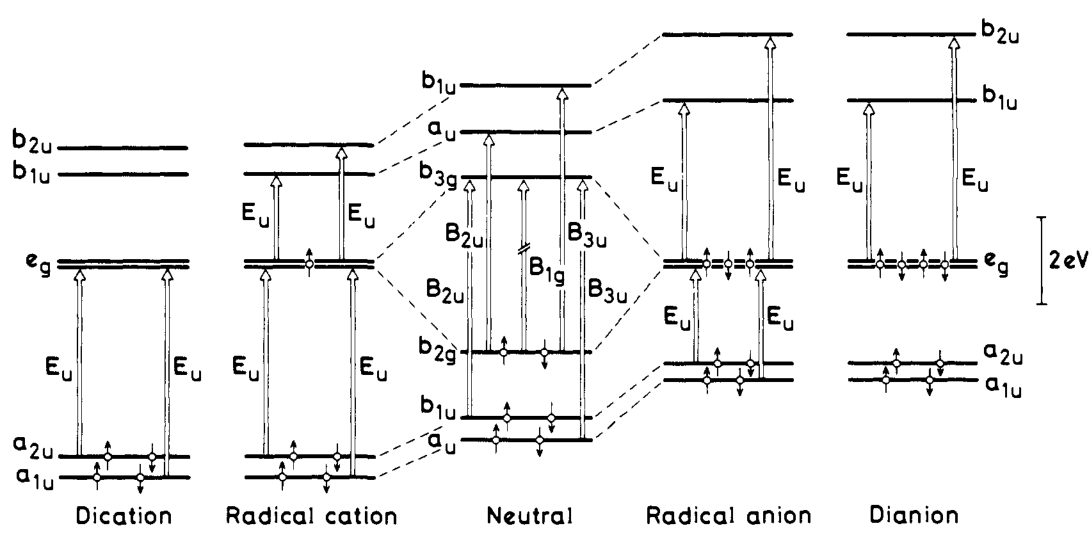

Figure 2. Electronic transitions between SCF energy levels of several highest occupied and lowest unoccupied MO's in the five redox stages of tetraoxaporphyrin. For the dication, neutral molecule, and dianion (closed-shell systems), these levels were calculated by the PPP method. Those of the radical cation and radical anion (open-shell systems) 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 the vertical mirror planes is specified in Figure 3.

than the neutral tetraoxaisophlorin.[4] Interestingly, the fluorescence band is not its mirror image, but the two maxima (495 and 530 nm) of the emission spectrum are a reflection of those in the intermediate absorption region (487 and 452 nm).

Comparison with Porphyrins. As stated in the Introduction, the tetraoxaporphyrin dication and its four consecutive reduction stages are isoelectronic with free base porphyrin and its anions. Comparison of the electronic spectra for the corresponding species in the two series is, however, not straightforward, as the free base porphyrin deviates from the D_{4h} symmetry and as its derivatives, formed exclusively by electron uptake into its π-system, are not available. One is, therefore, restricted to compare the redox stages of tetraoxaporphyrin with their metalloporphyrin counterparts. Zinc complexes seem to be appropriate for this aim, as the metal does not significantly take part in the reduction processes. Literature reports on such processes exist, in particular, for zinc 5,10,15,20-tetraphenylporphyrin (Zn-TPP), of which several consecutive reduction potentials have been measured.[2a,d,e,i] Disregarding the phenyl substituents, the porphyrin π-systems of Zn-TPP and its reduced derivatives are isoelectronic with the corresponding redox stages of tetraoxaporphyrin. Thus, the electronic absorption spectra of the neutral Zn-TPP and its radical anion, dianion, trianion, and tetraanion should be comparable to those of the tetraoxaporphyrin dication and its radical cation, neutral derivative (tetraoxaisophlorin), radical anion, and dianion, respectively. In the Zn-TPP series, only the spectra of the first three stages have been reported.[2a–c,h] Despite the bathochromic shift caused by the phenyl substitution, these spectra correlate fairly well with those of corresponding redox stages of tetraoxaporphyrin. The main characteristics of all these spectra are strong short-wave absorptions (Soret bands) and less intense ones at longer wavelengths.

