Dimerization and π Bonding of a Zinc Porphyrin Cation Radical. Thermodynamics and Fast Reaction Kinetics

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Abstract: Zinc octaethylporphin radical cation is shown to form a diamagnetic dimer in methanol–chloroform, 10:1, at low temperatures. At 293°, the ΔH of dimerization is -17.5 ± 0.4 kcal/mol^{-1} and ΔS is -38 ± 1 cal deg^{-1} mol^{-1}. The rate constant of dimerization, obtained by the temperature-jump method under these conditions, is $1.3 \pm 0.2 \times 10^8$ M^{-1} sec^{-1}. and that of dissociation is $5.0 \pm 0.7 \times 10^3$ sec^{-1}. The stability of the dimer is attributed to a novel $\pi-\pi'$ bond formed by overlap of the half-filled π orbitals in the face-to-face dimer of porphyrin rings. The nmr and optical spectra agree with this assignment. The oxidation of zinc octaethylporphin in the solid state and the preparation of the solid dimer containing approximately 10% of the monomeric radical are also described. Bulk magnetic susceptibility measurements, determination of the elementary cell by X-ray spectroscopy, optical, infrared, and mass spectroscopy, as well as elemental analysis are all consistent with the formulation of this solid as $(ZnOEP \cdot Br_2)_2$.

The ability of porphyrins to form definite aggregates determines many of their physical and biological properties. Optical absorption, quantum yield of fluorescence, magnetic resonances, and the activity towards ligands at the central metal ion are very dependent on the state of aggregation of these pigments. Our knowledge of chlorophyll aggregates and photosynthesis has been reviewed.[2] Examples of metalloporphyrins which form aggregates are hemes,[3] chlorophyll,[4] protochlorophyllide,[5a] and bacteriochlorophyll.[5b] In most cases, aggregation leads to a bathochromic shift and a broadening of the main absorption peaks. The most detailed structural information has been obtained from the shift of specific proton magnetic resonances in chlorophyll aggregates by Katz's[6] group.

We have found a new kind of $\pi-\pi$ dimer in the metalloporphyrin series: zinc porphyrin cation radicals form diamagnetic dimers with an intense absorption band at 930 nm. The equilibrium of this dimer with the monomeric radical has been shown to be highly temperature dependent.[7] A similar absorption in cooled solutions of MgOEP$^+$ has been observed by Fajer, *et al.*[8] We now report a thermodynamic and kinetic investigation of the reaction

$$2ZnP^+ \rightleftharpoons (ZnP)_2{}^{2+} \tag{1}$$
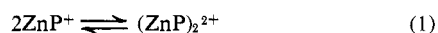
Experimental Section

Thermodynamic Data. Absorption measurements were made on a Cary 14 spectrophotometer. For measurements in the near infrared, diaphrams and neutral density glasses were introduced into the sample and reference compartments to protect the sample from the intense white light source The oxidation procedure with Fe(ClO$_4$)$_3$ and the preparation of materials have been described.[7]

The controlled temperatures were obtained by a cell holder cooled with Dry Ice–acetone for low temperatures or by a flowing liquid thermostat for intermediate temperatures. The sample temperature was measured before and after each absorption experiment. The temperature difference never exceeded 2°. The cell windows were blown dry with nitrogen gas at low temperatures. At the end of each experiment the oxidation was reversed with triethylamine, and full recovery of the ZnOEP was always observed. The concentration in most experiments was 2.7×10^{-5} M ZnOEP.

Esr measurements were made with the same solution on a Varian E-3 and a Bruker 414s spectrometer, both equipped with a variable-temperature accessory. The temperature in the solution was checked occasionally and found to agree within 2° with that recorded. A flat thin cell was used. The intensity of the signal at 55° was taken as the 100% radical point and the zero signal at $-30°$ as the pure dimer. The line width and g value of the radical are unaffected by temperature.

Fast Kinetic Measurement. The kinetics of the dimerization were studied on an improved version of the Eigen–de Maeyer temperature-jump[9] apparatus, the details of which have been described[10] elsewhere. The low solubility of the ZnOEP prevented measurements at higher concentrations. Temperature jumps were executed at 20°. A discharge voltage of 14 kV resulted in a rise of 2°. The absorption at 655 nm was observed with a photomultiplier. Five temperature jumps were executed on each sample at intervals of 5 min for temperature equilibration. The evaluation of the data followed standard procedures.[9]

Solid ZnOEP·Br$_2$. (a) From Solution. ZnOEP (100 mg) was suspended in 100 ml of methylene chloride (analytical grade Merck) and oxidized under nitrogen atmosphere with a slight excess of gaseous bromine. The end point of the oxidation was determined with a hand spectroscope. The solvent was then quickly removed in a flash evaporator, and the green residue was dried at 60° under high vacuum.

