Molecular Orbital Calculations on Porphine and Tetrahydroporphine

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Molecular Orbital Calculations on Porphine and Tetrahydroporphine*

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The first three electronic transitions of porphine and the first five electronic transitions of tetrahydroporphine are predicted as simple one-electron *LCAO* molecular orbital transitions (with overlap included). The electron densities and bond orders in the ground states are also computed. The observed levels are tentatively assigned to the predicted levels with the help of comparisons with spectra of other aza-amine derivatives of conjugated hydrocarbons. Probable degeneracies and polarizations are determined. The blue shift and loss of intensity of the first electronic transition, in going from tetrahydroporphine to the larger conjugated system of porphine, is typical of the change from a "long-field" to a "round-field" molecule (see previous paper) and is shown to occur in several other "long-field" systems when additional conjugated atoms are added at the side of the system.

INTRODUCTION

THE wide occurrence of porphine derivatives in nature, and their essential role in photosynthesis, makes the understanding of their electronic structures a most important matter.

In this paper we shall investigate the electronic structures of porphine (I) and tetrahydroporphine (II), using molecular orbital theory in its simplest form. We shall attempt to interpret certain interesting features of their electronic spectra on the assumption that their ground state and excited states are adequately described by single electron configurations. The notation used will be that of Coulson and Longuet-Higgins.[1]

A theoretical discussion of the structure of these molecules has been recently given by Simpson, using the free-electron model.[2] Also Rabinowitch earlier brought together experimental data on the spectra of these and related compounds (porphyrins, chlorins, and bacterio-chlorophyll) and discussed the interpretation of their spectra.[3] Further references may be found in these two papers.

THEORY

It is assumed that the longest wave-length electronic bands of I and II arise from transitions involving the π electrons, not the σ electrons. Attention will therefore be restricted to the former.

TABLE I. A_{2u} MO in porphine.

x	2.39138	0.77287	0.00000	−2.16425
c_1	0.17070	−0.29912	0.00000	0.06615
c_2	0.23750	0.06794	0.00000	−0.20933
c_3	0.19863	0.17581	0.35355	0.19344
c_{21}	0.19863	0.17581	−0.35355	0.19344

[1] C. A. Coulson and H. C. Longuet-Higgins, Proc Roy. Soc. (London) A191, 39 (1947).
[2] W. T. Simpson, J. Chem. Phys. 17, 1218 (1949).
[3] E. Rabinowitch, Rev. Mod. Phys. 16, 226 (1944).

It is convenient to express the molecular orbitals (*MO*) of the electrons as linear combinations of suitable atomic orbitals (*LCAO*). Each *MO* is then written in the form

$$\psi = \sum_r c_r \phi_r, \tag{1}$$

where ϕ_1 to ϕ_{24} are the $2pz$ orbitals of atoms 1 to 24. For simplicity it is assumed that the atomic orbitals (*AO*) are orthogonal and normalized, viz.

$$\int \phi_r \phi_s d\tau = 1 \text{ if } r = s, \; 0 \text{ if } r \neq s. \tag{2}$$

On these assumptions, the energy of an electron in ψ is given by the usual secular equations

$$(\alpha_r - \epsilon)c_r + \sum_{s \neq r} \beta_{rs} c_s = 0, \qquad (r = 1, 2, \cdots, 24), \tag{3}$$

where

$$\phi_r = \int \phi_r H \phi_r d\tau, \qquad \beta_{rs} = \int \phi_r H \phi_s d\tau. \tag{4}$$

In solving these equations for the molecules under investigation we assume that

$$\beta_{rs} = \begin{cases} \beta & \text{if atoms } r \text{ and } s \text{ are bonded,} \\ 0 & \text{otherwise,} \end{cases} \tag{5}$$

where β has the same value for all CC and CN bonds. We also assume that α_r has the same value α for all the atoms. This is, of course, not correct: nitrogen is more electronegative than carbon, and will certainly have a lower value of α_r. However, it is most convenient to begin by assuming all the α's equal, and to correct the resulting energies later, using the equation

$$\partial \epsilon / \partial \alpha_r = c_r^2. \tag{6}$$

TABLE II. B_{2u} MO in porphine.

x	2.00000	0.618034	−1.618034
c_1	0.22361	−0.25583	0.09972
c_2	0.22361	0.09972	−0.25583
c_{21}	0.22361	0.31623	0.31623

TABLE III. A_{1u} MO in porphine.

