

in the host lattice to allow the copper ion to take up the same specific tetragonally elongated symmetry as in the pure crystal, and, therefore, a dynamic Jahn-Teller effect is not observed. From the differing orientations of the  $g$  tensors in the doped and pure crystals, it can be inferred that together with the tetragonal distortion a rotation of about  $10^\circ$  takes place around the elongated axis. The orientation angle data for the pure complex shows that the axes of the  $g$  tensor are not coincident with the copper-oxygen bond directions. This was also found to be the case for the pyridine  $N$ -oxide complexes, and as for these species the principal axis of the  $g$  tensor (assuming it to be basically axial) is directed into the region of the ligand N-O bond. This is in agreement with the now well-established result that this group of complexes deviate markedly from octahedral symmetry with regard to their electronic properties.<sup>18</sup>

As a final point we note that there is no significant spin exchange between the two magnetically inequivalent sites in the pure complex. This can be seen qualitatively, in that the  $g$  tensors for the sites in the pure and doped crystals agree well with one another, and quantitatively from simulation of the ESR spectra, taking into account exchange interaction with the help of the modified Bloch equations. These calculations show the exchange constant to be very small. In fact, the exchange must be in the order of the copper hyperfine splitting

since the latter cannot be observed in the pure system. The line width is, however, still determined by the hyperfine splitting and is maximal in the direction of the maximum  $g$  value where also the largest hyperfine splitting is expected. The line shape is in between Lorentzian and Gaussian, proving again that the exchange is small. In the case of the monoclinic phase of the pyridine  $N$ -oxide nitrate complex, the exchange is also small, as a consequence (at Q-band frequency) two lines are observed.<sup>19</sup> This is in contrast to the pure trigonal pyridine  $N$ -oxide complexes where the exchange interaction is much larger and amounts to about  $0.7 \text{ cm}^{-1}$ . The relevant copper-copper distances are 9.45 and 10.55 Å for the trigonal and monoclinic pyridine  $N$ -oxide complexes and 11.57 Å for the picoline  $N$ -oxide complex.

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**Registry No.**  $\text{Cu}(\text{CH}_3\text{C}_5\text{H}_4\text{NO})_6(\text{ClO}_4)_2$ , 35828-27-4;  $\text{Zn}(\text{CH}_3\text{C}_5\text{H}_4\text{NO})_6(\text{ClO}_4)_2$ , 24470-65-3.

**Supplementary Material Available:** Anisotropic thermal parameter and structure factor tables for Cu- and  $\text{Zn}(\text{CH}_3\text{C}_5\text{H}_4\text{NO})_6(\text{ClO}_4)_2$  (8 pages). Ordering information is given on any current masthead page.

(18) Mackay, D. J.; Evans, S. V.; McMeeking, R. F. *J. Chem. Soc., Dalton Trans.* 1978, 160.

(19) Keijzers, C. P.; Wood, J. S., unpublished work.

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## Synthesis and Properties of Tetraphenylporphyrin Molecules Containing Heteroatoms Other Than Nitrogen. 6. Electrochemical Studies

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When the two NH groups in tetraphenylporphyrin (TPP) are replaced by the group 6A heteroatoms S, Se, and Te, bonding interactions within the porphyrato core are formed as is apparent from their short distances as found in X-ray structure analysis and is also supported by MO calculations. Because of the heterosubstitution there is a change in the energies of the frontier orbitals in such a way that the LUMO is stabilized. The HOMO is stabilized because the short distances between the chalcogen atoms give rise to the formation of  $d\pi-d\pi$  orbitals, which interact with the frontier orbitals. These stabilization mechanisms are expressed by positive shifts of both the reduction and the oxidation potentials as measured by cyclic voltammetry. It appears that there is a linear relationship between the difference between the first oxidation and first reduction potential (which decreases with the increasing bonding interaction) and  $1/\lambda_{\text{max}}$  ( $\text{cm}^{-1}$ ) of the Soret transition. The decrease of the first reduction potential relates linearly to the chemical shifts of the  $\beta$ -hydrogens in the  $^1\text{HMR}$  spectra. For the para-substituted  $\text{S}_2\text{TPP}$  molecules the Hammett constant  $\rho$  for the first oxidation reaction is abnormally large. This is connected with the nonplanarity of the cation radicals. The optical spectrum of the  $\text{Se}_2\text{TPP}$  cation radical provides support for this suggestion.