Anal. Calcd for $C_{36}H_{44}N_4ZnBr_2$: C, 57.0; H, 5.85; N, 7.41; Br, 21.1. Found: C, 56.4; H, 5.97; N, 7.43; Br, 21.6.

(b) From Crystals. Orthorhombic prisms of ZnOEP, $0.8 \times 0.3 \times 0.05$ mm, were obtained by crystallization from dioxane–methylene chloride. Their density was determined by suspension in aqueous potassium carbonate solutions. The Weissenberg diagrams were obtained in the usual way. An elementary cell of $23.3 \pm 0.5 \times 15.3 \pm 0.5 \times 9.9 \pm 0.5$ Å was found, indicating four porphyrin molecules per cell (mol wt 596, density 1.16 g cm^{-3}). The space group was $pm2_1n$ or $Pmmn$. The crystals were oxidized for 10 min with bromine vapor. Longer exposure of the crystals to bromine led to their destruction.

Anal. Found: C, 58.15; H, 6.45; N, 7.28; Br, 17.6.

(1) (a) Gesellschaft für Molekularbiologische Forschung; (b) Rockefeller University.

(2) R. G. Clayton in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., 1966, p 609.

(3) G. Blauer and B. Zvilichocsky, *Arch. Biochem. Biophys.*, **127**, 749 (1968).

(4) J. C. Goedher in ref 2, p 147.

(5) (a) C. J. Seliskar and B. Ke, *Biochem. Biophys. Acta*, **153**, 685 (1968); (b) J. G. Komen, *ibid.*, **22**, 9 (1956).

(6) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Amer. Chem. Soc.*, **85**, 3809 (1963).

(7) J. H. Fuhrhop and D. Mauzerall, *ibid.*, **91**, 4174 (1969).

(8) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *ibid.*, **92**, 3451 (1970).

(9) M. Eigen and L. de Maeyer in "Techniques of Organic Chemistry," Vol. VIII, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 895.

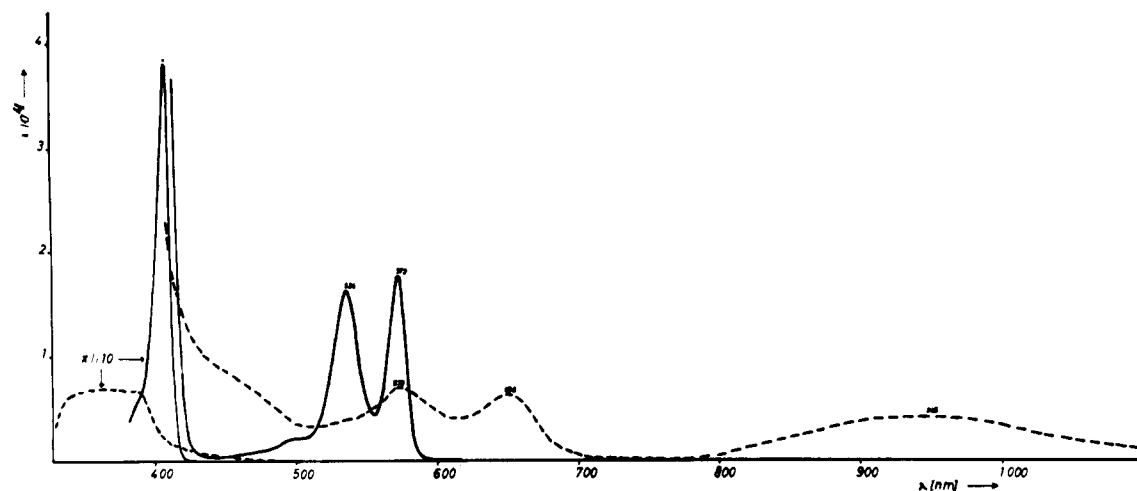(10) D. Riesner, R. Römer, and G. Maass, *Eur. J. Biochem.*, **15**, 85 (1970).

