ACTA CHEMICA SCANDINAVICA 22 (1968) 1317–1326

Semi-empirical Molecular Orbital Studies of Neutral Porphin, PH_2, the Dianion P^{2-} and the Dication PH_4^{2+}

M. SUNDBOM

Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden

The π and σ lone pair electron system of the porphin molecules PH_2, P^{2-} and PH_4^{2+} has been studied in a modified Pariser-Parr-Pople method. The electronic transitions of both $\pi-\pi^*$ and $n-\pi^*$ types are calculated. The calculated electronic spectrum is in satisfactory agreement with experiment. A new interpretation of the Soret band splitting is given.

I. INTRODUCTION AND SUMMARY

In several enzymes a porphyrin constitutes the central part of the prosthetic group. Investigations of porphyrins and metal-porphyrins are therefore of importance for the interpretation of their activity in the metabolism of the living cell. The present semi-empirical MO study of the pure porphin molecule, PH_2, is a first step in an intended theoretical investigation of metal-porphyrins. An extensive list of review articles on porphyrins can be found in Ref. 1.

The molecule PH_2 is a tetrapyrrole planar compound, shown in Fig. 1. Its structure has been determined by X-ray diffraction analysis by Webb and Fleischer.[2] The two inner hydrogen atoms of PH_2 are attached to opposite

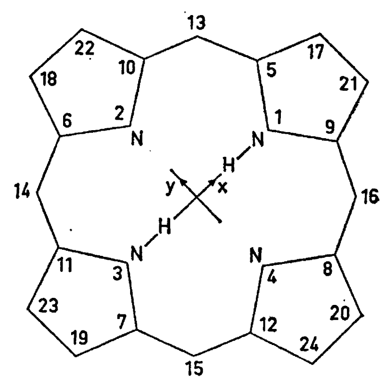

Fig. 1. The porphin skeleton.

nitrogens and perhaps hydrogen-bonded to neighbouring nitrogens.[2-4] The symmetry of PH_2 is thus D_{2h}. For comparison the ions P^{2-} and PH_4^{2+} of assumed symmetry D_{4h} have also been studied by the present method. In Fig. 1 the xy-plane is the plane of the molecule with the inner protons on the x-axis. For the neutral PH_2 molecule the xy-degeneracy is removed.

The simple Hückel method has been applied to PH_2 by many authors,[5-9] but this method does not allow a satisfactory assignment of the spectrum. Weiss, Kobayashi and Gouterman[10] have applied the SCF semi-empirical Pariser-Parr-Pople method to PH_2 and a series of other porphyrins. They used a few different standard sets of semi-empirical parameters and were able to give a good overall interpretation of the spectrum up to the intense Soret band. In order to account for the experimental fact that the visible Q_y band is stronger than the Q_x band, they had to change their parameter sets by introducing nonzero values of resonance integrals, β_{ij}, between next nearest neighbours.

The present study predicts the Soret (B) band to split even more than the visible (Q) band. For both Q and B the calculated energy and intensity are lower for the x-polarized state than for the y-polarized state. Further the lowest $n-\pi^*$ transition is predicted to be in the Soret region.

The semi-empirical method and the scheme for parameter evaluation of the present study are briefly described in section II. The results of the investigation are presented and discussed in section III. The SCF—MO's have been evaluated by means of a data machine programme written by P. Eisenberger, T. Alm and B. Roos. This programme also calculates the energy levels of excited states by mixing all configurations obtained from single excitations. The CDC 3600 machine at the University of Uppsala and the UNIVAC 1107 at Stadsförbundet, Stockholm, have been used for the present calculations.

II. METHOD AND DETAILS OF THE CALCULATIONS

The Pariser-Parr-Pople (PPP) method in the SCF—MO—LCAO form has been adopted. In a series of papers[11-13] from this laboratory a scheme for the evaluation of the semi-empirical parameters of this method has been suggested and applied to unsaturated pure hydrocarbons and to nitrogen containing molecules. This scheme has also been applied in the present study of porphyrin. The previously obtained parameter values are collected in Table 1. This parameter set is a fixed set determined from experimental data of a chosen set of small standard molecules and it has been successfully applied in investigations of molecules containing nitrogen atoms.[13]

In all calculations of the present study the molecular geometry assumed is that published by Webb and Fleischer[2] (*cf.* Table 3).