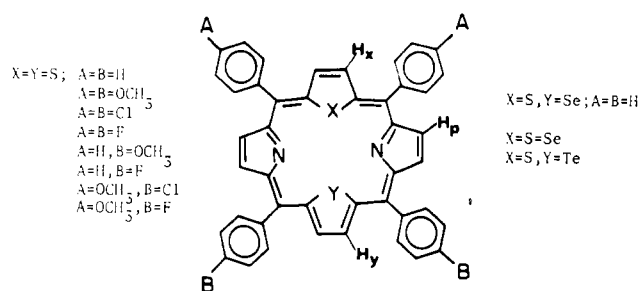
### Introduction

Electrochemistry as a tool for the study of the physical properties of porphyrins and metalloporphyrins has been extensively used recently.<sup>2</sup> The influence of the metal ion, the axial ligand, and the para substituents on the half-wave potentials is well established.<sup>3-18</sup>

The effect of substituents on the oxidation and reduction reactions of the  $\pi$  system of tetraphenylporphyrin (TPP) was investigated by Kadish et al. by cyclic voltammetry in methylene chloride<sup>18</sup> and in other solvents.<sup>14</sup> In all solvents it was found that electron-donating substituents shift the oxidation and the reduction potentials to more positive values. Elec-

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 (2) Smith, K. M. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1975; Chapter 14.  
 (3) Fuherhop, J.-H.; et al. *J. Am. Chem. Soc.* 1973, 95, 5140-5147.  
 (4) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* 1970, 92, 2982.  
 (5) Walker, F. A.; et al. *J. Am. Chem. Soc.* 1975, 97, 2390-2397.  
 (6) Felton, R. H.; Linschitz, H. *J. Am. Chem. Soc.* 1966, 88, 1113-1116.  
 (7) Clark, D. W.; Hush, N. S. *J. Am. Chem. Soc.* 1965, 87, 4238-4242.  
 (8) Fajer, J.; et al. *J. Am. Chem. Soc.* 1970, 92, 3451-3459.

(9) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* 1974, 7, 26-32.  
 (10) Kadish, K. M.; et al. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 1014-1016.  
 (11) Felton, R. H.; et al. *J. Am. Chem. Soc.* 1971, 93, 6332-6334.  
 (12) Kadish, K. M.; et al. *J. Am. Chem. Soc.* 1974, 96, 591, 592.  
 (13) Kadish, K. M.; et al. *J. Am. Chem. Soc.* 1975, 97, 282-288.  
 (14) Kadish, K. M.; Morrison, M. M. *J. Am. Chem. Soc.* 1976, 98, 3326-3328.  
 (15) Kadish, K. M.; Morrison, M. M. *Inorg. Chem.* 1976, 15, 980-982.  
 (16) Walker, F. A.; et al. *J. Am. Chem. Soc.* 1976, 98, 3484-3489.  
 (17) Kadish, K. M.; Larson, C. *Bioinorg. Chem.* 1977, 7, 95-105.  
 (18) Kadish, K. M.; Morrison, M. M. *Bioinorg. Chem.* 1977, 7, 107-115.



**Figure 1.** New heterosubstituted and para-substituted tetraphenylporphyrins.

tron-attracting substituents on the other hand, shift the potentials to more negative values. When the  $E_{1/2}$  values were plotted vs. the Hammett substituent constant  $\sigma$ ,<sup>19</sup> a linear free-energy relationship were obtained. Both ring reduction to yield the  $\pi$ -anion radical and ring oxidation to yield the  $\pi$ -cation radical showed sensitivity to para substitution, and an average value of  $0.07 \pm 0.01$  V was found for the Hammett reaction constant  $\rho$ .

