245. *Theoretical Studies of the Macrocyclic Pigments. Part I. The Structure of Bacteriochlorophyll.*

By J. R. Barnard and L. M. Jackman.

Molecular-orbital calculations have been performed on chlorin and a tetrahydroporphin of C_{2v} symmetry. It is found that the predicted centres of gravity for the longest-wavelength transitions lie in the order C_{2v} tetrahydroporphin < porphin < chlorin < D_{2h} tetrahydroporphin. This is in agreement with spectra in the tetraphenylporphin series, where the porphin and the chlorin lie between two tetrahydro-compounds of unknown structure. It follows that bacteriochlorophyll is related to the tetrahydroporphin of D_{2h} symmetry in which the two pairs of hydrogen atoms are located on opposite pyrrole rings. This effect of symmetry is also observed in the polycyclic aromatic hydrocarbons related to coronene.

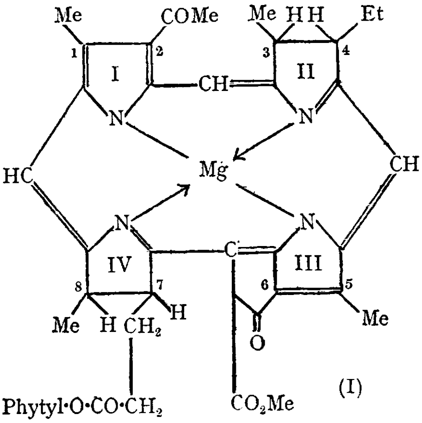
There are only two structural features in which bacteriochlorophyll differs from chlorophyll-*a*. This close relation is exemplified by the conversion of the former into 2-acetyl-2-devinylphæophorbide-*a* which has been synthesised from chlorin-e_6.[1] The degradation is effected by the removal of the magnesium atom, the phytyl residue, and the (? two) extra hydrogen atoms.[2] Bacteriochlorophyll has an acetyl group at position 2 and differs in its state of hydrogenation. The preservation of long-wavelength absorption (*ca.* 7500 Å)

---

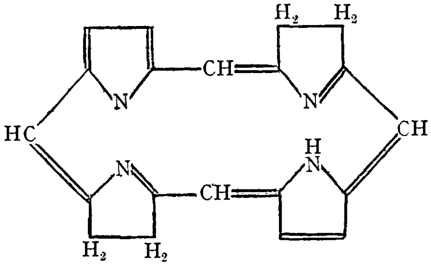
[1] Cf. Stoll and Wiedemann, *Fortschr. chem. Forsch.*, 1952, **2**, 538 and references there cited.
[2] Fischer, Lambrecht, and Mittenzwei, *Z. physiol. Chemie*, 1938, **253**, 1.

and the ease of dehydrogenation [3] suggest that the two extra hydrogen atoms are located on one of the three pairs of peripheral or β-positions of ring I, II, or III (see structure I).* Thus, apart from the stereochemistry of the various asymmetric centres, the only outstanding problem regarding the structure of bacteriochlorophyll is the decision between these three pairs of positions.

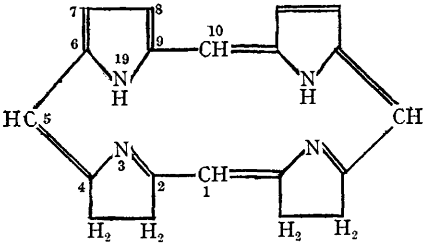
Mittenzwei [3] has suggested that ring II carries the extra hydrogen atoms and that bacteriochlorophyll has the structure (I). He has shown that oxidative degradation of bacteriochlorophyll derivatives yields small quantities of an oil which was possibly ethylmethylsuccinic anhydride. As this compound is not produced when chlorophyll derivatives are similarly degraded Mittenzwei claims that it must have arisen from a hydrogenated ring II. Seely [5] recently criticised the significance of these findings on the grounds that the failure of chlorophyll derivatives to yield ethylmethylsuccinic anhydride does not exclude the possibility of its having arisen from ring IV by decarboxylation before degradation of the bacteriochlorophyll derivatives. Seely suggested that the extra hydrogen atoms may be in either ring I or ring III, probably the latter.