1. *PH_2, neutral porphin.* The neutral porphin molecule has symmetry D_{2h}. The degree of hydrogen bonding is still a question open to discussion. In the present investigation two extreme cases have been considered:

(a) No hydrogen bond
(b) "Very strong" hydrogen bond: all four nitrogens have been assumed to be equivalent, giving the molecule the symmetry D_{4h}.

Table 1. Semi-empirical parameters for heteroatomic molecules containing nitrogen.

Carbon [11,12]		Nitrogen [13]					
		Pyridine-nitrogen π-parameters		Pyrrole-nitrogen π-parameters		Pyridine-nitrogen σ-parameters	
$R_{CC}^\circ =$	1.397 Å	$R_{CN}^\circ =$	1.338 Å	$R_{CN}^\circ =$	1.338 Å		
$\gamma_{\pi\pi}$	11.97 eV	$\gamma_{\pi\pi}$	15.44 eV		15.44 eV	$\gamma_{\sigma\sigma}$	17.53 eV
γ_{CC}°	6.91 eV	γ_{CN}°	7.16 eV		6.34 eV	$\gamma_{\sigma\pi}$	13.95 eV
δ_{CC}^γ	−3.99 eV/Å	δ_{CN}^γ	−3.99 eV/Å		−3.99 eV/Å	$K_{\sigma\pi}$	1.57 eV
β_{CC}°	−2.42 eV	β_{CN}°	−2.72 eV		−2.25 eV	W_σ	−10.96 eV
δ_{CC}^β	3.05 eV/Å	δ_{CN}^β	2.63 eV/Å		2.63 eV/Å	$\gamma_{\sigma 1 \pi 2}$	7.33 eV
W_C°	−9.84 eV	W_N°	−1.57 eV		−8.52 eV		
ΔW_C°	0.07 eV	$\Delta W_N^\circ(C)$	0.14 eV		0.14 eV		
δ_{CC}^W	9.22 eV/Å	$\Delta W_C^\circ(N)$	0.03 eV		0.03 eV		
		δ_{CN}^W	5.60 eV/Å		5.60 eV/Å		

In case (a) the two nitrogen atoms bounded to hydrogen atoms have been treated as pyrrole-nitrogens and the other two nitrogens as pyridine-nitrogens (*cf.* Table 1). The σ lone pairs of the pyridine-nitrogens have been included in the calculations for a rough estimate of the $n-\pi^*$ transitions.

In case (b) the σ lone pairs have not been included and the values of the semi-empirical parameters of the π system have been chosen as the arithmetic mean of pyrrole- and pyridine-type values.

Let θ be a parameter describing the "degree of hydrogen bonding". $\theta = 0$ for no hydrogen bond and $\theta = 1$ for "very strong" hydrogen bond. The "real" molecule may be defined to have a splitting of the Q band equal to the experimentally found splitting. The spectrum for the real case can then be obtained by linear interpolation between the calculated spectra for cases (a) and (b). The benzene solution spectrum of PH_2 measured by Rimington, Mason and Kennard [14] gives

$$\Delta Q_{exp} = E_{max}(Q_y) - E_{max}(Q_x) = 2700 \text{ cm}^{-1} \quad (1)$$

corresponding to a value of $\theta = 0.68$.

2. *P^{2-}*. P^{2-} has symmetry D_{4h}. All four nitrogen atoms have been treated as pyridine nitrogens. The values of the one-center two-electron integrals have been chosen corresponding to a value of the charge $Z_N = -0.5$.

3. *PH_4^{2+}*. PH_4^{2+} has been assumed to be planar with symmetry D_{4h}. This is of course an oversimplification because the mutual repulsion of the central hydrogens probably results in a tilting of the pyrrole rings.