The Hammett constants for the oxidation reactions to yield  $\pi$ -cation radicals were found relatively more sensitive to para substitution and varied from 0.064 V for free-base TPP (in  $CH_2Cl_2$ ), to 0.089 V for the nickel complex  $TPPn^{II}$  (in  $CH_2Cl_2$ ).<sup>15</sup>

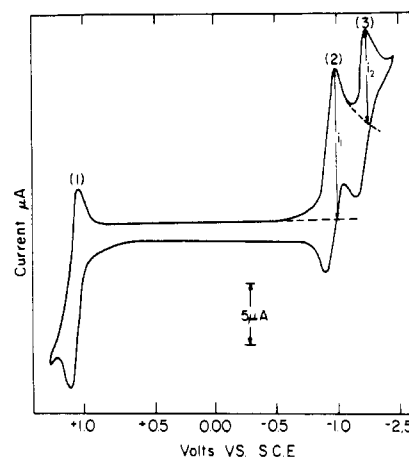
When the two NH groups in TPP are replaced by the group 6A heteroatoms S, Se, and Te,<sup>20–22</sup> bonding interactions within the porphyrin core are found, as is apparent from the short distances between these heteroatoms as well as between the heteroatoms and the nitrogens found in the X-ray structure analyses<sup>23</sup> (Figure 1). Recent MO calculations<sup>24</sup> support this bond formation. It was found that new molecular orbitals contribute to this bonding interaction, in which the major contribution is that of the chalcogen atoms. The above results are supported by EPR and optical spectra of the different cation and anion radicals of these new heterosubstituted tetraphenylporphyrins.<sup>25</sup>

The bonding interactions within the core cause changes in the aromatic pathways. This is expressed in the chemical shifts of the different hydrogens in the  $^1H$  NMR. We recently published the high-resolution  $^1H$  NMR studies which showed that the inner and outer aromaticity pathways are affected by heterosubstitution as well as by para substitution.<sup>26</sup>

It appears that all the physical properties of these porphyrins are affected by these new interactions. We felt that some information on the energies of the outer orbitals is needed for future and deeper understanding of the relationships among the different physical properties of these porphyrins. Therefore we present here the results of an electrochemical study which was carried out by cyclic voltammetry in methylene chloride of different heterosubstituted and para-substituted tetraphenylporphyrin molecules.

### Experimental Section

The porphyrins were prepared as described in ref 20–22, and in ref 30. The purification was on basic alumina. The cyclic voltammetry



**Figure 2.** Typical cyclic voltammogram of  $3 \times 10^{-3}$  M  $S_2$ TPP in  $CH_2Cl_2$  and 0.1 M TBAP. The scan rate is 50 mV/s. The numbers in parentheses refer to redox reactions corresponding to eq 1–3.

**Table I.** Reversible Half-Wave Potentials for Different Heterosubstituted Tetraphenylporphyrins in  $CH_2Cl_2$  ( $E_{1/2}$  in V vs. SCE)

porphyrin	1st oxidn (1)	1st redn (2)	2nd redn (3)	$\Delta_{redox}^a$	$X \cdots Y, ^b$ Å
TPP	1.03	-1.23	-1.55	2.26	4.40
$S_2$ TPP	1.18	-0.94	-1.21	2.12	3.02
$S_2Se$ TPP <sup>c</sup>	1.17	-0.91	-1.19	2.08	2.89
$Se_2$ TPP <sup>d</sup>	1.14	-0.88	-1.18	2.02	2.85
$S_2Te$ TPP <sup>e</sup>	dec (?)	-0.82	-1.10		2.65

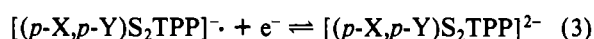
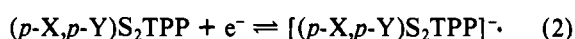
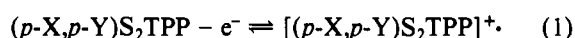
<sup>a</sup>  $E_{1/2}(1) - E_{1/2}(2)$ . <sup>b</sup> Figure 1. <sup>c</sup> Tetraphenyl-21-selena-23-thiaporphyrin. <sup>d</sup> Tetraphenyl-21,23-diselenaporphyrin. <sup>e</sup> Tetraphenyl-21-tellura-23-thiaporphyrin.