x	0.61803	-1.61803
c_1	0.18587	-0.30075
c_2	0.30075	0.18587

TABLE IV. B_{1u} MO in porphine.

x	1.618034	-0.618034	$-2\,000000$
c_1	0.09972	-0.25583	0.22361
c_2	0.25583	-0.09972	-0.22361
c_3	0.31623	0.31623	0.22361

With these assumptions, the secular equations take the form

$$(\alpha-\epsilon)c_r+ \sum_{s\ \text{bonded to}\ r} \beta c_s=0, \qquad (7)$$

or, more briefly,

$$-xc_r+ \sum_{s\ \text{bonded to}\ r} c_s=0, \qquad (8)$$

where $x=(\epsilon-\alpha)/\beta$.

MOLECULAR ORBITALS IN PORPHINE

The symmetry group of porphine is D_{4h}. The π MO are, by definition, all antisymmetric with respect to the molecular plane, and therefore belong to the species A_{2u}, B_{2u}, A_{1u}, B_{1u}, and E_g.

Species A_{2u}

The molecular orbitals of species A_{2u} may be written in the form

$$\psi(A_{2u})=c_1(\phi_1+\phi_5+\phi_6+\phi_{10}+\phi_{11}+\phi_{15}+\phi_{16}+\phi_{20})$$
$$+c_2(\phi_2+\phi_4+\phi_7+\phi_9+\phi_{12}+\phi_{14}+\phi_{17}+\phi_{19})$$
$$+c_3(\phi_3+\phi_8+\phi_{13}+\phi_{18})$$
$$+c_{21}(\phi_{21}+\phi_{22}+\phi_{23}+\phi_{24}).$$

The secular Eqs. (8) demand that

$$-xc_1+c_1+c_2=0$$
$$-xc_2+c_1+c_3+c_{21}=0$$
$$-xc_3+2c_2=0$$
$$-xc_{21}+2c_2=0.$$

Eliminating the coefficients c_r we obtain

$$\begin{vmatrix} 1-x, & 1, & 0, & 0 \\ 1, & -x, & 1, & 1 \\ 0, & 2, & -x, & 0 \\ 0, & 2, & 0, & -x \end{vmatrix}=0=x^4-x^3-5x^2+4x.$$

This equation has four real roots $x_j(j=1, 2, 3, 4)$, so there are 4 MO of species A_{2u}, with energies $\epsilon_j=\alpha+\beta x_j$. The ratios of the coefficients c_r for each of these are obtained by substituting the appropriate x_j back into the equations; and their absolute magnitudes are fixed by the condition that the MO be normalized, viz.,

$$8c_1{}^2+8c_2{}^2+4c_3{}^2+4c_{21}{}^2=1.$$

The values of x_j and the corresponding values of c_r are given in Table I below.

Species B_{2u}

The MO of species B_{2u} have nodal planes through atoms 3, 8, 13, and 18. They have the general form

$$\psi(B_{2u})=c_1(\phi_1-\phi_5-\phi_6+\phi_{10}+\phi_{11}-\phi_{15}-\phi_{16}+\phi_{20})$$
$$+c_2(\phi_2-\phi_4-\phi_7+\phi_9+\phi_{12}-\phi_{14}-\phi_{17}+\phi_{19})$$
$$+c_{21}(\phi_{21}-\phi_{22}+\phi_{23}-\phi_{24}).$$

The fact that c_3 etc., are zero means that the MO in this species satisfy the secular equations for an isolated 5-membered ring of unsaturated atoms. The solutions are given in Table II.

Species A_{1u}

The orbitals of this species have nodal planes through the nitrogen atoms as well as through the corner carbon atoms. They therefore satisfy the secular equations for butadiene. Their general form is

$$\psi(A_{1u})=c_1(\phi_1-\phi_5+\phi_6-\phi_{10}+\phi_{11}-\phi_{15}+\phi_{16}-\phi_{20})$$
$$+c_2(\phi_2-\phi_4+\phi_7-\phi_9+\phi_{12}-\phi_{14}+\phi_{17}-\phi_{19}).$$

The energies and normalized AO coefficients are given in Table III below.