Figure 1. Absorption spectrum of ZnOEP in CHCl₃-MeOH, 1:10 (———); same solution oxidized with bromine at room temperature (— — —).
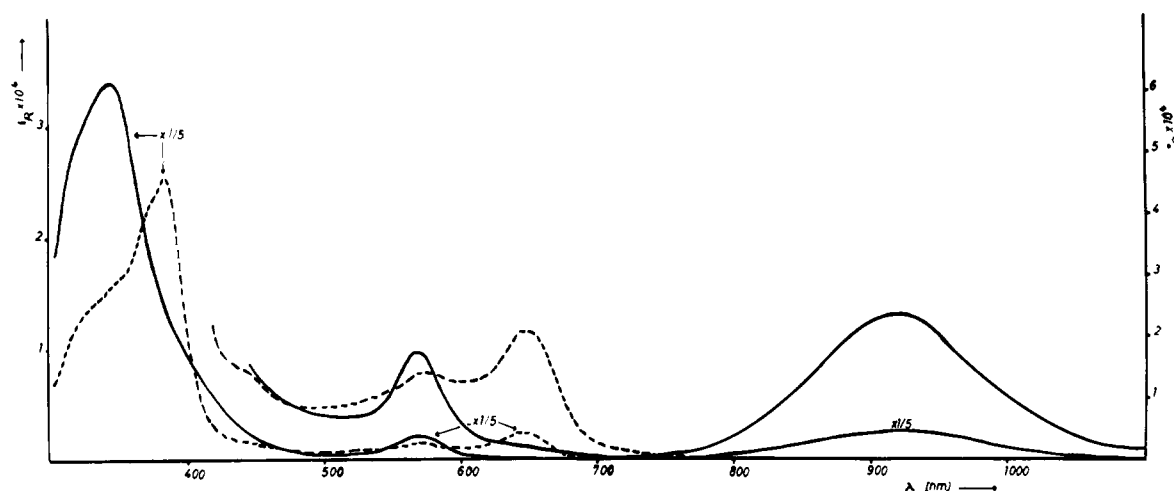

Figure 2. Absorption spectra of zinc octaethylporphyin radical cation at 55° (— — —) and its dimer at —30° (———). Solvent, MeOH-ChCl₃, 10:1; oxidant, Fe(ClO₄)₃.

(c) **Magnetic Susceptibility.** ZnOEP·Br₂ (300 mg) prepared by method a was placed in a quartz tube under nitrogen and attached to the Gouy balance. At 8.8 kG the dimer was diamagnetic, but less so then OEP itself. Calibration of the balance showed that less than 12% of the porphyrin could contain an unpaired electron.

(d) **Absorption Spectra.** ZnOEP·Br₂ (5 mg) prepared by method a was pulverized with KBr and pressed into a pellet 15 mm in diameter and 0.5 mm thick. This disk was attached to a 1-mm diaphragm and its spectra recorded in the Cary 14 vs. an identical blank disk and diaphragm. The spectrum showed the product to be >90% dimer and <10% radical.

(e) **Ir Spectra.** ZnOEP·Br₂ (15 mg) from method a was pressed into a pellet with 1 g of CsI. The spectrum recorded from 200 to 4000 cm⁻¹ did not show any strong new bands as compared with the spectrum of ZnOEP

(f) **Nmr Measurements.** A Varian HA-100 spectrometer was used, equipped with the variable-temperature probe. ZnOEP (10 mg) was suspended in 0.6 ml of d_3-acetonitrile and oxidized under nitrogen with a slight excess of bromine. At room temperature only broad peaks of the ethyl groups were discernible. The spectra sharpened at 0°, and the data quoted (see below) were taken at —30°. $meso$-d_4-ZnOEP treated under identical conditions as ZnOEP showed no signals at τ 5.65, confirming the assignment of this signal to the methine protons.

Results and Discussion

The Electronic Spectra. The absorption spectra of the starting zinc octaethylporphin (ZnOEP) and the mixture of cation and dimer found on oxidizing this

solution are shown in Figure 1. The spectra of the cation and the dimer separately are shown in Figure 2. The spectra of the ZnOEP⁺ is qualitative as expected for an aromatic hydrocarbon with an electron removed from the highest filled molecular orbital. The visible bands move to the red while the allowed Soret transition is broadened and weakened. A molecular orbital description of these radicals has been given by Fajer, et al.[8]

The outstanding characteristic of the dimer is the strong absorption band in the near-infrared. This is a fully allowed transition, having an oscillator strength of about 0.75. It is most likely a charge transfer transition analogous to the band at 800 nm (ϵ ~12,000) observed by Hausser and Murrell[11] in a cooled solution of N-ethylphenazyl radical. In our case the optical transition would be from the dimer ground state to a dication–neutral porphyrin pair. We will discuss the electronic structure of the dimer in the Conclusion, after presenting evidence that it is in fact a dimer and that the ground state is a singlet.