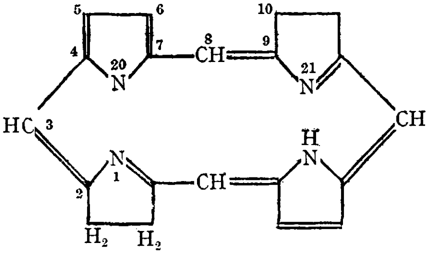
(I)



(II)



(III)



(IV)

We agree with Seely that Mittenzwei's proof of structure is by no means rigid. We now provide, by the application of the empirical L.C.A.O. M.O. method, some support for the correctness of structure (I).† Our studies suggest marked spectral differences for the two tetrahydroporphin models (II) and (III) which, if they exist, would allow an unambiguous

---

* There is now conclusive evidence that ring IV in chlorophyll has a 3 : 4-dihydropyrrole structure.[4]

† Professor Longuet-Higgins (personal communication) has stressed the fact that too much reliance should not be placed on simple M.O. methods when applied to the calculation of transition energies and that more refined calculations using self-consistent orbitals would be better adapted for this purpose. We are undertaking a more detailed treatment.

[3] Mittenzwei, *ibid.*, 1942, **275**, 93.

[4] Ficken, Johns, and Linstead, Chem. Soc. Spec. Publ. No. 3, 1955.

[5] Seely, U.S. Atomic Energy Commn. U.C.R.L. 2417, 1953.

decision between the two types. This effect is dependent on symmetry and may be quite general for large conjugated loops. Analogous observations in other systems of known constitution tend to confirm the theoretical findings. Longuet-Higgins, Rector, and Platt [6] accounted for the bathochromic shift which accompanies hydrogenation of the porphin nucleus to the bacteriochlorophyll level by assuming structure (II) for the latter and used the simple M.O. method including overlap. We have extended the calculations to the C_{2v} model, (III), as well as to chlorin, the dihydro-level. We find that the structure (III) is not associated with a bathochromic shift.

The π-electron system of porphin itself has the symmetry of the point group D_{4h}.* Like many conjugated systems with D_{3h} or higher symmetries the low-lying π-electron transitions are to an unoccupied degenerate M.O. In consequence the spectrum predicted from simple M.O. theory might be expected to be altered, perhaps considerably, by configuration interaction.[7] Although Longuet-Higgins *et al.*[6] originally suggested that this alters the intensities of porphin rather than the predicted frequencies,* we have thought it better to compare the predicted spectra of the two tetrahydro-models with that of chlorin as none of these structures has degenerate levels and configuration interaction will be less serious than in porphin.

In applying M.O. methods to porphin molecules two rather serious approximations, besides those implicit in the general method, have to be made. These concern the value of α_N, the Coulomb integral for nitrogen, and the variation of α_i, the Coulomb integral of the i'th atom with its charge density q_i. It is convenient to express α_N in terms of α_C by means of equation (1) in which β is the resonance integral for a carbon–carbon double bond:

$$\alpha_N = \alpha_C + \beta\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Values of δ ranging from 0·6 to 2·0 are found in the literature.[8] We have attempted to avoid the necessity of selecting one value for δ by examining an extreme range of values (*viz.*, 0—2·0). This is readily done by using the method of Coulson and Longuet-Higgins [9] in which the change in α is treated as a perturbation. $\delta\varepsilon_r$, the first order perturbation energy for the r'th M.O., is given by equation (2)

$$\delta\varepsilon_r = \sum c^2_{ir} \, . \, \delta\alpha_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where c_{ir} is the coefficient of the atom i in the r'th M.O. Longuet-Higgins *et al.*[6] have already applied this correction, with $\delta = 1$, to porphin and D_{2h} tetrahydroporphin (II). We have also calculated sets of data in which α_N has been varied with q. The results for porphin, chlorin, and the two tetrahydroporphins have been collected in Table 1. Only the first transitions have been considered. The energy values have also been converted into wavelengths by use of conversion factors obtained by assuming the energy for the first transition of chlorin to correspond to 6375 Å, the experimentally determined position of the longest-wavelength band in chlorin, the structure of which has been rigidly proved.[10] The value of β used to convert the energy into frequency is also included in Table 1 and may be compared with the values for β of —23,000 and —30,000 cm.$^{-1}$ which best reproduce the experimental values in the polycyclic aromatic hydrocarbon series and the polyenes respectively.[7]