MO Models. The spectral patterns observed for the five redox stages of tetraoxaporphyrin (Figure 1) point to substantial differences in the symmetry and electronic structure, particularly between the charged systems and the neutral tetraoxaisophlorin. In order to interpret the absorption spectra, MO calculations by the PPP SCF CI method[6] have been performed on the five redox stages, starting from D_{4h} symmetry. The SCF energy levels of the relevant highest occupied and lowest unoccupied orbitals are presented schematically in Figure 2. As expected, the three diamagnetic species (dication, neutral, and dianion) proved to be closed-shell systems. For the two diions, the D_{4h} symmetry is preserved. Its important feature is a degenerate pair of frontier MO's, e_g, with an occupancy number *zero* in the dication and *four* in the dianion. In the neutral tetraoxaisophlorin, the symmetry is lowered from D_{4h} to D_{2h} due to double-bond localization along the 20-membered perimeter, as indicated by the π-bond orders given in Figure 3. Thus, the degenerate pair, e_g, splits into the HOMO b_{2g} and the LUMO b_{3g}, yielding a singlet ground state through the double occupancy of b_{2g}. This structure, as predicted by the PPP calculations, requires some comments which are presented in the Appendix.

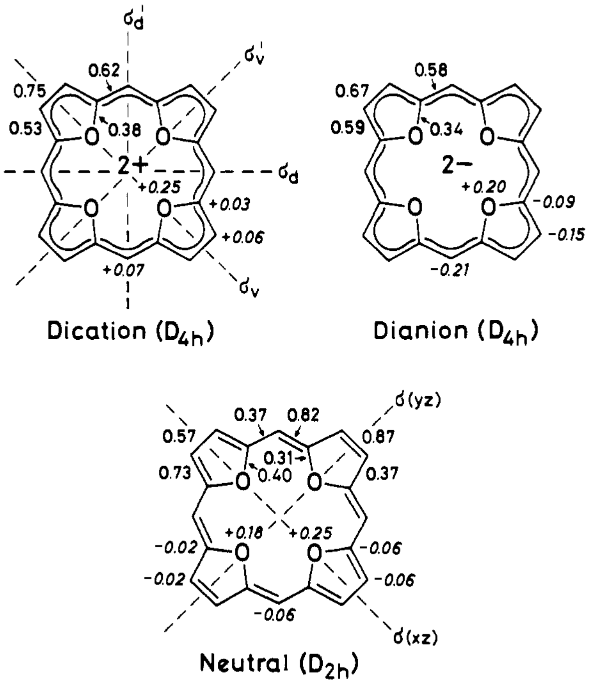

Figure 3. π-Bond orders (upper halves of the formulas) and π-charge populations (lower halves of the formulas, in italics) of the tetraoxaporphyrin diions and the neutral compound (tetraoxaisophlorin) as calculated by the PPP method. The traces of the vertical mirror planes are indicated by dashed lines.

For the two paramagnetic open-shell systems (radical cation and radical anion), the PPP SCF calculations[7] failed to converge

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(6) Used for configuration interaction, in each case: five highest occupied and five lowest unoccupied orbitals. Energy parameters for O, in eV: $\Delta U(O) = IP(O) - IP(C) = -21.48$; $\beta(C\text{–}O) = -2.38$; $\gamma_{\mu\mu} = +22.90$. Core charge of O: 2.0. For a recent publication on the PPP method, see: *Int. J. Quantum Chem.* **1990**, *37*, issue in honor of R. Pariser, R. G. Parr, and J. A. Pople.

(7) The method used followed the theory by: Longuet-Higgins, H. C.; Pople, J. A. *Proc. Phys. Soc., London* **1955**, *A68*, 591.