Dimerization of radicals with resulting optical spectral changes ranging from minor to extensive are quite

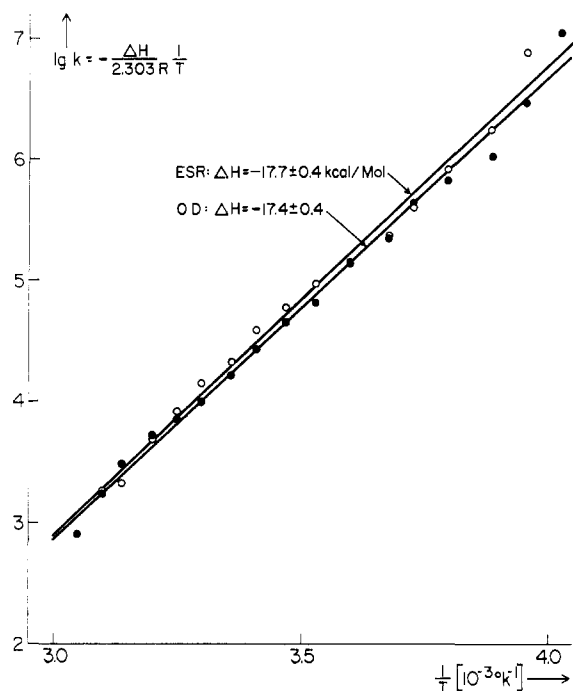(11) K. H. Hausser and J. N. Murrell, J. Chem. Phys., 27, 500 (1957).

$$\lg k = -\frac{\Delta H}{2.303\,R}\frac{1}{T}$$

ESR: $\Delta H = -17.7 \pm 0.4$ kcal/Mol

OD: $\Delta H = -17.4 \pm 0.4$

Figure 3. Van't Hoff plots of the equilibrium constant for the dimerization of ZnOEP$^+$ (●) from absorption and (○) from esr.

(a)   (b)

Figure 4. Typical oscillograms of temperature jumps of 2° at 655 nm and 20° in CHCl$_3$–MeOH, 10:1, with 0.5 M LiClO$_4$ at (a) 5.25 $\times$ 10^{-5} M, 20 μsec cm^{-1}, 10 mV cm^{-1}, and (b) 2.1 $\times$ 10^{-5} M, 50 μsec cm^{-1}, 2 mV cm^{-1}.

common: sodium benzophenoneketyl,[12] phenanthrenesemiquinone,[13] 4-carbomethoxypyridinyl,[14] pyridinyl biradicals,[15] and Wurster's Blue.[11] In fact dimerization was a complication in Michaelis' classical analysis[16] of the redox titration curves which initiated this field of chemistry.

Thermodynamics of Dimer Formation. The equilibrium constant of reaction 1 could be determined spectrophotometrically knowing the total concentration of pigment (C_0) and the extinction coefficients of the radical (ϵ_R) and dimer (ϵ_D). The latter were obtained from spectra at the highest and lowest temperatures, respectively. The concentration of dimer was calculated from the absorbancy at a given wavelength by the relation

$$[dimer] = (A - \epsilon_R C_0)/(\epsilon_D - 2\epsilon_R)$$

Wavelengths of 655 and 945 nm were both used, the calculated equilibrium constants agreeing to ±11% over the whole range of temperature −25 to +55°, corresponding to a range of 10^4 in the equilibrium constant. Good isosbestic points were obtained. The solvent mixture chloroform–methanol, 1:10, was chosen because of the convenient temperature range. The equilibrium constant could also be determined by measurement of the esr signal of the radical cation. The constant agreed very well with that obtained spectrophotometrically. This agreement and the internal consistency of the analysis strongly argue that we are dealing with a simple dimerization. Further proof for reaction 1 will be given in the section on kinetics. The logarithm of the equilibrium constants determined

(12) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).
(13) T. L. Staples and M. Swaz, *ibid.*, **92**, 5022 (1970).
(14) M. Itoh and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 3959 (1967).
(15) M. Hoh and E. M. Kosower, *ibid.*, **90**, 1843 (1968).
(16) L. Michaelis and M. P. Schubert, *Chem. Rev.*, **22**, 437 (1938).

by spectrophotometry and by esr are plotted *vs.* the reciprocal of the absolute temperature in Figure 3. The slopes of these plots obtained by a least-squares computation allow calculation of the rather large ΔH of the dimerization: by spectra, -17.4 ± 0.4, and by esr, -17.7 ± 0.4 kcal mol^{-1}. The heat of dimerization of large organic radicals is about -2 kcal mol^{-1}, *e.g.*, N-ethylphenazyl in ethanol[17] and sodium fluorenone in dimethoxyethane.[12] Porphyrin cation dimers are thus exceptionally stable. We believe this is caused by a face-to-face π bond (see Conclusion).