measurements were performed on 20 mL of  $3 \times 10^{-3}$  M solutions of the porphyrins in  $CH_2Cl_2$  and 0.1 M tetrabutylammonium perchlorate (TBAP), at 25 °C. The solutions were degassed for 15 min with  $CH_2Cl_2$ -saturated argon. Methylene chloride was Fluka spectroscopic grade and was shown to be electrochemically pure under our conditions. Typical scan rates were 50 mV/s. The working electrode was a Metrom Pt wire, and the counterelectrode was a Metrom Pt foil (1 cm<sup>2</sup>). The saturated calomel electrode was connected with the solution by a bridge. This bridge contained saturated solution of TBAP in  $CH_2Cl_2$  in the solution end and saturated solution of TBAP in methanol in the calomel end. The potentiostat was homemade, IR compensation was used, and the voltammograms were recorded on a Hewlett Packard XY-recorder. The middistances between oxidation and reduction peaks were taken as measured half-wave potentials and were reproducible within 5 mV.

### Results and Discussion

A typical cyclic voltammogram of tetraphenyl-21,23-dithiaporphyrin ( $S_2$ TPP) in methylene chloride is shown in Figure 2. In all cases investigated, similar voltammograms were obtained, i.e., two reduction peaks and one oxidation peak. Further oxidation was accompanied by decomposition.

The electrode processes (oxidation and reduction) did not satisfy all the diagnostic criteria for reversible charge transfer.<sup>27</sup> Thus although the potential of the response was in agreement with  $E_p^a - E_p^c = 59 \pm 5$  mV, the anodic to cathodic current ratio  $i_p^a/i_p^c$  was far from unity. It can thus be concluded that the electrode processes which confirm that reactions 1–3 are



- (19) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420–427.  
 (20) Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540–6544.  
 (21) Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Tetrahedron Lett.* **1978**, 167–170.  
 (22) Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Tetrahedron Lett.* **1978**, 1885, 1886.  
 (23) Frolow, F.; Rabinovich, D.; Ulman, A.; Manassen, M., manuscripts in preparation.  
 (24) Hill, R.; Gouterman, M.; Ulman, A., manuscript in preparation.  
 (25) Richardson, P.; Fajer, J.; Ulman, A.; Manassen, J., to be submitted for publication.  
 (26) Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *J. Am. Chem. Soc.* **1979**, *101*, 7055–7059.

- (27) Weissberger, A.; Rossiter, B. W. "Electrochemical Methods"; Wiley: New York, 1971; Part IIA, pp 536–540.

**Table II.** Half-Wave Potentials ( $E_{1/2}$  in V vs. SCE) for (*p*-A, *p*-B) $S_2$ TPP<sup>a</sup> in  $CH_2Cl_2$ 

A	B	1st oxidn (1)	2nd redn (2)	2nd redn (3)
OCH <sub>3</sub>	OCH <sub>3</sub>	1.01	-1.01	-1.25
H	OCH <sub>3</sub>	1.07	-0.98	-1.21
F	OCH <sub>3</sub>	1.075	-0.955	-1.175
Cl	OCH <sub>3</sub>	1.14	-0.99	-1.23
H	F	1.17	-0.95	-1.20
H	H	1.18	-0.94	-1.21
F	F	1.23	-0.91	-1.17
Cl	Cl	1.26	-0.87	-1.15

<sup>a</sup> Of Figure 1.

not reversible. From Figure 2 it appears that the currents of the two reduction processes are not equal. These observations indicate that chemical reactions are coupled to the electrochemical processes and will be discussed elsewhere.

In Table I a summary of the half-wave potentials for the oxidation and reduction reactions is given for the heterosubstituted tetraphenylporphyrins. For comparison the half-wave potentials of TPP are included. The difference between the first oxidation potential and the first reduction potential ( $\Delta_{redox}$ ) is also given.

In order to understand the electrochemical reactions better, we undertook a systematic synthesis of symmetrically and unsymmetrically para-substituted  $S_2$ TPP molecules<sup>28</sup> (Figure 1) and studied the effect of electron-attracting and electron-donating groups on the electrochemical half-wave potentials. In Table II the values of  $E_{1/2}$  are given for the various substituted  $S_2$ TPP molecules.