Fortunately we have certain empirical criteria which we may legitimately use to limit the choice of δ and its variation with charge density. If we select chlorin as a reference compound, the calculated data for the first transition must fulfil two conditions: (1) At least one of the two tetrahydro-structures (II) and (III) must have its first transition of lower energy than the first transition of chlorin. This follows from the fact that bacteriochlorophylls always have their longest-wavelength band some 1000 Å to longer wavelengths

---

* This symmetry is partially destroyed by the presence of the two pyrrolic hydrogen atoms but the assumption of D_{4h} symmetry is a reasonable approximation.

[6] Longuet-Higgins, Rector, and Platt, *J. Chem. Phys.*, 1950, **18**, 1174.
[7] See Platt, *ibid.*, p. 1168, for a qualitative discussion of configuration interaction.
[8] Cf. Davies, *Trans. Faraday Soc.*, 1955, **51**, 449.
[9] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.
[10] Eisner and Linstead, *J.*, 1955, 3742.

than that of the corresponding chlorins. (2) The first transition of a chlorin is always observed to be of lower energy than that of the corresponding porphin. The M.O. method with configuration interaction included should predict this sequence. But since configuration interaction tends to reduce the energies of first transitions and since its effect will be greater in porphin than in chlorin, it follows that simple M.O. theory without configuration interaction should predict the same sequence.

Two important conclusions may now be drawn from Table 1. First, the theory predicts that even for the extreme range of δ considered the tetrahydroporphin (II) of symmetry D_{2h} always has its longest-wavelength band at longer wavelengths than that (III) of C_{2v} symmetry. Secondly, if the choice of δ and its variation with q is limited to those values which fulfil the two foregoing empirical criteria (*i.e.*, for values of δ between about 0·7 and 1·6), the predicted long-wavelength absorption of the D_{2h} model (II) lies above that of chlorin, while that of the C_{2v} compound lies below that of chlorin.

TABLE 1. *The energies, wavelengths, and symmetry types predicted for the longest-wavelength bands of porphin and its hydro-derivatives.*

	δ:	0	0·6 [a]			0·8	1·0 [a]			1·2	1·4 [a]			2·0
Porphin	$\Delta y/\beta$	0·391	0·543	0·491	0·435	0·588	0·627	0·583	0·534	0·665	0·641	0·662	0·620	0·529
	λ (Å)	6300	5700	5300	4760	5590	5520	5180	4720	5470	5890	5070	4690	9040
		A_{2u}–E_g		A_{2u}–E_g		A_{2u}–E_g		A_{2u}–E_g		A_{2u}–E_g	A_{1u}–E_g	A_{2u}–E_g	A_{2u}–E_g	A_{1u}–E_g
Chlorin	$\Delta y/\beta$	0·386	0·486	0·408	0·325	0·516	0·542	0·471	0·395	0·568	0·592	0·526	0·456	0·756
	λ (Å)	6375	6375	6375	6375	6375	6375	6375	6375	6375	6375	6375	6375	6375
		B_1–B_1		B_1–B_1		B_1–B_1		B_1–B_1		B_1–B_1		B_1–B_1		B_1–B_1
D_{2h} Tetra-hydroporphin	$\Delta y/\beta$	0·380	0·514	0·446	0·383	0·497	0·449	0·468	0·464	0·402	0·356	0·374	0·393	0·225
	λ (Å)	6480	6020	5840	5410	6620	7700	6380	5430	9010	10600	8970	7400	21200
		B_{1u}–B_{3g}		B_{1u}–B_{3g}		A_u–B_{3g}	A_u–B_{3g}	A_u–B_{3g}	B_{1u}–B_{3g}	A_u–B_{3g}		A_u–B_{3g}		A_u–B_{3g}
C_{2v} Tetra-hydroporphin	$\Delta y/\beta$	0·482	0·648	0·601	0·551	0·668	0·640	0·664	0·656	0·620	0·597	0·601	0·551	0·530
	γ (Å)	5110	4780	4330	3760	4920	5410	4500	3840	5845	6320	5580	5280	9030
		B_1–B_1		B_1–B_1		A_2–B_1	A_2–B_1	A_2–B_1	B_1–B_1	A_2–B_1	A_2–B_1	B_1–B_1	B_1–B_1	A_2–B_1
$-10^4\beta$ (cm.$^{-1}$)		4·06	3·23	3·84	4·83	3·04	2·89	3·35	3·97	2·76	2·65	2·98	3·44	2·09