Table II. Proton-Hyperfine Coupling Constants, a_{H_μ} (in mT), and g Factors of the Radical Ions of Tetraoxaporphyrin

	a_{H_μ}		
position μ	5,10,15,20	2,3,7,8,12,13,17,18	g
radical cation	0.198 ± 0.003	0.122 ± 0.003	2.0027 ± 0.0001
radical anion	0.197 ± 0.002	0.129 ± 0.002	2.0031 ± 0.0001

when starting from perfect D_{4h} symmetry. Convergence could be achieved by introducing a perturbation that lowers the symmetry, but is is questionable whether the results of these calculations should be taken at their face value, as they depend on the nature and extent of the perturbation.[8] Therefore, the MO energy levels of the dication and the dianion have been assumed to be also adequate for a qualitative treatment of the corresponding monoions. This is all the more justified as ESR studies of the radical cation and the radical anion (see below) indicate that these ions have an effective D_{4h} symmetry characteristic of the diions. The pair of the relevant frontier MO's (e_g in D_{4h}) is thus degenerate or nearly degenerate with an occupancy number *one* in the cation and *three* in the anion (Figure 2). The electronic configuration of the dianion is related to that of the dication, as the vacancies in the former correspond to the occupancies in the latter. An analogous relation holds for the electronic configuration of the radical anion with respect to that of the radical cation. This situation is reminiscent of the pairing properties exhibited by the alternant hydrocarbons and their radical ions.[9a,10a,11a]

Assignments of Electronic Bands. Figure 2 shows the allowed transitions between the SCF MO's for the five redox stages (of the forbidden transitions, only the LUMO ← HOMO one in the neutral compound is taken into consideration). According to this diagram, two bands of the dication represent D_{4h}-symmetry-allowed E_u transitions from the doubly occupied MO's a_{2u} and a_{1u} to the vacant degenerate pair e_g. The more intense transition (PPP, 3.6 eV; exptl 370 nm or 3.4 eV) involves 56 and 44% contributions from $e_g \leftarrow a_{1u}$ and $e_g \leftarrow a_{2u}$, respectively, whereas a composition with an inverse ratio gives rise to the less intense one (PPP, 1.9 eV; exptl 524 nm or 2.4 eV). Similarly, the two bands of the dianion are predicted to be the D_{4h}-symmetry-allowed E_u transitions from the 4-fold occupied degenerate pair e_g to the vacant MO's b_{1u} and b_{2u}. The more intense transition (PPP, 3.5 eV; exptl 412 nm or 3.0 eV) is expected to have 73 and 27% contributions from $b_{2u} \leftarrow e_g$ and $b_{1u} \leftarrow e_g$, respectively, while the less intense one (PPP, 1.7 eV; exptl 644 nm or 1.9 eV) consists of these components with an inverse ratio.

For the radical cation and the radical anion, the electronic transitions are here discussed in terms of D_{4h} symmetry. An inspection of Figure 2 points to additional low-energy transitions which have no counterparts in the corresponding diions. These D_{4h}-symmetry-allowed E_u transitions occur from the singly occupied degenerate pair e_g or nearly degenerate e_g-like orbitals to the vacant MO's b_{1u} and b_{2u} in the radical cation and from the doubly occupied MO's a_{2u} and a_{1u} to the triply occupied pair e_g in the radical anion. They can mix with the other E_u transitions which are analogous to those in the corresponding diions. Configuration interaction should thus account for both the larger number of bands and the red shifts of the long-wave bands by ca. 0.5 eV on going from the dication and dianion to the radical cation and radical anion, respectively.[12]

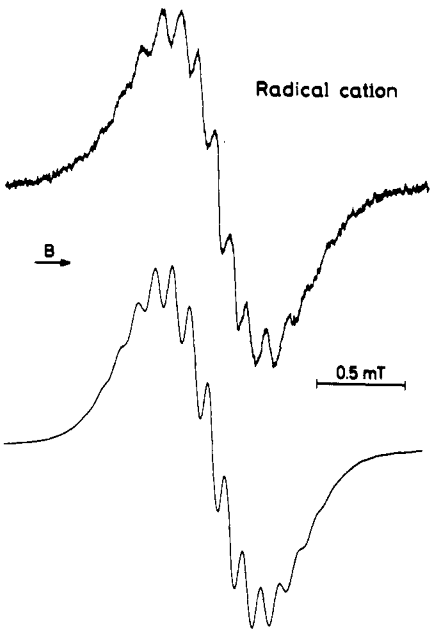

Figure 4. ESR spectrum of the radical cation of tetraoxaporphyrin (top) and its computer simulation (bottom): solvent, DMF; counterion, ClO_4^-; temperature, 273 K. The simulation makes use of the coupling constants given in Table II: line shape, Lorentzian; line width, 0.15 mT.