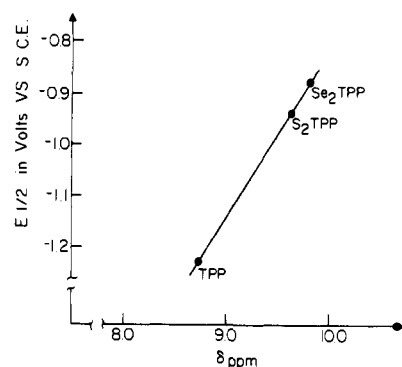
The effect of substituting two NH groups in TPP by two S atoms on the first oxidation and reduction potentials is a shift of both to more positive values (Table I), but the effect on the reduction process is larger. By subsequent substitution of S by Se and Te the first reduction potential continues to decrease, while the first oxidation potential stays more or less constant or even decreases somewhat. Consequently  $\Delta_{redox}$  decreases with increasing bonding interactions between the heteroatoms. These shifts indicate different stabilization mechanisms of the HOMO and the LUMO as can also be learned from MO calculations.<sup>24</sup> In the discussion of the high-resolution <sup>1</sup>H NMR results<sup>26</sup> we suggested that the bonding interactions between the chalcogen atoms act as an electron drain on the molecular  $\pi$  system. As a result large downfield shifts of the proton resonances were observed. This electron-drain effect can be compared to the effect which transition metals have on the electrochemical behavior of metalloporphyrins and is called "the inductive effect" by Fuhrhop.<sup>3</sup> The observed positive shifts of the reduction potentials can be related to this inductive or electron-drain effect, which the heterosubstitution has on the outer orbitals.

The stabilization of the HOMO, which occurs on substitution of NH groups by S atoms is to be explained by participation of the empty d orbitals of the chalcogen atoms. This mechanism is valid *only* when the bonding interaction is considered. Thus the short distances found in the X-ray analysis demand the definition of four  $d\pi-d\pi$  orbitals:

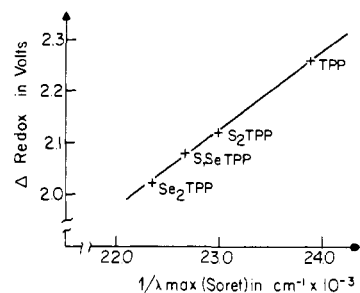
$$\phi_{1,2} = d_{xz}(1) \pm d_{xz}(2)$$

$$\phi_{3,4} = d_{yz}(1) \pm d_{yz}(2)$$

These new orbitals have the right symmetry to interact with the outer porphyrin orbitals, and MO calculations show indeed that a considerable stabilization is achieved by this d participation. Thus without the participation of the empty d



**Figure 3.** Plot of  $E_{1/2}$  of the first reduction potential vs. the chemical shifts ( $\delta$ ) of the  $\beta$ -hydrogens.



**Figure 4.** Plot of  $\Delta_{redox}$  in V vs. the energy of the Soret transitions ( $1/\lambda_{max}$ ,  $cm^{-1}$ ).

orbitals a repulsion is found between the two heteroatoms, and in the case of  $Se_2$ TPP a distance of 4.0 Å should have been found instead of the experimental value of 2.85 Å.

The difference between these two stabilization mechanisms provides an explanation for the different behavior of the oxidation and reduction potentials. Thus the inductive effect suggested for the stabilization of the LUMO increases with the increasing bonding interactions, and as a result the reduction potential shifts to more positive values. On the other hand, while the d orbitals stabilize the HOMO, the introduction of heteroatoms with electronegativities smaller than that of nitrogen can be expected to destabilize the filled orbitals by providing larger electron densities.<sup>29</sup> As a result we find a positive shift when sulfur is introduced but almost a constant value (or even an opposite trend) for further substitution.