The free energy and the entropy of the dimerization are calculated for the ZnOEP$^+$ dimer and are given in Table I. The large negative entropy is most likely

Table I. Thermodynamic Data for the Dimerization of ZnOEP$^+$ in Methanol–Chloroform, 10:1

T, °K	Log K	$-\Delta G$, kcal mol^{-1}	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, cal deg^{-1} mol^{-1}
253	6.5	7.5		
263	5.8	7.0		
273	5.4	6.7		
283	4.8	6.2		
293	4.4 $\pm$ 0.1	5.9 $\pm$ 0.1	17.5 $\pm$ 0.4	38 $\pm$ 1
305	4.0	5.5		
313	?.7	5.2		
323	3.2	4.8		

caused by interactions with the solvent. The description in terms of the Born charging of the dielectric[18] at least gives the correct sign because the dielectric constant of solvents such as methanol decreases with increasing temperture.

Reaction Kinetics. An example of the relaxation process when a solution of the radical cation and dimer is subjected to a temperature jump is shown in Figure 4. The plot of the logarithm of the radical concentration differences at infinite time and at time t (Figure 5) is a straight line, demonstrating that only one process is involved in this equilibrium. The relaxation time is related to the rate constants of dimerization[9] by the following expression

$$1/\tau = 4k_{12}C_R + k_{21}$$

where k_{12} and k_{21} are respectively the rate constants for recombination and dissociation and C_R is the concentration of free radical. By combining this equation and the law of mass action, the following expression, independent of knowledge of the absolute radical concentration, can be derived.

$$1/\tau^2 = 8k_{12}k_{21}C_0 + k_{21}^2$$

(17) K. H. Hausser, *Z. Naturforsch. A*, **11**, 20 (1956).
(18) G. H. Nancollas, *Quart. Rev., Chem. Soc.*, **14**, 402 (1960).
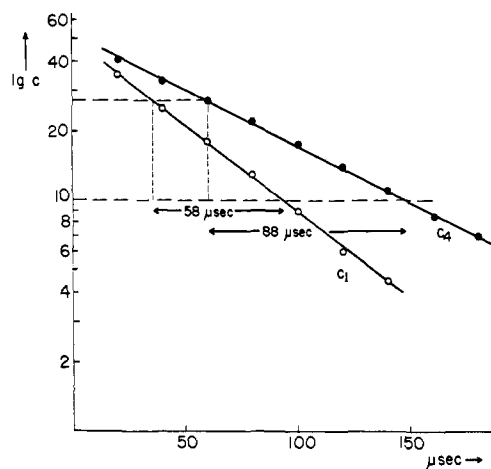
Figure 5. Plots of the logarithm of the absorbance change *vs.* time for the temperature jumps of Figure 4. The concentration in arbitrary units is measured as the difference between the final concentration and that at time t. The dotted line indicates the relaxation time, τ.

Figure 6. Plot of the inverse square of the relaxation time, τ, *vs.* the concentration of ZnOEP.

Table II. Solvent Dependence of Dimerization of $ZnOEP^+$

Solvent	Dimer, %
CH_2Cl_2	0
$CHCl_3$	0
$CHCl_3-CH_3OH$, 1:10	45
CH_3CN	60
H_2O^a	100

[a] This was zinc hematoporphyrin. The concentration of radical in all cases was about 10^{-5} M; temperature, 20°.

