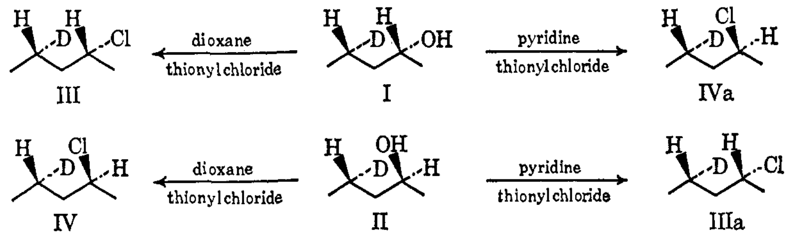
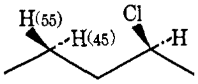
Scheme I[10]



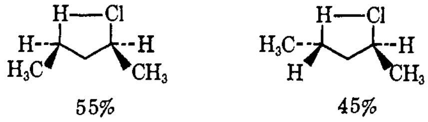
II lead to essentially the same results from the opposing reactions. Concurrently the intensity of the M − Cl ion is independent of stereochemistry. It follows from the data that the over-all stereospecificities, and deuterium incorporation,[11] for the reaction sequences outlined in Scheme I are the same. More important is the fact that the loss of the diastereotopic deuterium atoms[12] as deuterium chloride takes place to unequal extent. Since the deuteriums are related to each other in III and IV (or IIIa and IVa) exactly as the two C-4 hydrogens are related in 2-pentyl chloride (of a single configuration), the results can be summarized as shown in Scheme II.

Scheme II[10,13]



These results are compatible with a concerted elimination of hydrogen chloride (in contrast to loss of Cl· followed by H·). The simplest manner to envision such a reaction would be through a five-membered cyclic transition state. If this is so, the *mass spectral difference* between the diastereotopic hydrogens is remarkable since the competing transition states would be expected to differ by substantially less than 1 kcal![17] It is noteworthy that the favored thermochemical isomer of 1,3-dimethylcyclopentane (*i.e.*, *cis*) corresponds to the favored transition state for this elimination (Scheme III).

Scheme III



Further significance for these findings rests in the fact that an electron-impact-induced reaction occurring in compounds of widely variant structure has been shown to be sensitive to subtle structural features, and, in addition, this sensitivity is *only* a function of the transition state of the reaction.[18] It follows that studies along these lines will act as a probe into the effects of structure on these activated complexes as well as a means of correlating similar and dissimilar transition states of related electron-impact and condensed-phase processes.[22]

Acknowledgment. We are grateful for support of this research to the Petroleum Research Fund of the American Chemical Society (Grant No. 1104-Gl) and to Research Corporation for a Frederic Gardner Cottrell grant in aid.

---

(10) The diagrams in Schemes I and II are not designed to suggest conformation but rather to display convenient representations of the stereochemistry.

(11) The deuterium incorporation was quantitative as evidenced by the mass spectrum of the ketone derived by oxidation of a mixture of I and II. Further, this ketone was reduced with lithium aluminum hydride and the product was converted to chloride by reaction in dioxane and pyridine as described above. The two chlorides gave identical mass spectra.

(12) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 1 ff.

(13) The numbers correspond to the relative loss of DCl from III (IIIa) and IV (IVa). The values given have been corrected for the expected 10–20% nonspecific[5,14] displacement of tosylate by deuterium in the reduction step. This will be an accurate reflection of the relative hydrogen loss if the isotope effect for loss of DCl in III and IV is the same (not necessarily one). A referee has alternatively suggested that the observed effect may be due to different isotope effects for each isomer (III and IV). We do not favor this explanation because it is difficult to understand why the two isomers should show such a difference especially in view of the only small over-all discrimination against deuterium observed in closely related reactions.[15,16] At any rate the fundamental difference must ultimately reside in the differing stereochemical environments of the two deuterium atoms, and the following discussion is couched in these terms.

(14) W. A. Sanderson and H. S. Mosher, *J. Am. Chem. Soc.*, 88, 4185 (1966).

(15) A. M. Duffield, S. D. Sample, and C. Djerassi, *Chem. Commun.*, 193 (1966), and references included therein.

(16) M. M. Green and J. Schwab, *Tetrahedron Letters*, 2955 (1968).

(17) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 202. This assumes a puckered ring and relief of equivalent eclipsing interactions in the isomers by replacement of the two CH_2 groups in cyclopentane by H and Cl. Lack of puckering would lower the energy difference. See also the discussion of E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 250.