The central part of the ion has been considered to consist of two pyrrole nitrogen atoms, two pyridine nitrogen atoms, and two protons (Fig. 2). The parameter values, "α_μ", obtained from this configuration, have then been symmetrized in the following manner:

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \tfrac{1}{2}(``\alpha_1" + ``\alpha_2") \quad (2)$$

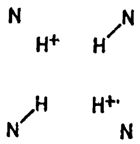

Fig. 2. The assumed atomic arrangement for the central part of PH_4^{2+}; *cf.* section II, 3.

III. RESULTS AND DISCUSSION

1. *Molecular orbitals.* The molecular orbital energies of porphin, are presented in Table 2. The vertical ionization potentials of PH_2 obtained from the energy of the highest filled orbital is 6.56 eV for case (a) and 6.58 eV for case (b). (*cf.* section II, 1).

As far as is known to the author there is no published observed ionization potential of porphin. For phthalocyanine the ionization potential is determined to be 7.0 ± 0.5 eV from field emission microscopy.[15]

Table 2. Molecular orbitals, φ_i, and orbital energies ε_i for PH_2.

PH_2 with no hydrogen bond (*cf.* section II, 1 case a.) Symmetry D_{2h}		PH_2 with "outsmeared" hydrogen bond (*cf.* section II, 2 case b.) Symmetry D_{4h}	
φ_i	ε_i (a.u.)	φ_i	ε_i (a.u.)
1 b_{1u}	−0.4954	1 a_{2u}	−0.4905
1 b_{3g}	−0.4874	1 e_g	−0.4765
1 b_{2g}	−0.4721	1 b_{1u}	−0.4494
2 b_{1u}	−0.4508	1 b_{2u}	−0.4092
1 a_{1u}	−0.4119	2 e_g	−0.3567
3 b_{1u}	−0.3673	2 a_{2u}	−0.3424
2 b_{3g}	−0.3667	2 b_{1u}	−0.3365
1 $a_{1g}(\sigma)$	−0.3653	3 e_g	−0.3332
1 $b_{3u}(\sigma)$	−0.3653	1 a_{1u}	−0.2426
2 b_{2g}	−0.3606	3 a_{2u}	−0.2412
3 b_{3g}	−0.3535	4 e_g	−0.0361
4 b_{1u}	−0.3211	2 b_{2u}	0.0298
3 b_{2g}	−0.3122	3 b_{1u}	0.1118
2 a_{1u}	−0.2452	5 e_g	0.1297
5 b_{1u}	−0.2417	2 a_{1u}	0.1383
4 b_{3g}	−0.0421	3 b_{2u}	0.1773
4 b_{2g}	−0.0338	6 e_g	0.1808
3 a_{1u}	0.0296	4 a_{2u}	0.1843
6 b_{1u}	0.1032		
5 b_{3g}	0.1173		
5 b_{2g}	0.1318		
4 a_{1u}	0.1354		
5 a_{1u}	0.1795		
6 b_{3g}	0.1796		
6 b_{2g}	0.1960		
7 b_{1u}	0.1962		

2. *Bond lengths and π-electron densities.* The following bond order-bond length relations [13,16] have been used

$$R_{\mu\nu}(\mathrm{CC}) = 1.517 - 0.180\ p_{\mu\nu} \quad (3)$$

$$R_{\mu\nu}(\mathrm{CN}) = 1.458 - 0.180\ p_{\mu\nu} \quad (4)$$

The results of the bond length calculation are collected in Table 3 where also experimental data and the theoretical results by Weiss *et al.*[10] are presented. For comparison the observed bond distances for pyrrole [17] are also included in Table 3. The obtained π-electron densities are given in Table 4.

Table 3. Calculated and observed bond distances for neutral pure porphin, PH_2. All values in Å. The numbering of the atoms is given in Fig. 1. For comparison the observed bond distances of tetraphenyl porphyrin (TPP) and pyrrole are also included.