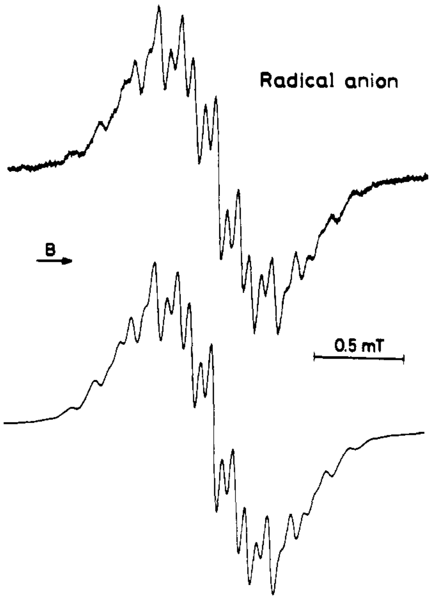

Figure 5. ESR spectrum of the radical anion of tetraoxaporphyrin (top) and its computer simulation (bottom): solvent, DME; counterion, K^+; temperature, 198 K. The simulation makes use of the coupling constants given in Table II: line shape, Lorentzian; line width, 0.12 mT.

Four allowed transitions in the range 300–500 nm are predicted in Figure 2 for the neutral tetraoxaisophlorin of D_{2h} symmetry.

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[8] A perturbation was introduced with use of the geometry determined by X-ray crystallography for the perchlorate salt of tetraoxaporphyrin dication.[3a] This geometry slightly deviates from perfect D_{4h} symmetry. The results of an open-shell PPP SCF CI calculation[7] starting with such a structure are provided as supplementary material. Whereas the results for the closed-shell systems (diions and the neutral compound) are identical with those obtained by starting from perfect D_{4h} symmetry, there is a notable modification for the open-shell systems (radical ions). The radical cation and the radical anion are now predicted to adopt D_{2h} symmetry like the neutral compound but in contrast to the dication and dianion. The doublet ground state of the radical ions is almost degenerate, as its separation from the lowest excited state amounts to only 0.04 and 0.01 eV for the cation and the anion, respectively.

[9] Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966: (a) Chapter 1.9; (b) Chapter 8.3.

[10] Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York–London, 1961: (a) Chapter 2.6; (b) Chapter 5.8.

[11] Heilbronner, E.; Bock, H. *The HMO-Model and Its Application*; Wiley: London–New York, and Verlag Chemie: Weinheim, 1976: (a) Chapter 5.3; (b) Chapter 6.5.

[12] Tentatively, while discussing the electronic spectra of the radical ions, one may consider the results of calculations described in footnote 8. It has been stated here that these results (given as supplementary material) predict a near-degeneracy of the ground state for the two ions. The lowest excited state, which is separated from the ground state by only 0.04 eV or less, should be thermally populated at ambient temperature. Interestingly, the electronic bands of the radical ions can be accommodated by ignoring this low-lying excited state. In particular, the very strong transitions at short wavelengths (PPP, 3.2–3.8 eV; exptl 330–400 nm or 3.2–3.7 eV) and the prominent long-wave maxima (cation: PPP, 1.6 eV; exptl 681 nm or 1.8 eV; anion: PPP, 1.2 eV; exptl 888 nm or 1.4 eV) are well accounted for.

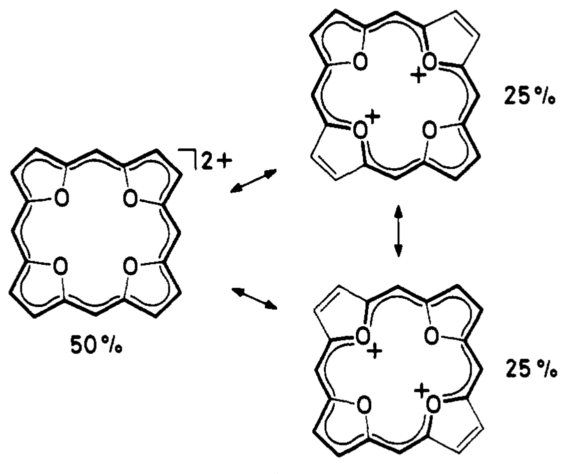

Figure 6. Mesomeric formulas of the tetraoxaporphyrin dication.