The linear relation between C_0, the total concentration, and the reciprocal of the square of the relaxation time is in fact observed (Figure 6). This is a kinetic proof of the validity of the simple dimerization reaction 1 which is independent of the equilibrium measurements. Although k_{21} can be obtained from the intercept in Figure 6, the resulting value is very inaccurate. It was therefore replaced by k_{12}/K, since the equilibrium constant at 20° is accurately known. Using the slope of the line in Figure 6, the following rate constants were calculated.

$$k_{12} = (1.31 \pm 0.17) \times 10^8 \, \text{l. mol}^{-1} \, \text{sec}^{-1}$$

$$k_{21} = (4.95 \pm 0.65) \times 10^3 \, \text{sec}^{-1}$$

The rate constants calculated from the kinetic data alone were consistent with the above. The association rate constant is only twice as large as that found[19] for a water-soluble porphyrin preparation. The authors of that paper discussed changes of water structure as causing the rate to be much slower than diffusion controlled. In our case the factor of 10 below the encounter limited rate constant is most easily explained by electrostatic and steric factors. The ion pairs must adopt a particular orientation if the porphyrin rings approach to the van der Waals limit with the counterions on opposite sides of the sandwich.

Influence of Solvents and Counterions on the Dimerization. The solvent has a pronounced effect on the radical–dimer equilibrium. The relative concentration of the dimer in different solvents at 20° is given in Table II. The general trend is that solvents of higher dielectric constant stabilize the dimer. We believe the polarization of the solvent decreases the electrostatic repulsion of the face-to-face dimer of the ion pairs. The dielectric constants of solvents such as methanol increase on cooling, and thus lower temperatures favor dimerization. The observation that the dimer of $MgOEP^+ClO_4$ is formed more readily in methylene chloride than in methanol[8] may be explained by specific solvation of the Mg atom on the position opposite to

(19) R. R. Das, R. F. Pasternack, and R. A. Plane, *J. Amer. Chem. Soc.*, **92**, 3312 (1970).
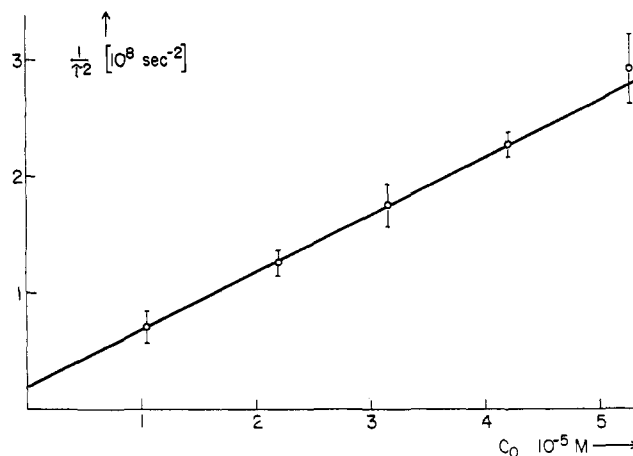
the counterion. This would prevent close contact of the porphyrin rings.

In many cases of radical ion dimerization, the counterion is often found to affect[12,13] the equilibrium. We measured the equilibrium constant in methanol-chloroform, 10:1, in the presence of 0.4 M lithium perchlorate, lithium bromide, and tetramethylammonium bromide. Only a small increase in the amount of dimer, presumably a salting-out effect, was observed.

The Nmr Spectrum of the Dimer. Whereas the radical $ZnOEP^+$ yields only broad nmr signals, the dimer in acetonitrile at $-30°$ produced a well-defined spectrum: CH_3 of ethyl at τ 9.2, CH_2 of ethyl at τ 7.4, and methine C–H at τ 5.65. The latter assignment was confirmed by the absence of this particular signal in the dimer prepared from *meso-d_4*-ZnOEP. The same methine protons in ZnOEP have a resonance at τ -0.05. The diamagnetic shift in the dimer is about 10 times larger than that found in chlorophyll dimers.[6] These results, combined with the observation that porphyrin radicals only yield very broad absorption peaks, show that the ground state of the dimer is diamagnetic and that considerable changes in the electronic structure, particularly in those levels contributing to the large ring currents in the porphyrin molecule, have occurred.

Preparation of the Dimer in the Solid State. When a concentrated solution of $ZnOEP^+$ Br^- in chloroform was diluted with petroleum ether, a green precipitate formed. This substance was diamagnetic in the Gouy balance (see Experimental Section), showed a strong absorption at 930 nm in KBr disk, and gave an elemental analysis consistent with one Br_2 per ZnOEP.