[a] The first set refers to δ; the second to $(\delta + 1 - q)$, and the third to $(\delta + 2 - 2q)$.

It is fortunate that there exists one series in which all four compounds and their spectra are probably known, *viz.*, the *meso*tetraphenyl series. Dorough and Miller [11] have prepared the two tetrahydro-pigments and have established their higher state of hydrogenation by dehydrogenation to the chlorin.* Results for the longest-wavelength band of these compounds are given in Table 2, together with similar values for other incomplete series.

TABLE 2. *Wavelengths* (Å) *of the longest-wavelength bands of some porphin derivatives.*

*meso*Tetraphenylporphin,[a] 6480.
*meso*Tetraphenylchlorin,[a, b] 6550.
Tetrahydrotetraphenylporphin compound α,[b] 7500.
Tetrahydrotetraphenylporphin compound β,[b] 5910.
Porphin,[c] 6160.
Chlorin,[c] 6375.
Oxophæoporphin-a_5 monomethyl ester, 6455.
2-Acetyl-2-devinylmethylphæophorbide *a*,[e] 6850.
Bacteriophæophytin,[f] 7500.

[a] Ball, Dorough, and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 2278; [b] Dorough and Miller, *ibid.*, 1952, **74**, 6106; [c] Eisner and Linstead, *J.*, 1955, 3742; [d] Fischer, Lautsch, and Lin, *Annalen*, 1938, **534**, 1; [e] Fischer and Riedmair, *ibid.*, 1933, **505**, 87; [f] Weigl, *J. Amer. Chem. Soc.*, 1953, **75**, 999.

It is seen in the *meso*tetraphenyl series that the two tetrahydro-pigments are in fact in the predicted positions relative to the chlorin. The remarkable spectral difference predicted

---

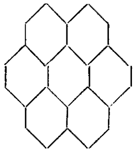
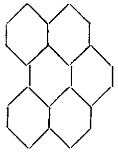
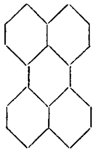
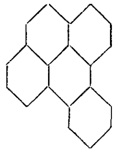
* The proof that these compounds are actually at the tetrahydro- rather than the hexahydro-level is still required, although Seely [5] has some evidence for the separate existence of the hexahydro-derivative which, if correct, locates the longest-wavelength band at 6420 Å for the zinc derivative.

[11] Dorough and Miller, *J. Amer. Chem. Soc.*, 1952, **74**, 6106.

for the two types of symmetry is therefore experimentally established and we can with confidence assign structure (I) to bacteriochlorophyll.

Our results seem quite general for the symmetry changes involved, for the predictions based on calculations in the porphin series may be successfully applied to the polycyclic aromatic hydrocarbon series. Longuet-Higgins *et al.*[6] have already noted the parallelism between the series porphin, chlorin, and D_{2h} tetrahydroporphin, and the series coronene, 1 : 2-benzoperylene, and perylene. We now find that C_{2v} tetrahydroporphin and 1 : 2-benzopyrene may be included in the respective series (cf. Table 3).