Bond	Bond length					
	PH_2				TPP	Pyrrole
	Calc. Present work. Symmetry D_{2h} *cf.* section II, 1, case a.	Calc. Present work. Symmetry D_{4h} *cf.* section II, 1, case b.	Calc.[10]	Obs.[2]	Obs.[24]	Obs.[25]
5– 1	1.379	1.361	1.402	1.367 *a*	1.374	1.374
6– 2	1.349	1.361	1.355	1.367 *a*	1.364	—
13– 5	1.404	1.407	1.402	1.386	1.400	—
13–10	1.409	1.407	1.409	1.386	1.400	—
17– 5	1.429	1.441	1.420	1.442	1.428	1.381
18– 6	1.454	1.441	1.443	1.442	1.455	—
21–17	1.375	1.367	1.378	1.342	1.355	1.417
22–18	1.360	1.367	1.363	1.342	1.347	—

[a] The arithmetic mean of the values published by Webb and Fleisher.

Table 4. π-Electron densities. The numbering of the atoms is given in Fig. 1.

Atom No.	π-Electron density				
	PH_2 symmetry D_{2h} *cf.* section II, 1 case a	PH_2 symmetry D_{4h} *cf.* section II, 1 case b	P^{2-}	PH_4^{2+}	Pyrrole from previous calc.[13]
1	1.673	1.457	1.202	1.728	1.656
2	1.217	1.457	1.202	1.728	
5	0.968	0.948	0.997	0.983	1.072
6	0.956	0.948	0.997	0.983	
13	1.057	1.068	1.099	0.968	—
17	1.051	1.039	1.103	0.919	1.099
18	1.029	1.039	1.103	0.919	

Table 5. Calculated and observed electronic transitions of neutral pure porphin, PH_2. For comparison the observed solution spectrum of free base deuteroporphyrin IX dimethyl ester and the vapour phase spectrum of meso-tetraphenylporphyrin are reproduced. Transition frequencies in kK.

Generic names Ref. 19, 21.	PH_2								PH_2			Free base deuteropor-phyrin IX-dimethyl ester	TPP		
	Calculations								Observation			Observation	Observation		
	Present work: *cf.* section II, 1								Rimington *et al.*[14] in benzene			Caughey *et al.*[21] in chloroform	Mullins *et al.*[23] in vapour		
	real case			case a			case b								
	ν	f	pol	ν	f	pol	ν	f	ν_{max}	range [a]	log ε	ν_{max} [b,c]	ν_{max} [d]	range [a]	log ε
Q	13.6	0.002	x	12.5	0.0005	x	14.7	0.004	17.75	16.0–18.5	1.37	16.16 (0–0)	—	16.1–21.7	—
	16.3	0.012	y	16.4	0.016	y			20.43	18.5–22.2	4.2	18.87 (0–0)			
B	26.4	0.53	x	25.2	0.32	x	28.9	0.97	25.22	23.8–27.0→	5.4	25.06	24.7	22–27	5.6
	30.9	1.8	y	31.8	2.22	y							27.6s	27–29→	5.3
$n-\pi^*$	—			31.6	0.0001	z	—								
N	35.2	2.5	x	35.0	2.88	x	35.5	1.70				31.55			
	35.7	0.6	y	35.8	0.09	y									
L	40.2	1.0	x	40.2	1.12	x	40.1	0.90				~37.59			
	42.4	0.5	y	43.5	0.39	y									
	47.0	0.5	x	46.4	0.63	x	48.4	0.15							
	48.7	0.05	y	48.9	0.007	y									
	50.9	0.04	x	49.7	0.0004	x	51.3	0.11							
	51.2	0.10	y	50.2	0.09	y									

[a] An arrow after the last value indicates a cut-off in the measurements. [b] No observations beyond 40 kK. [c] No absorption curves published. [d] s shoulder.