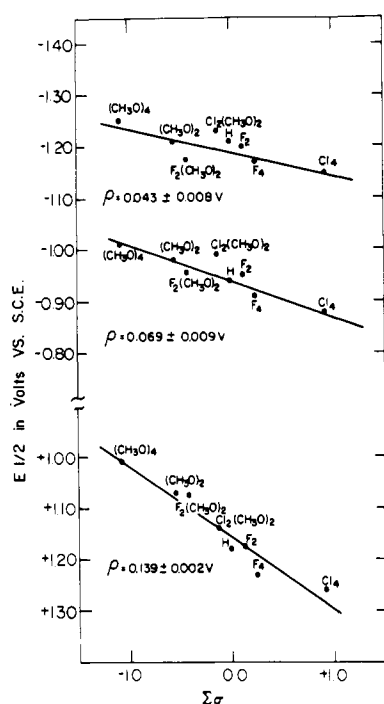
It has been shown before<sup>30</sup> that there is a linear relationship between the chemical shifts in the <sup>1</sup>H and <sup>13</sup>C NMR of the heterocycles thiophene, selenophene, tellurophene, and furane and the electronegativities of the corresponding heteroatoms. This kind of relationship cannot be found here. However, according to the model suggested above, the first reduction potential may serve as a measure for the molecular "electron affinity" in these systems, instead of the individual electronegativities which do not take into account the bonding interactions in the core. Thus a linear relationship between the chemical shifts and the first reduction potentials can be expected. This relationship is illustrated in Figure 3.

The Soret transition is the major  $\pi \rightarrow \pi^*$  transition in the optical spectra of porphyrins and is the only transition which contains  $x$ - and  $y$ -polarized components. It thus may serve as the best expression for the various effects chalcogen substitution has on the outer orbitals of the porphyrin molecule. Experimentally it is the only transition which shows a gradual red shift with heterosubstitution. In Figure 4 is shown how this red shift relates linearly to the quantity of  $\Delta_{redox}$  of Table I.

(28) Ulman, A.; Manassen, J. *J. Chem. Soc., Perkin Trans. 1* 1979, 1066-1069.

(29) Neot-Mer, M.; Adler, A. D. *J. Am. Chem. Soc.* 1972, 94, 4763, 4764.

(30) Gronowitz, S.; et al. *Acta Chem. Scand., Ser. B* 1974, B28, 175-184.



**Figure 5.** Plot of  $E_{1/2}$  vs.  $\Sigma\sigma$  for the electrode reactions (1)–(3) ( $T = 25^\circ\text{C}$ , solvent  $\text{CH}_2\text{Cl}_2$ , electrolyte TBAP (0.1 M), concentration of porphyrin  $3 \times 10^{-3}$  M).

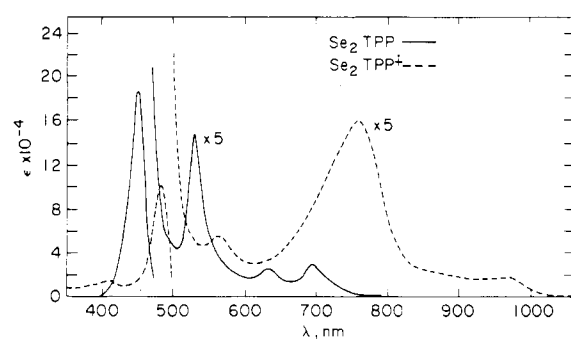
The results of Table II can be treated according to the Hammett linear free-energy relationship,<sup>31</sup> which in our case becomes

$$E_{1/2} = \rho \Sigma\sigma$$

where  $\rho$  is given in volts. Its value depends on the kind of electron-active group, the electrolyte, and the temperature.<sup>32</sup>  $\Sigma\sigma$  is used here instead of 4 because of the unsymmetrically para-substituted  $\text{S}_2\text{TPP}$  molecules. Figure 5 illustrates the results.