They occur from the doubly occupied MO's b_{2g}, b_{1u}, and a_u to the vacant ones b_{3g}, a_u, and b_{1u}, and they belong pairwise to B_{2u} and B_{3u}. The more intense B_{2u} transition (PPP, 3.6 eV; exptl 343 nm or 3.6 eV) has 78 and 22% contributions from $b_{3g} \leftarrow b_{1u}$ and $a_u \leftarrow b_{2g}$, respectively, whereas for the less intense one (PPP, 3.0 eV; exptl 452 and 487 nm or 2.8 and 2.6 eV) the ratio is inverse. Analogously, the more intense B_{3u} transition (PPP, 3.9 eV; exptl 315 nm or 3.9 eV) consists of 70% $b_{1u} \leftarrow b_{2g}$ and 30% $b_{3g} \leftarrow a_u$, while in the less intense one (PPP, 3.5 eV; exptl 422 nm or 3.0 eV) the two components mix with an inverse ratio. In addition, there is a low-energy, forbidden B_{1g} transition which arises almost entirely from $b_{3g} \leftarrow b_{2g}$ (LUMO ← HOMO). This transition (PPP, 1.3 eV), appearing as a very weak and broad long-wave absorption (exptl, 600–900 nm or 2.0–1.4 eV), is characteristic of $4n\pi$-electron systems in which such a transition involves alternating compression and expansion of adjacent bonds.[13] As stated above, the emission band is not a mirror image of this absorption, but a reflection of the allowed long-wave B_{2u} transition (Figure 1). Fluorescence due to emission from the second excited state has been observed for π-electron systems like azulene and its derivatives,[14a] [18]annulene,[14b] thioketones,[14c] and cycl[3.3.3]azine,[14d] which have a low-lying first excited state.

ESR Spectra. Figures 4 and 5 display the ESR spectra of the radical cation and the radical anion, along with their computer simulations. Table II lists the *g* factors and the hyperfine coupling constants due to sets of four and eight equivalent protons. The close similarity of the hyperfine data for the two radical ions is consistent with a single occupancy of the degenerate pair of MO's e_g or nearly degenerate e_g-like orbitals in the cation and a corresponding triple occupancy in the anion (Figure 2). PPP calculations, as well as a Hückel model which makes use of standard heteroatom parameters ($\alpha_O = \alpha + 2\beta$ and $\beta_{CO} = 0.8\beta$),[10b,11b] indicate that the pertinent pair of MO's is almost entirely localized on the 20-membered π-perimeter with a negligible participation of the bridging oxygen atoms. Averaging over the two degenerate Hückel MO's yields 0.070 and 0.044 as the squared LCAO coefficients at the proton-bearing centers μ = 5, 10, 15, 20 and 2, 3, 7, 8, 12, 13, 17, 18, respectively. McLachlan corrections ($\lambda = 1.2$)[15] modify the first value to 0.084, leaving the second one essentially unchanged. These π-spin populations, ρ_μ, are in good agreement with the observed proton coupling constants a_{H_μ} (Table II) when the McConnell equation,[16] $a_{H_\mu} = Q\rho_\mu$, is applied to them with a proportionality factor $|Q| = 2.6 \pm 0.3$ mT.

The ESR lines are unusually broad (widths 0.15 mT for the cation and 0.12 mT for the anion), as compared to those generally found for radical ions in solution (0.01–0.02 mT). Moreover, they could not be saturated, even by a microwave power of 200 mW, which precluded the use of ENDOR spectroscopy. Both features are characteristic of radicals in a degenerate or a nearly degenerate ground state exhibiting a dynamic Jahn–Teller effect,[17] as expected for a single or triple occupancy of e_g or almost degenerate e_g-like MO's.

Concluding Remarks

The electronic structure of the five redox stages of tetraoxaporphyrin can be interpreted by MO models in several ways, depending on which physical and chemical properties are addressed.