3. *Electronic spectra.* The absorption spectra of neutral pure porphin, PH_2, dissolved in benzene and in ethanol have been examined by Rimington *et al.*[14] As far as is known to the author there are no published data on the spectra of the dianion, P^{2-}, and the dication PH_4^{2+}, of pure porphin. Falk[18a] in his book "Porphyrins and Metalloporphyrins" has published spectra of the dications of some different porphyrins, measured by Dempsey.[19] His data show that the Soret band of the dication is displaced to longer wavelength in relation to the corresponding neutral porphyrin. According to Falk[18b] this red shift of the Soret band is also found for the dianion.

In the present study the transition energies have been calculated by configurational interaction including all singly excited states. The obtained results are presented in Tables 5 and 6 together with available experimental data. In discussing the spectra I have used the generic names introduced by Platt[20] and Caughey, Deal, Weiss and Gouterman.[21] The present study predicts the sequence of the four lowest allowed $\pi-\pi^*$ transitions to be Q_x, Q_y, B_x, and B_y in accordance with low-temperature polarization spectral data of porphin by Sevchenko, Solov'ev, Mashenkov and Shkirman.[22] Q_x is predicted to have lower intensity than Q_y. The absorption spectrum reported

Table 6. Calculated electronic transitions of PH_2, P^{2-} and PH_4^{2+}. Observed solution spectrum of the free base and the dication of deuteroporphyrin IX dimethyl ester. Transition frequencies in kK.

	Calculations present work						Observations Dempsey[18a,19] In aqueous sodium dodecyl sulphate			
	PH_2 *cf.* Table 5		P^{2-}		PH_4^{2+}		Deuteroporphyrin IX dimethyl ester *cf.* Table 5		Dication of deuteroporphyrin IX dimethyl ester	
	ν	f	ν	f	ν	f	ν_{max}[a]	log ε	ν_{max}[a]	log ε
$\pi-\pi^*$	13.6	0.002	11.7	0.015	14.9	0.012	17.6	3.91	18.2	4.17
	16.3	0.012					20.1	4.18		
	26.4	0.53	26.2	0.94	32.9	0.37	25.1	5.29	24.9	5.60
	30.9	1.8								
	35.2	2.5	34.2	1.13	34.4	3.81				
	35.7	0.6								
	40.2	1.0	42.3	0.09	37.3	0.001				
	42.4	0.5								
			43.3	1.11						
	47.0	0.5	48.3	0.50	50.5	0.006				
	48.7	0.05								
	50.9	0.04	52.7	0.13	51.6	0.006				
	51.2	0.10								
$n-\pi^*$	31.6	0.0001	24.4	0.006						
	57.4	0.0006	48.7	0.003						

[a] No observations beyond 26 kK.

by Rimington *et al.*[14] verifies this prediction. Caughey *et al.*[21] report solution spectra of substituted metal and free base deuteroporphyrins in the region 650—250 mμ. In Table 5 their data of free base deuteroporphyrin IX dimethyl ester in chloroform solution are reproduced. Their observed band at $\sim$31 550 cm^{-1} may be assigned to the calculated transitions at 35 200 cm^{-1} (N_x) and 35 700 cm^{-1} (N_y). The observed band at $\sim$37 590 cm^{-1} may be assigned to the calculated band at 40 200 cm^{-1} (L_x). In doing this assignment, I make the very probable assumption that the corresponding bands in unsubstituted porphin are only slightly shifted in comparison with deuteroporphyrin IX dimethyl ester. The difference between calculated and observed band maxima is thus of the order of 4000 cm^{-1}. Previous calculations [13] on large molecules with the present method and parameter scheme show differences of the same order of magnitude between calculated spectra and observed solution spectra. In this context it should be noted that the calculated spectra of the present investigation ought to be compared with vapour phase spectra, as our parameter sets have been determined to fit vapour phase spectra of small standard molecules. Mullins, Adler and Hochstrasser [23] report the spectra of meso-tetraphenylporphyrin (TPP) in benzene and in vapour. They observed the Soret band to be red shifted by 780 cm^{-1} in going over from vapour to benzene solution.