TABLE 3. *Comparison of the longest-wavelength* (Å) *bands of* meso-*tetraphenylporphins and polycyclic aromatic hydrocarbons.**

D_{6h}	C_{2v}	D_{2h}	C_{2v}
			
3415 3360 3255 3195 3165	3875 3670 3480 3310	4340 4060 3870 3860	3315 3165 3040
D_{4h}	C_{2v}	D_{2h}	C_{2v}
Porphin	Chlorin	Tetrahydro	Tetrahydro
6480	6550	7500	5910

* The data for the hydrocarbons refer to the *p*-bands (Clar, " Aromatische Kohlenwasserstoffe," Springer, Berlin, 1952.

The results described here provide an example of the manner in which the methods of theoretical chemistry, in spite of their many approximations, can be employed for solving structural problems. We have purposely avoided the choice of a single value for δ. It is gratifying to note, however, that the experimental results are best reproduced by $\delta \sim 1$ which is the value generally assumed for this parameter.[12] Further the values of β in this region agree satisfactorily with the value usually assumed (see p. 1174). If the value of δ is approximately unity, the 7500 Å band of D_{2h} tetrahydroporphin is due to the A_u–B_{3g} transition and is polarised parallel to the long axis. The method of correction for the variation of α with q_i is, at best, a very crude approximation. We have used the q_i's derived for the all-carbon model and have only considered the variation of δ for the four nitrogen atoms. Although the errors involved cannot alter the present conclusions a more satisfactory treatment is necessary for the predictions of other properties of these molecules.

CALCULATIONS

We have corrected all M.O. energies for overlap by the usual method [13] in which

$$y_r = 4x_r/(4 + x_r)$$

where

$$x_r = (\varepsilon_r - \alpha)/\beta$$

ε_r being the enery of the r'th M.O. This is an approximation to the more accurate correction used by Wheland [14] when the coulomb integrals vary.

As no account of spin interaction is included the predicted transition energies refer to the centres of gravity of the singlet–singlet and singlet–triplet transitions. We have made no explicit correction for the effect of the two pyrrolic hydrogen atoms. Their effect is probably

---

[12] Brown, *Quart. Rev.*, 1952, **6**, 63.

[13] Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025.

[14] *Idem, ibid.*, 1942, **64**, 900.

small and acts so as to reduce α_N. It is therefore absorbed by the range of values considered for the variation of δ_i with q_i.

Porphin and D_{2h} *Tetrahydroporphin.*—The M.O. energies and c_i's have been calculated by Longuet-Higgins, Rector, and Platt.[6] We have used these values to calculate the additional data for the various δ's.

Chlorin.—A recent theoretical treatment of this compound gives secular equations which include explicit corrections for the pyrrolic hydrogen atoms but take no account of the variation of α_i with q_i.[15] Chlorin belongs to the symmetry group C_{2v}, the M.O. wave functions being bases of the irreducible representations B_1 and A_2. The roots of the secular equations and the corresponding coefficients are given in Table 4. Table 5 lists the charge densities at the various positions.

TABLE 4. *Values of* x_r *and* c_{ir} *for chlorin.*

Representation A_2.

x_r	−2·0655	−1·9197	−1·6180	−0·9247	−0·4680	0·4472	0·6180	1·0985	1·5805	2·2517
c_1	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
c_2	0·0605	0·1491	0·0000	0·4176	0·1700	0·3851	0·0000	0·2844	0·1885	0·0782
c_3	−0·1250	−0·2863	0·0000	−0·3862	−0·0796	0·1722	0·0000	0·3124	0·2979	0·1760
c_4	0·1976	0·4005	0·0000	−0·0605	−0·1328	−0·3081	0·0000	0·0588	0·2824	0·3181
c_5	−0·0174	−0·3175	−0·1730	0·2734	−0·1030	−0·0897	−0·3897	−0·2042	0·1294	0·2554
c_6	−0·1618	0·2091	0·2799	−0·1923	0·1810	0·2679	−0·2408	−0·2830	−0·0778	0·2570
c_7	0·3515	−0·0839	−0·2799	−0·0956	0·0183	0·2096	0·2409	−0·1067	−0·2524	0·3233
c_8	−0·2984	0·1168	0·0000	0·1119	−0·4342	0·0461	0·0000	0·2095	−0·3401	0·1862
c_9	0·2648	−0·1404	0·2799	−0·0079	0·1850	−0·1890	−0·2409	0·3368	−0·2851	0·0958
c_{10}	−0·2485	0·1527	−0·4529	−0·1046	0·3476	−0·1306	−0·1489	0·1605	−0·1105	0·0295
c_{20}	−0·2659	−0·1649	0·1730	0·1688	0·2447	−0·2203	0·3897	−0·0437	0·0190	0·2849
c_{21}	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000