(18) This study presents the first detection of a mass spectrometric difference between two compounds with identical ground states (it is reasonably assumed that the configuration at the deuterated carbon has essentially no effect on the ground-state properties of these compounds). There are two previous cases of electron-impact-induced competitive reactions which take place at different rates only by virtue of transition-state differences.[19,20] The alternative possibility in this case, that the elimination is a function of the conformer populations of 2-pentyl chloride, seems unlikely especially in the light of the conformational changes which are prerequisites for elimination of hydrogen chloride and water in cyclohexyl compounds.[16,21]

(19) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, 89, 2711 (1967).

(20) E. P. Smith and E. R. Thornton, *ibid.*, 89, 5079 (1967).

(21) C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Letters*, 807 (1963).

(22) The Barton reaction[23] and the mass spectral elimination of water, processes which we propose obey similar driving forces, are being compared in detail by the present technique.

(23) M. Akhtar, "Advances in Photochemistry," Vol. 2, Interscience Publishers, New York, N. Y., 1964, pp 263–303.

Mark M. Green
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

Received February 26, 1968

The Molecular Geometry of Vanadyl Deoxophylloerythroetioporphyrin. An Analog of Chlorophyll

Sir:

The crystal and molecular structure of vanadyl deoxophylloerythroetioporphyrin (VO-DPEP) has been solved by three-dimensional X-ray techniques and is in the latter stages of analysis. The weighted *R* factor is

Table I. Intramolecular Atomic Distances (Ångströms) for VO-DPEP[a]

V–O	1.63 (2)	Ring C		Bridge Carbons	
V–N(A)	2.12 (2)				
V–N(B)	2.08 (2)	N(C)–C(11)	1.40 (2)	C(5)–C(4)	1.36 (3)
V–N(C)	1.97 (2)	N(C)–C(14)	1.39 (3)	C(5)–C(6)	1.38 (3)
V–N(D)	2.14 (2)	C(11)–C(12)	1.47 (3)	C(10)–C(9)	1.42 (3)
V–C(5)	3.48 (2)	C(12)–C(13)	1.41 (3)	C(10)–C(11)	1.45 (3)
V–C(10)	3.54 (2)	C(13)–C(14)	1.39 (3)	C(15)–C(16)	1.41 (2)
V–C(15)	3.48 (2)			C(20)–C(1)	1.40 (3)
V–C(20)	3.51 (2)			C(20)–C(19)	1.36 (3)
N(A)–N(B)	2.88 (2)				
N(B)–N(C)	2.77 (2)	Ring D		Substituents	
N(C)–N(D)	2.81 (2)				
N(D)–N(A)	2.99 (2)	N(D)–C(16)	1.38 (3)	C(2)–C(21)	1.51 (2)
N(A)–N(C)	3.98 (2)	N(D)–C(19)	1.44 (2)	C(3)–C(22)	1.64 (3)
N(B)–N(D)	4.11 (2)	N(16)–N(17)	1.46 (3)	C(22)–C(23)	1.50 (4)
Ring A		N(17)–N(18)	1.37 (4)	C(7)–C(24)	1.56 (3)
		N(18)–N(19)	1.49 (3)	C(8)–C(25)	1.54 (3)
		Ring E		C(25)–C(26)	1.51 (4)
N(A)–C(1)	1.41 (3)			C(12)–C(27)	1.52 (2)
N(A)–C(4)	1.40 (3)	C(13)–C(14)	1.39 (3)	C(17)–C(30)	1.57 (3)
C(1)–C(2)	1.47 (3)	C(14)–C(15)	1.37 (3)	C(30)–C(31)	1.59 (4)
C(2)–C(3)	1.39 (3)	C(15)–C(29)	1.56 (3)	C(18)–C(32)	1.51 (2)
C(3)–C(4)	1.48 (3)	C(29)–C(29)	1.62 (2)	Average	1.55 (2)
Ring B		C(28)–C(13)	1.63 (3)		
N(B)–C(6)	1.38 (3)				
N(B)–C(9)	1.40 (2)				
C(6)–C(7)	1.47 (3)				
C(7)–C(8)	1.36 (3)				
C(8)–C(9)	1.49 (3)				

[a] Least-squares estimated standard deviations are given in parentheses.