(i) In order to account for the successive reduction of the dication to the radical cation, the neutral compound, the radical anion, and the dianion, it is sufficient to consider the frontier MO's, which are stepwise filled up by one, two, three, and four electrons, respectively. In the diions of D_{4h} symmetry, these MO's are degenerate (e_g). This statement holds also essentially for the radical ions which have an effective D_{4h} symmetry on the hyperfine time scale and are subject to a dynamic Jahn–Teller effect. In the neutral tetraoxaisophlorin, formation of a biradical is avoided by lowering the symmetry from D_{4h} to D_{2h} and by splitting the MO's e_g into b_{2g} and b_{3g}. Such behavior closely resembles that of $4n\pi$-electron perimeters of D_{4h} symmetry, exhibiting a degenerate pair of nonbonding MO's.[9b]

(ii) For the electronic transitions in the range 300–900 nm (Figure 1), two MO's at lower and two at higher energy have to be considered, in addition to e_g or b_{2g} and b_{3g} (Figure 2). Again, the resulting MO scheme is similar to that of $4n\pi$-perimeters of D_{4h} or D_{2h} symmetry.[9b] This is because the relevant MO's are essentially restricted to the 20-membered perimeter of tetraoxaporphyrin, so that the contribution of the four oxygen atoms can be disregarded.

(iii) Structural features such as π-charge distribution involve participation of all occupied π-MO's. For the dication of tetraoxaporphyrin and its reduced congeners, many of the lower lying MO's exhibit substantial coefficients at the four oxygen atoms, in contrast to the few uppermost ones which are responsible for the observed electron transfers and excitations. Consequently, each of the oxygen atoms is predicted to bear a substantial π-charge population, as indicated in Figure 3. This population amounts to +0.25 in the dication, so that the four oxygen atoms share one unit of positive charge and a second unit is distributed over the 20 carbon π-centers of the perimeter. The dication can thus be adequately represented by the superposition of the three mesomeric formulas depicted in Figure 6. On passing from the dication to the neutral compound and to the dianion, the positive π-charge populations at the oxygen atoms are expected to decrease by only ca. 10% on each two-electron reduction step. Consequently, the additional electrons should be mainly accommodated by the carbon π-centers of the perimeter. For the neutral compound, tetraoxaisophlorin, such a distribution requires that the π-perimeter must bear almost a whole unit of negative charge (Figure 3), a structural feature which readily accounts for the sensitivity of this compound to air oxidation.

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Appendix

Bond-length alternation along the 20-membered π-perimeter of tetraoxaisophlorin is not only predicted by the PPP SCF CI method, but also results from AM1[18] and MNDO[19] calculations

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which started with D_{4h} symmetry (equalized C–C bond lengths of 140.9 pm) and optimized the geometry while preserving the planarity. For the tetraoxaporphyrin dication and dianion, the optimized structures had still D_{4h} symmetry with C–C bond lengths of 140 ± 3 pm, whereas for the tetraoxaisophlorin the symmetry was lowered to D_{2h} with these bond lengths alternating between 136 ± 2 and 145 ± 2 pm (AM1) or 138 ± 2 and 147 ± 2 pm (MNDO).

At present, experimental evidence for double-bond localization solely rests upon the observation of the weak long-wave absorption assigned to the $b_{3g} \leftarrow b_{2g}$ transition. X-ray crystallographic structure analysis of tetraoxaisophlorin[4] shows an averaged geometry, caused by superposition of reflexes arising from molecules differently oriented in the unit cells. Neither is reduction of symmetry from D_{4h} to D_{2h}, as a consequence of double-bond localization, indicated by ^{1}H and ^{13}C NMR spectra above 138 K.[4] Hereto, one may consider the corresponding results for the recently synthesized 2,3,7,8,12,13,17,18-octaethyl-*N,N′,N″,N‴*-tetramethylisophlorin[20] which is iso-π-electronic with tetraoxaisophlorin but, in contrast to this molecule, has a nonplanar geometry. The ^{1}H NMR spectra of the octaethyl-*N,N′,N″,N‴*-tetramethylisophlorin, taken in the range 201–377 K, exhibit a dynamic process diagnostic of an interconversion between two degenerate structures with localized double bonds. The coalescence temperature and the free energy of bond-shift activation are T_c = 289 K and ΔG^{*} = 55.2 kJ/mol (13.2 kcal/mol).[20] A ΔG^{*} value of 55.7 kJ/mol (13.3 kcal/mol), which is equal within the limits of experimental error, results from the formula[21]