It is clear from Figure 5 that ring oxidation to yield the  $\pi$ -cation radical is appreciably more sensitive to para substitution than ring reduction to yield the  $\pi$ -anion radical. This is in marked contrast to results found for TPP.<sup>14</sup> The  $\rho$  value of  $0.069 \pm 0.009$  V for the reduction of free-base  $\text{S}_2\text{TPP}$  is in good agreement with the value given for TPP and metalloporphyrins ( $0.069 \pm 0.007$  V). The Hammett reaction constant for the oxidation process ( $0.139 \pm 0.002$  V), on the other hand, is about twice as high as the one given for TPP ( $0.07 \pm 0.01$  V) and is even higher than the value reported for the dissociation of (*p*-X)TPP conjugate acids ( $0.125$ ).<sup>29</sup>

In order to understand the abnormally high  $\rho$  value for the oxidation reactions, we have to consider the optical spectrum



**Figure 6.** Optical spectrum of the  $\text{Se}_2\text{TPP}$  cation radical in THF at  $25^\circ\text{C}$ .

of the cation radical obtained for  $\text{Se}_2\text{TPP}$  as is given in Figure 6. The Soret transition and  $Q_{IV}$  band show a red shift and decrease in intensity, while a broad and strong band appears in the visible region (620–820 nm). There is thus a great similarity between this optical spectrum of the cation radical and that of the conjugate acid,<sup>21</sup> and this may indicate a similarity also in structure, i.e., considerable nonplanarity. When an electron is abstracted from the HOMO the bonding interactions between the heteroatoms are weakened, and as a result of the electrostatic and steric interactions in the core the different heterocycles tend to tilt out of the NLS plain to form a conjugate acid like structure.<sup>33</sup> The result of this structural change is a rotation of the phenyl rings toward the porphyrin plane, which is accompanied by much larger overlap between their  $\pi$  systems. The result of these changes is the larger Hammett reaction constant.

### Conclusions

In this study the electrochemical oxidation and reduction of heterosubstituted and para-substituted tetraphenylporphyrins were investigated. The following effects were described and could be explained: (a) The oxidation and reduction potentials are shifted in a positive direction with heterosubstitution. (b)  $\Delta_{\text{redox}}$  decreases with heterosubstitution. (c) The first reduction potentials represent the “electron affinity” of the heterosubstituted porphyrins and relate linearly to the chemical shifts of the peripheral hydrogens. (d)  $\Delta_{\text{redox}}$  relates linearly to  $1/\lambda_{\text{max}}$  of the Soret transitions. (e) The Hammett reaction constant  $\rho$  is abnormally large for the oxidation of the para-substituted  $\text{S}_2\text{TPP}$  molecules. This can be explained by assuming a nonplanar structure for the  $\pi$ -cation radicals, which is in agreement with its optical spectrum.

These effects were shown to be in agreement with the  $^1\text{H}$  NMR results described in ref 26 and the tentative MO model suggested there, which was confirmed by MO calculations.

**Registry No.** TPP, 917-23-7;  $\text{S}_2\text{TPP}$ , 57511-57-6;  $\text{S}_1\text{SeTPP}$ , 66951-07-3;  $\text{Se}_2\text{TPP}$ , 66951-06-2;  $\text{S}_1\text{TeTPP}$ , 68231-96-9; (*p*- $\text{OCH}_3$ , *p*- $\text{OCH}_3$ ) $\text{S}_2\text{TPP}$ , 71248-63-0; (*p*-H, *p*- $\text{OCH}_3$ ) $\text{S}_2\text{TPP}$ , 71221-21-1; (*p*-F, *p*- $\text{OCH}_3$ ) $\text{S}_2\text{TPP}$ , 71221-25-5; (*p*-Cl, *p*- $\text{OCH}_3$ ) $\text{S}_2\text{TPP}$ , 72389-69-6; (*p*-H, *p*-F) $\text{S}_2\text{TPP}$ , 72359-17-2; (*p*-F, *p*-F) $\text{S}_2\text{TPP}$ , 71221-20-0; (*p*-Cl, *p*-Cl) $\text{S}_2\text{TPP}$ , 71221-19-7;  $\text{Se}_2\text{TPP}^{\bullet+}$ , 76299-76-8.

(31) Leffler, J. E.; Grunwald, E. “Rates and Equilibria of Organic Reactions”; Wiley: New York, 1963; pp 172–179.

(32) Zuman, P. “Substituent Effect in Organic Polarography”; Plenum Press: New York, 1970.

(33) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735–2748.