Representation B_1.

x_r	−3·1447	−2·0306	−1·6180	−1·5167	−0·3519	0·0000
c_1	0·1278	0·2877	0·0000	0·5074	0·3327	0·3780
c_2	−0·1370	−0·2921	0·0000	−0·3848	−0·0586	0·0000
c_3	0·1661	0·3054	0·0000	0·0762	−0·3122	−0·3780
c_4	−0·2192	−0·3281	0·0000	0·2692	0·1684	0·0000
c_5	0·0256	0·2395	−0·2021	−0·2648	0·2578	0·0000
c_6	0·1643	−0·1582	0·3271	0·1325	−0·2591	0·0000
c_7	−0·3268	0·0818	−0·3271	0·0639	−0·1666	0·0000
c_8	0·2820	−0·1291	0·0000	−0·0098	0·3226	−0·3780
c_9	−0·2780	0·1805	0·3271	−0·0491	0·0531	0·0000
c_{10}	0·0884	−0·0596	−0·1249	0·0195	−0·0393	0·0000
c_{20}	0·2546	0·1213	0·2021	−0·2196	−0·0049	0·3780
c_{21}	0·2593	−0·1777	−0·4043	0·0647	−0·3020	0·0000
x_r	0·6180	0·7183	1·0965	1·7365	2·1314	2·3612
c_1	0·0000	0·1995	0·3315	0·4795	0·1695	0·0683
c_2	0·0000	0·0717	0·1818	0·4163	0·1806	0·0806
c_3	0·0000	−0·1481	−0·1322	0·2434	0·2155	0·1221
c_4	0·0000	−0·1780	−0·3267	0·0064	0·2786	0·2077
c_5	−0·2538	0·2760	−0·2151	−0·1063	0·1977	0·1661
c_6	−0·1568	0·3763	0·0909	−0·1909	0·1427	0·1846
c_7	0·1568	−0·0057	0·3148	−0·2253	0·1065	0·2697
c_8	0·0000	−0·1246	0·2652	−0·0743	−0·0964	0·2501
c_9	−0·1568	−0·0838	−0·0240	0·0963	−0·3120	0·3208
c_{10}	0·4106	0·2973	−0·2490	0·1308	−0·2758	0·2356
c_{20}	0·2538	−0·2558	−0·0109	−0·1260	0·1807	0·2022
c_{21}	−0·5076	−0·2332	−0·0438	0·1110	−0·2928	0·2717

TABLE 5. *Charge densities in chlorin.*

Position	1	2	3	4	5	6	7	8	9	10	20	21
q_i	1·1117	1·0428	1·0996	1·0771	1·0968	1·0947	1·0802	1·0046	1·0786	1·0915	1·2921	0·9715

C_{2v} *Tetrahydroporphin.*—As in chlorin the M.O. wave functions are bases of the irreducible representations A_2 and B_1. A further simplification can be made as the A_2 wave functions are bases of the irreducible representations A_2' and B_1' of the group corresponding to A_2 which is of

---

[15] Matlow, *J. Chem. Phys.*, 1955, **23**, 673.

course isomorphous with C_{2v}. In this way the ninth-order secular determinant of A_2 factorises seventh- and second-order determinants. Table 6 lists the roots of the secular equations and the corresponding coefficients. The charge densities are given in Table 7.

TABLE 6. *Values of x_r and c_{ir} for C_{2v} tetrahydroporphin.*

Representation A_2.