The present calculations show that for PH_2 the B band splits more than the Q band in contradiction to the assignment made by Weiss, Kobayashi and Gouterman.[10] Their investigation gave the result that the Q band splits much more than the B and meant that this result was experimentally verified by the work of Rimington *et al.*[14] The spectrum reported by Rimington *et al.*[14] is in the region 650—350 mμ and is thus not enough extended towards the high energy region to allow an interpretation of the splitting of the B band. The two observed peaks at 394.3 and 390.6 mμ of PH_2 in ethanol at -180°C may be interpreted as two vibrational bands belonging to B_x.

In metal alkyl porphyrins Caughey *et al.*[21] report a broad band (N) with maximum between 330—320 mμ, while in the corresponding free base porphyrin this band is reduced to a shoulder or inflection. They interpret these facts as a splitting of the B band, making it much broader in going over from D_{4h} to D_{2h} symmetry.

The calculated f-values of the four bands, B_x, B_y, N_x, and N_y must not be looked upon as very strict predictions. The relative intensities between these bands may be somewhat different. With this fact in mind it is possible to give an interpretation of the splitting of the B band in PH_2:

I suggest that the B band is split to an extent comparable to the splitting of the Q band. The narrow intense Soret band observed at 396 mμ [14] in benzene solution can be assigned as B_x. If B_y is a broad band at $\sim$350 mμ with a half width comparable to the half width found for the N-band, this B_y band might be completely hidden or look like a tail of the intense narrow peak at 396 mμ. This interpretation of the B_y band explains why the N-band of most free base porphyrins is reduced to a shoulder or inflection as found by Caughey *et al.*[21] An attempt to give a rough sketch of this interpretation is reproduced in Fig. 3. This interpretation is also in agreement with the polarization data by Sevchenko *et al.*[22] For more asymmetric bands than sketched in Fig. 3

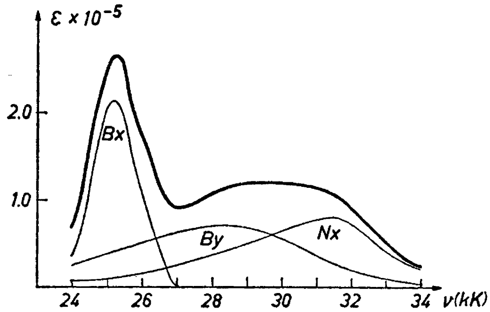

Fig. 3. An interpretation of the splitting of the B-band for PH_2, based on the result of the present investigation; *cf.* section III in text.

the B_y band might dominate over B_x in the region where Sevchenko *et al.* found a negative polarization.

Furthermore the vapour phase spectra of TPP and CuTPP reported by Mullins *et al.*[23] confirm this interpretation of the splitting of the B band. Their data for TPP show an intense peak at 24 700 cm^{-1} ($\varepsilon_{max} \sim 4.2 \times 10^5$) followed by a minimum at $\sim$27 000 cm^{-1} ($\varepsilon \sim 1.72 \times 10^5$) and then a region with increasing optical density having a shoulder at about 27 600 cm^{-1}. No observations beyond 29 000 cm^{-1} ($\varepsilon \sim 2.89 \times 10^5$) are reported. (A question to be posed is why no such region is observed in the benzene solution spectrum of TPP). For CuTPP no such region is observed neither in the solution spectrum nor in the vapour phase spectrum. These facts can be interpreted as a splitting of the B-band of TPP by 3300 cm^{-1} or more.

No observed $n-\pi^*$ bands of PH_2 have been published as far as is known to the author. The results of the present study show that the lowest allowed $n-\pi^*$ transition appears in the Soret region and therefore it is probably covered by intense $\pi-\pi^*$ bands.