$$\Delta G^{*} = 19.13T_c\left(9.97 + \log\frac{T_c}{\delta\nu}\right)\ [\mathrm{J/mol}]$$

where $\delta\nu$ = 230 Hz is the difference in the positions of coalescing NMR signals of the NCH$_3$ protons. Application of this formula to tetraoxaisophlorin with $\delta\nu$ = 120 Hz[22] and $T_c < 138$ K yields $\Delta G^{*} < 26.5$ kJ/mol (6.3 kcal/mol). The drastic lowering of T_c and ΔG^{*}, on going from the octaethyl-*N,N′,N″,N‴*-tetramethylisophlorin to tetraoxaisophlorin, is presumably due to the planar geometry of the latter as opposite to the saddle-like conformation of the former.[20] In this respect, it is worth mentioning that, in order to observe an analogous bond shift in the ^{13}C NMR spectra of heptalene, the solution must be cooled down to T_c = 113 K.[23] Presumably, a temperature well below 138 K is likewise necessary to detect this phenomenon in the NMR spectra of tetraoxaisophlorin, a requirement which can hardly be met in fluid solution, considering the poor solubility of the compound and the restricted choice of suitable solvents.

Supplementary Material Available: Figure S1 showing transitions between the SCF MO's of the five tetraoxaporphyrin redox stages as determined by PPP calculations starting from a perturbed D_{4h} geometry[8] (it corresponds to Figure 2 in the paper), Figure S2 displaying the SCF CI energy levels of the ground and relevant excited states resulting from these calculations, Table SI listing the characteristics of the pertinent electronic transitions[12] (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Vibrational Analysis of a Locked 14-*s-cis* Conformer of Retinal

Mary E. M. Cromwell,[1a,c] Ronald Gebhard,[1b,d] Xiao-Yuan Li,[1a,e] Elvira S. Batenburg,[1b] Johan C. P. Hopman,[1b] Johan Lugtenburg,[1b] and Richard A. Mathies*,[1a]

Contribution from the Departments of Chemistry, University of California, Berkeley, California 94720, and Leiden University, 2300 RA Leiden, The Netherlands.

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Abstract: A 12-*N*-ethano retinal Schiff base is synthesized to study the vibrational properties of a C_{14}–C_{15} *s-cis* conformer of retinal. The synthesis of the 12-*N*-ethano retinal Schiff base and seven of its isotopomers is described. Raman and FTIR spectra of this compound and its isotopic derivatives are analyzed and the normal mode assignments compared to MNDO normal coordinate calculations. The frequency of the C_{14}–C_{15} stretch at 1096 cm^{-1} is ~100 cm^{-1} below typical values for *s-trans* conformers of retinal polyenes, supporting previous arguments that *s-cis* conformers will have characteristically low frequencies for the C–C stretch of the *s–cis* bond (Smith et al., *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 967–971). Deuteriation at the 15-position produces two modes at 950 and 1044 cm^{-1} that contain C_{15}D rock character. The elevated frequency (1044 cm^{-1}) of the high-frequency component is a marker band for the C=N *syn* geometry and confirms an earlier analysis of the sensitivity of the C_{15}D rock frequency to Schiff base configuration (Ames et al., *Biochemistry* **1989**, *28*, 3681–3687). This work on retinals with chemically defined configuration and conformation provides a basis for further analysis of the geometry of these bonds in retinal-containing pigments.

Introduction

Retinal is the chromophore in visual pigments and in the light-transducing proteins found in halobacteria. Optical excitation of these pigments initiates a photochemical *cis–trans* double-bond isomerization of the retinal prosthetic group that occurs on a femtosecond time scale.[2,3] In visual pigments, this photoisomerization initiates an enzymatic cascade[4] that ultimately causes

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(1) (a) University of California, Berkeley. (b) Leiden University. (c) Present address: Genentech, Inc., 460 Point San Bruno Blvd., South San Francisco, CA 94080. (d) Present address: Organon Int. B.V., P.O. Box 20, 5340 B.H. Oss, The Netherlands. (e) Present address: Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

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