	A_2'		B_1'						
x_r	−1·6180	0·6180	−2·0000	−1·4812	−0·6180	0·3111	1·0000	1·6180	2·1701
c_1	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
c_2	0·0000	0·0000	0·0816	0·2779	0·3804	0·3621	0·2887	0·2351	0·0408
c_3	0·0000	0·0000	−0·1633	−0·4117	−0·2351	0·1126	0·2887	0·3804	0·0886
c_4	0·0000	0·0000	0·2449	0·3318	−0·2351	−0·3270	0·0000	0·3804	0·1515
c_5	0·0000	0·0000	−0·3266	−0·0798	0·3804	−0·2144	−0·2887	0·2351	0·2401
c_6	0·0000	0·0000	0·4082	−0·2136	0·0000	0·2603	−0·2887	0·0000	0·3696
c_7	0·2629	0·4254	−0·2449	0·1981	−0·1902	0·1477	0·0000	−0·1176	0·2810
c_8	0·4254	0·2629	0·0816	−0·0798	0·1176	−0·2144	0·2887	−0·1902	0·2401
c_9	−0·4254	−0·2629	0·0816	−0·0798	0·1176	−0·2144	0·2887	−0·1902	0·2401
c_{10} ...	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
c_{19} ...	−0·2629	−0·4254	−0·2449	0·1981	−0·1902	0·1477	0·0000	−0·1176	0·2810

Representation B_1.

x_r	−2·1242	−2·0000	−1·7855	−1·0977	−0·4303	0·0000
c_1	0·0801	0·2357	0·4148	0·3974	0·2243	0·3536
c_2	−0·0851	−0·2357	−0·3703	−0·2181	−0·0483	0·0000
c_3	0·1007	0·2357	0·2464	−0·1580	−0·2035	−0·3536
c_4	−0·1287	−0·2357	−0·0696	0·3916	0·1361	0·0000
c_5	0·1727	0·2357	−0·1221	−0·2718	0·1450	0·3536
c_6	−0·2382	−0·2357	0·2876	−0·0932	−0·1983	0·0000
c_7	0·0261	0·2357	−0·2539	0·2410	−0·2484	0·0000
c_8	0·1828	−0·2357	0·1658	−0·1714	0·3052	0·0000
c_9	−0·4143	0·2357	−0·0421	−0·0529	0·1171	0·0000
c_{10} ...	0·3901	−0·2357	0·0472	0·0964	0·5443	0·3536
c_{19} ...	0·3072	0·0000	−0·1375	0·1331	0·1886	−0·3536
x_r	0·6495	1·0000	1·5345	1·9191	2·3346	
c_1	0·2187	0·3333	0·3255	0·4082	0·0333	
c_2	0·0710	0·1667	0·2498	0·3916	0·0389	
c_3	−0·1725	−0·1667	0·0577	0·3435	0·0575	
c_4	−0·1831	−0·3333	−0·1612	0·2675	0·0953	
c_5	0·0563	−0·1667	−0·3050	0·1699	0·1649	
c_6	0·2179	0·1667	−0·3069	0·0585	0·2898	
c_7	−0·2703	0·3333	−0·1449	−0·0124	0·2331	
c_8	−0·3935	0·1667	0·0846	−0·0822	0·2543	
c_9	0·0148	−0·1667	0·2747	−0·1453	0·3606	
c_{10} ...	0·0454	−0·3333	0·3580	−0·1515	0·3089	
c_{19} ...	0·3582	0·0000	−0·0210	−0·0453	0·2786	

TABLE 7. *Charge densities in C_{2v} tetrahydroporphin.*

Position ...	1	2	3	4	5	6	7	8	9	10	19
q_i	1·1153	1·0429	1·1115	1·0517	1·0946	1·0892	1·1049	1·1068	1·0937	0·9694	1·2578

We thank Dr. R. P. Linstead, C.B.E., F.R.S., for helpful discussion and encouragement, and the Department of Scientific and Industrial Research for a maintenance grant (to J. R. B.).

DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[*Received, September* 16*th*, 1955.]