Table II. Interatomic Angles (degrees) for VO-DPEP[a]

Ring A		Ring C		Ring E	
N(A)	111	N(C)	101	C(13)	108
C(1)	108	C(11)	117	C(14)	119
C(2)	105	C(12)	98	C(15)	106
C(3)	111	C(13)	112	C(28)	99
C(4)	104	C(14)	112	C(29)	108
Ring B		Ring D		Bridge Carbons	
N(B)	106	N(D)	106	C(5)	128
C(6)	108	C(16)	109	C(10)	119
C(7)	111	C(17)	111	C(15)	125
C(8)	103	C(18)	104	C(20)	126
C(9)	111	C(19)	110		
		Other Angles			
N(A)–C(1)–C(20)	130	C(2)–C(1)–C(20)	122	V–N(A)–C(1)	121
N(A)–C(4)–C(5)	124	C(3)–C(4)–C(5)	132	V–N(A)–C(4)	126
N(B)–C(6)–C(5)	125	C(7)–C(6)–C(5)	127	V–N(B)–C(6)	127
N(B)–C(9)–C(10)	128	C(8)–C(9)–C(10)	121	V–N(B)–C(9)	126
N(C)–C(11)–C(10)	125	C(12)–C(11)–C(10)	119	V–N(C)–C(11)	131
N(C)–C(14)–C(15)	129	C(12)–C(13)–C(28)	140	V-N(C)–C(14)	126
N(D)–C(16)–C(15)	120	C(17)–C(16)–C(15)	131	V–N(D)–C(16)	129
N(D)–C(19)–C(20)	126	C(18)–C(19)–C(20)	124	V–N(D)–C(19)	123

[a] Least squares estimated standard deviations are ±2° for all angles.

8.4% with isotropic *B*'s for all the atoms except vanadium and the four atoms of ethylene chloride, which were refined with anisotropic *B*'s. The ethylene chloride is present as a solvent molecule of crystallization.

The significance of the VO-DPEP structure in relation to the chemistry of chlorophyll was called to the authors' attention by Earl W. Baker of Mellon Institute, who also prepared and isolated the compound.[1] The VO-DPEP is similar to other porphyrins and porphines whose structures have been determined by similar techniques,[2] except that a fifth ring E has been introduced, making the molecule a closer analog of chlorophyll. Figure 1 shows the two-dimensional arrangement of the atoms in the molecule and Tables I and II list the pertinent intramolecular bond lengths and angles.

Crystals of the material were grown by slow vapor-phase diffusion of methanol into a nearly saturated solution of VO-DPEP in ethylene chloride.[3] The crystals grew as small rhombic plates and the VO-DPEP crystallized in a 1:1 ratio with ethylene chloride. Pertinent crystal data are: space group $P2_1/a$; a = 17.963 (3),

---

(1) E. W. Baker, A. H. Corwin, E. Klesper, and P. E. Wei, *J. Org. Chem.*, in press.

(2) Numerous papers can be cited. See, for example, (a) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963); (b) D. F. Koenig, *Acta Cryst.*, **18**, 663 (1965); (c) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughy, *J. Am. Chem. Soc.*, **87**, 2312 (1965); (d) L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965).

(3) G. Donnay and C. B. Storm, *Mol. Cryst.*, **2**, 287 (1967).

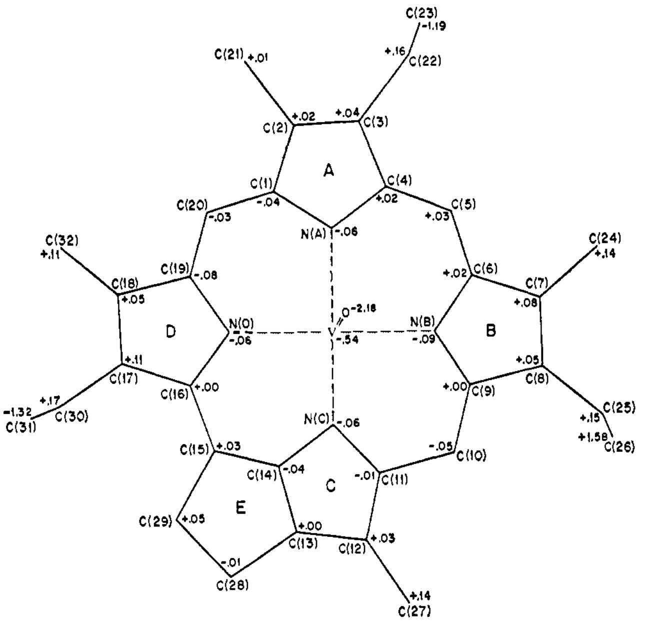


Figure 1. The two-dimensional structure of VO-DPEP projected onto the plane defined by the four nitrogen atoms. The smaller numbers at each atom specify the displacement in ångströms from the best least-squares plane using all the atoms except V, O, and the methyl and ethyl side groups.

b = 13.961 (1), c = 14.090 (3) Å; β = 116.97° (1); Z = 4; empirical formula $C_{32}H_{34}N_4VO \cdot C_2H_4Cl_2$.