The calculated spectrum of the dianion, P^{2-}, shows a small red shift of the B band compared to the B_x band of PH_2, in agreement with experimental findings.[18b] For PH_4^{2+} this work predicts the B band to be at shorter wavelength than the B_x band of PH_2, while Dempsey [19] observed a red shift of B for porphyrin dications in aqueous sodium dodecyl sulphate. In previous theoretical investigations [13] on hydrocarbons and heteroatomic molecules containing nitrogen it was found that the location of the strong bands is particularly sensitive to variations in the assumed geometry. In the present study the geometry of PH_4^{2+} has been assumed to be the same as for PH_2. This assumption is probably too rough to allow an interpretation of the shift of the strong B band for PH_4^{2+} as compared to PH_2. As mentioned previously there might be a distortion from planarity in PH_4^{2+} while PH_2 is found to be planar. P^{2-} is probably also planar and that can explain why the calculated spectrum is in better agreement with experiment for P^{2-} than for PH_4^{2+}.

Acknowledgement. This investigation has been supported by grants from the *Swedish Natural Science Research Council.* The data machine computations have been supported by *Kungl. Statskontoret.* The author wishes to express her gratitude to Prof. Inga Fischer-Hjalmars for her encouraging interest and valuable advise throughout the work. Thanks are also due to Dr. Björn Roos for useful discussions and to Mr. Lars Norén for skilful assistance in the numerical computations.

REFERENCES

1. Fischer-Hjalmars, I., Grabe, B., Roos, B., Skancke, P. N. and Sundbom, M. *Intern. J. Quant. Chem.*, Symposium issue (1967), 1 f, p. 233.
2. Webb, L. E. and Fleischer, E. B. *J. Chem. Phys.* **43** (1965) 3100.
3. Webb, L. E. and Fleischer, E. B. *J. Am. Chem. Soc.* **87** (1965) 667.
4. Becker, E. D., Bradley, R. B. and Watson, C. J. *J. Am. Chem. Soc.* **83** (1961) 3743.
5. Longuet-Higgins, H. C., Rector, C. W. and Platt, J. R. *J. Chem. Phys.* **18** (1950) 1174.
6. Matlow, S. L. *J. Chem. Phys.* **23** (1955) 673.
7. Pullman, B., Spanjaard, C. and Berthier, G. *Proc. Natl. Acad. Sci. U.S.* **46** (1960) 1011.
8. Gouterman, M., Wagnière, G. H. and Snyder, L. C. *J. Mol. Spectry.* **11** (1963) 108.
9. Chen, I. *J. Mol. Spectry.* **23** (1967) 144.
10. Weiss, C., Kobayashi, H. and Gouterman, M. *J. Mol. Spectry.* **16** (1965) 415.
11. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
12. Roos, B. *Acta Chem. Scand.* **21** (1967) 2318.
13. Fischer-Hjalmars, I. and Sundbom, M. *Acta Chem. Scand.* **22** (1968) 607.
14. Rimington, C., Mason, S. F. and Kennard, O. *Spectrochim. Acta* **12** (1958) 65.
15. Gomer, R. and Speer, D. A. *J. Chem. Phys.* **21** (1953) 73.
16. Fischer-Hjalmars, I. *Pure Appl. Chem.* **11** (1965) 571.
17. Bak, B., Christensen, D., Hansen, L. and Rastrup-Andersen, J. *J. Chem. Phys.* **24** (1956) 720; Bak, B. *Report at Nordisk Strukturkjemikermöte*, Oslo 1964.
18. Falk, J. E. *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam 1964; a) table 32, p. 239; b) pp. 74, 75.
19. Dempsey, B. *M. Sc. Thesis*, Univ. of Sydney 1961.
20. Platt, J. R. *J. Opt. Soc. Am.* **43** (1953) 252.
21. Caughey, W. C., Deal, R. M., Weiss, C. and Gouterman, M. *J. Mol. Spectry.* **16** (1965) 451.
22. Sevchenko, A. N., Solov'ev, K. N., Mashenkov, V. A. and Shkirman, S. F. *Dokl. Akad. Nauk SSSR* **163** (1965) 1367, or *Soviet Physics-Doklady* **10** (1966) 778.
23. Mullins, J. A., Adler, A. D. and Hochstrasser, R. M. *J. Chem. Phys.* **43** (1965) 2548.
24. Silvers, S. J. and Tulinsky, A. *J. Am. Chem. Soc.* **89** (1967) 3331.

Received December 2, 1967.