When crystalline ZnOEP was brought into contact with bromine vapor for a short time, it was also ox-
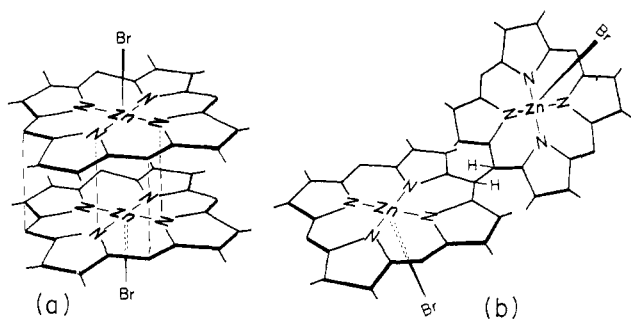
Figure 7. Proposed structures for the cation radical dimer: (a) $\pi-\pi'$ bond, one-half of the overlaps indicated by dashed lines; (b) meso carbon–carbon bond. Dashes on periphery indicate ethyl groups; meso carbon–hydrogen bonds and other π bonds are not shown.

idized to a green compound. This substance contained about 80% as much bromine as did the former precipitate.

Both oxidized species yielded a peak in the mass spectrum at $m/e \sim 12,00$, not found in the starting porphyrin. This again indicates the stability of the $(ZnOEP)_2{}^{2+}$ dimer.

Experiments with Other Metalloporphyrins. Zinc octaethylchlorin cation radical[20] did not yield a long-wavelength absorption under the conditions where $ZnOEP^+$ formed the dimer, e.g., acetonitrile, at $-12°$. The magnesium octaethylporphin radical cation showed essentially the same behavior as $ZnOEP^+$, but dimerized at lower temperatures. Copper and nickel octaethylporphin cation radicals did not yield any strong, long-wavelength absorption on cooling. However, spectral shifts do accompany the pronounced changes in esr spectra[7] with temperature previously noted in solutions of Ni and Pd octaethylporphyrin cation radicals. CuOEP was also oxidized in the solid state, but the resulting brown-green compound gave low carbon values in elemental analysis and could not be quantitatively reduced to CuOEP.

Zinc hematoporphyrin oxidized in water–methanol, 10:1, at 20° gave a pure dimer spectrum with a maximum at 945 nm (Table II).

Conclusion

The properties of the $ZnOEP^+$ dimer argue that it is an extreme form of the $\pi-\pi$ complex described by Hausser and Murrell.[11] As two identical radicals approach one another to the point that the electronic wave functions interact strongly, the doublet states will split into singlet and triplet states. The resulting dimer will have a singlet ground state only if the electron pairing results in sufficient concentration of electrons in the bonding region to overcome the inherently lower energy of the triplet state. The stability of the dimer justifies our assigning to it a definite, if novel, chemical bond. Two extreme models may be postulated for this bond (Figure 7). The conventional model contains a single bond between the meso carbons of the macrocycles. The novel model consists of multicentered overlap and pairing of the electrons in the previously half-filled π orbitals in a face-to-face dimer. We shall call it a $\pi-\pi'$ bond. A series of

intermediate stages between these extremes can be written, but we shall restrict our discussion to the end points.

The conventional model requires a hindered bond between the meso carbons. However, this may be rationalized by the observed weakness of the bond in the dimer, 17.5 kcal mol⁻¹, as compared to a normal carbon–carbon bond. Essentially this model is that of the progenitor of free radicals, viz., hexaphenylethane, which has a carbon–carbon bond energy of 11 kcal mol⁻¹. The nmr spectrum is, however, hard to fit to this model. One would expect some splitting of the meso protons in this phlorin-type molecule, whereas only one peak is observed.

The novel model explains the weak bonding as the limited overlap between the a_{2u} orbitals which are centered on nitrogens and meso carbons.[21] The repulsions of the other filled π orbitals limit the overlap and prevent a full $\pi-\pi$ bond from forming. On the assumption that the radicals are held at the van der Waals distance, ~ 3.5 Å, and assuming the self-consistent field overlap calculated by Mulliken, et al.,[22] the stabilization of this novel $\pi-\pi'$ bond would be ~ 20 kcal mol⁻¹. This could account for a good portion of the observed enthalpy of 17.5 kcal mol⁻¹. Any remainder has clearly to do with solvent interactions as discussed above. We also suggest that the observed energy of dimerization of one-tenth this value in other radical dimers is caused by a layer of solvent molecules separating the two radicals in the dimer. In these cases, a ground triplet state becomes quite possible.

The nmr spectrum of the dimer is compatible with this $\pi-\pi'$ bond. Clearly the center of symmetry would ensure only one class of ethyl and meso protons as is observed. Classically speaking, the cross conjugation between the rings will reduce the large ring currents and the protons reflect this decreased shielding. A less symmetric $\pi-\pi'$ bonding of the porphyrin planes coupled with rapid interchange of positions would lead to the same conclusions. Nmr measurements at very low temperatures, so far unobtainable, would be needed to resolve this fine point.