The intensities of 1911 independent reflections were measured by the 2θ scan technique using an automated General Electric XRD-5 diffractometer (Cu Kα radiation). The vanadium atom position was uniquely determined from a sharpened three-dimensional Patterson synthesis. The remaining structure was found by successive Fourier syntheses using all the observed intensities with phases calculated from the partial structure. No corrections were made for absorption or extinction. (μl = 0.9 for longest crystal dimension). The vanadium and chlorine scattering factors were corrected for the real and imaginary dispersion in the structure-factor calculations.

The refined structure indicates that the four nitrogens are coplanar within the standard error, and the vanadium atom lies 0.48 Å out of this plane.[4,5] The molecule as a whole is nearly planar but can perhaps be best described as having the shape of a very shallow saucer. In Figure 1 the numbers at the atom positions represent the displacements in ångströms from the best least-squares plane defined by all the atoms except the V═O group and the attached methyl and ethyl groups. The isotropic B's increase with distance from the vanadium atom, being 2.8 Å^2 for the four nitrogens and their 8 adjacently bonded carbon atoms, 3.2 Å^2 for the 14 outer carbon atoms, and 4.3 Å^2 for the substituent methyl and ethyl carbon atoms. These are average values, and no atom has a B greater than 5.5 Å^2. The B's for the ethylene chloride are extremely anisotropic, and it is likely that this thermal motion is the cause of the low limit of observable reflections ($2\theta \leq 80°$).

The results given above suggest that the strain introduced by the ring E is not localized but is transmitted throughout the entire molecule.[6] Bond distances and angles have lost the fourfold symmetry which characterizes many of the porphyrins and porphines.[2] Another effect of the E ring is that it appears to have "pushed" the N(C) atom in toward the vanadium, as the V–N(C) bond distance (1.97 Å) is significantly shorter (about 7 σ) than the other three vanadium–nitrogen distances (2.11 Å average).

Acknowledgment. We acknowledge the support of the U. S. National Institutes of Health, General Grant No. FR-05580-013.

---

(4) *Cf.* ref 2b and 2c.

(5) M. Zerner and M. Gouterman, *Inorg. Chem.*, **5**, 1699 (1966).

(6) A. H. Corwin, J. A. Walter, and R. Singh, *J. Org. Chem.*, **27**, 4280 (1962).

Roger C. Pettersen, Leroy E. Alexander
Mellon Institute
Pittsburgh, Pennsylvania 15213

Received March 11, 1968

The One-Electron Oxidation of Magnesium Octaethylporphin

Sir:

The porphyrins are central to the energy-transforming systems of biology: photosynthesis and respiration. Their function in these systems is based on their versatile redox properties. Although the reduction of porphyrins,[1-3] including photoreduction,[4] is partially understood, the behavior of these pigments on oxidation is far less clear.[5,6] We have found conditions for the reversible oxidation of a metalloporphyrin which lead to the formation of a rather stable free radical.

When a methanolic solution of magnesium octaethylporphin is titrated with iodine the pink color changes to green and the porphyrin fluorescence disappears. The spectrum of the product (Figure 1) shows bands at 398 (ϵ 71,000) and 683 nm (ϵ 23,000), with weak absorptions to wavelengths of >1 μm ($\epsilon \lesssim 10^3$); the strong absorption bands resemble those obtained from phlorins.[1-4] The reaction is reversed by simple back-titration with potassium iodide or other mild reducing agents. The redox potential of the system porphyrin–oxidation product is about equal to that of iodide–iodine in the same solvent. The overall form of the titration curve is complex because of the multiple equilibria involved between iodine and the solvent and possibly the por-

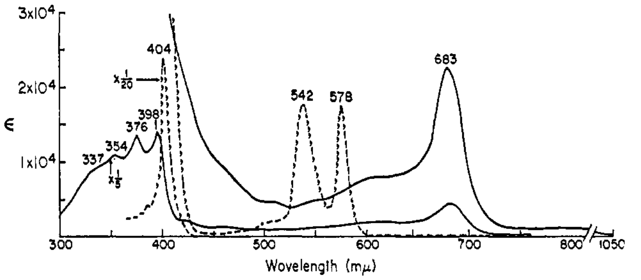


Figure 1. Absorption spectrum of magnesium octaethylporphin in methanol (----); after oxidation with $FeCl_3$ (——).

---

(1) R. B. Woodward, *Ind. Chim. Belge*, 1293 (1962).

(2) H. H. Inhoffen, P. Jäger, R. Mählhop, and K. D. Mengler, *Ann. Chem.*, 704, 188 (1967), and earlier references cited therein.

(3) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 818 (1963).

(4) D. Mauzerall, *ibid.*, 84, 2473 (1962).

(5) J. Barrett, *Nature*, **215**, 733 (1967).

(6) J. C. Goedheer, *Photochem. Photobiol.*, **6**, 521 (1967).