Several other pieces of evidence support the assignment of the $\pi-\pi'$ bond to the $ZnOEP^+$ dimer. The reduced pyrrole ring in the chlorin macrocycle distorts the system and prevents close approach of the porphyrin planes. Thus the fact that no dimer is observed with zinc octaethylchlorin is understandable. The distortion of the symmetry of the system also makes the highest filled π level (half-filled in the cation) of the a_{1u} type.[23] The spread of this orbital over some 14 carbon atoms might also weaken the $\pi-\pi'$ bond. It is thought that the unshared electron in $MgOEP^-$ is also in a largely a_{1u} orbital,[8] and this may account in part for its weaker tendency to dimerize. The increased solvation of the Mg atom would also hinder the close approach of the porphyrin planes. A comparison of the spectra of the cation and its dimer (Figure 2) indicates that the higher energy absorption band of both the visible and Soret groups appear to be con-

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(21) M. Gouterman, J. Mol. Spectrosc., **6**, 138 (1961).

(22) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys., **17**, 1248 (1949).

(23) C. Weiss, H. Kobayashi, and M. Gouterman, J. Mol. Spectrosc., **16**, 415 (1965).

served while the lower energy component is lost. If the a_{2u} orbital is heavily involved in the latter transitions, this result would be expected when the half-filled a_{2u} orbital is filled in the postulated $\pi-\pi'$ bond of the dimer. We assign the near-infrared band of the dimer to an internal charge transfer from the $\pi-\pi'$ bonding orbital to its antibonding counterpart. We thus predict that this band will be polarized perpendicular to the porphyrin planes in contrast to all the other porphyrin transitions which are restricted to the plane. This excitation may also cause photodissociation of the dimer, but the rapidity of the dimerization may make this prediction hard to detect experimentally. These predictions are unique to the $\pi-\pi'$ bonded dimer and could serve to distinguish this structure from alternatives such as a single bond between meso carbons.

Electron Population Analysis of Accurate Diffraction Data. III. Application of One- and Two-Center Formalisms to Tetracyanoethylene Oxide[1]

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Abstract: One- and two-center variable-coefficient scattering factor formalisms have been used to obtain a least-squares fit to accurate experimental diffraction data for tetracyanoethylene oxide. In some cases, calculations were carried out using both self-consistent-field isolated atom and standard molecular exponent Slater-type minimal basis sets. In general, refinements of selected one-center products of the first-order density matrix give net atomic charges in agreement with INDO results except for the cyano groups which appear neutral. When the two-center density pieces are included, the average charge of the cyano group is $-0.10\ (5)$ electron. A π to σ electron transfer at the cyano atoms relative to the INDO result is indicated by an analysis of the one-center density matrix refinement. This and similar previously observed charge migrations for certain atoms in α-oxalic acid dihydrate and cyanuric acid are interpreted in terms of a simulation of π density in the bonding region by appropriately thermally averaged σ orbitals. The absence of such migration in a refinement which explicitly includes two-center π-bond density pieces indicates this shift to be an artifact of the one-center approximation.

I n principle, the diffraction of X-rays by crystals is capable of providing detailed information concerning the time-averaged electron distribution. However, it has been shown by us and others that the spherical atom scattering factor formalism which is used in the conventional X-ray experiment introduces a bias into the least-squares refinement procedure which results in systematic errors in the derived parameters. While these errors are of minimal consequence as far as routine crystal structure analysis is concerned, they tend to almost completely obscure bond density features in, for example, Fourier difference maps. The standard X-ray diffraction approach is therefore inadequate for obtaining accurate charge densities.

Recently, considerable success has been achieved in resolving charge density features in several molecular crystals by using neutron diffraction experiments to obtain thermal and positional parameters which are unbiased by any assumed form of the scattering factor, since neutron form factors are constant functions of the magnitude of the scattering vector.[3-6] While the difference maps phased with these parameters have proved quite useful in qualitative discussions, it has become clear that more quantitative results are needed to facilitate a more convenient comparison with theoretical calculations.

The approach used here attempts to span an experimental charge distribution by a minimal basis set of atomic wave functions with variable coefficients. The density is a sum of the contribution from each molecular orbital.

$$\rho = \sum_i^{\text{occ}} \psi_i^* \psi_i$$

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