Species B_{1u}

The orbitals of this species are of the general form

$$\psi(B_{1u})=c_1(\phi_1+\phi_5-\phi_6-\phi_{10}+\phi_{11}+\phi_{15}-\phi_{16}-\phi_{20})$$
$$+c_2(\phi_2+\phi_4-\phi_7-\phi_9+\phi_{12}+\phi_{14}-\phi_{17}-\phi_{19})$$
$$+c_3(\phi_3-\phi_8+\phi_{13}-\phi_{18}).$$
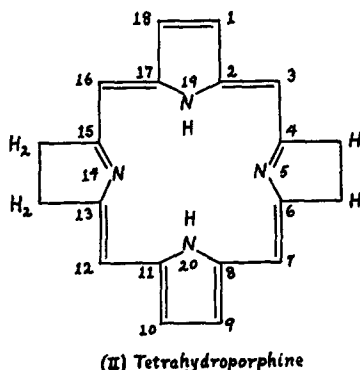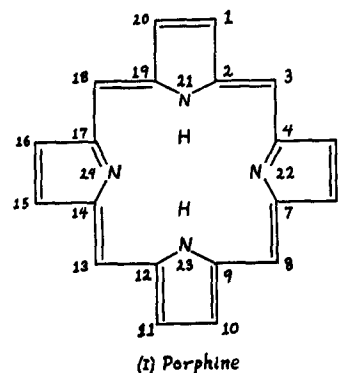

(I) Porphine

(II) Tetrahydroporphine

FIG. 1. Structure of porphine and tetrahydroporphine.

TABLE V. E_g MO in porphine.

x	2.25619	1.18994	0.61803	−0.35650	−1.61803	−2.08963
c_1	0.25427	0.22432	−0.34409	0.03958	0.08132	0 08811
c_2	0.31940	0.04261	0.13143	−0 05368	−0.21290	−0.27221
c_3	0.18324	−0.24524	0.00000	−0.32161	0 00000	0.22018
c_4	0.09401	−0.33442	−0.13143	0.16833	0.21290	−0.18789
c_5	0.02887	−0 15271	−0.08123	0.26160	−0.34448	0.22454
c_{21}	0.28314	0.07161	0.42533	0.30117	0.26316	0.26054

TABLE VI. π-electron densities and mobile bond orders in porphine.

$q_1 = 1.0846$	$p_{20,1} = 0.785$
$q_2 = 1.0711$	$p_{1,2} = 0.472$
$q_3 = 0.9656$	$p_{2,3} = 0.575$
$q_{21} = 1.2231$	$p_{2,21} = 0.579$

Since they have nodal planes through the nitrogen atoms, they satisfy the secular equations for a twenty-membered ring, and are relatively easily obtained. The solutions are given in Table IV.

Species E_g

The MO of species E_g occur in degenerate pairs, and though the energy of each pair is determinate, there is a certain freedom of choice in the forms of the MO. We shall use the following real forms:

$$\psi(E_g) = c_1(\phi_1 - \phi_{10} - \phi_{11} + \phi_{20}) + c_2(\phi_2 - \phi_9 - \phi_{12} + \phi_{19})$$
$$+ c_3(\phi_3 - \phi_8 - \phi_{13} + \phi_{18}) + c_4(\phi_4 - \phi_7 - \phi_{14} + \phi_{17})$$
$$+ c_5(\phi_5 - \phi_6 - \phi_{15} + \phi_{16}) + c_{21}(\phi_{21} - \phi_{23})$$

and

$$\psi'(E_g) = c_1(\phi_5 + \phi_6 - \phi_{15} - \phi_{16}) + c_2(\phi_4 + \phi_7 - \phi_{14} - \phi_{17})$$
$$+ c_3(\phi_3 + \phi_8 - \phi_{13} - \phi_{18}) + c_4(\phi_2 + \phi_9 - \phi_{12} - \phi_{19})$$
$$+ c_5(\phi_1 + \phi_{10} - \phi_{11} - \phi_{20}) + c_{21}(\phi_{22} - \phi_{24}).$$

The symmetry properties of ψ and ψ' are most easily seen by referring to the diagram (Fig. 2). The secular equations, for both ψ and ψ', are as follows:

$$-xc_1 + c_1 + c_2 = 0, \qquad -xc_4 + c_3 + c_5 = 0,$$
$$-xc_2 + c_1 + c_3 + c_{21} = 0, \qquad -xc_5 + c_4 - c_5 = 0,$$
$$-xc_3 + c_2 + c_4 = 0, \qquad -xc_{21} + 2c_2 = 0.$$

When expanded, the secular determinant factorizes into a quartic and a quadratic. The orbital energies and coefficients are as follows:

ELECTRON DENSITIES AND BOND ORDERS IN PORPHINE

It must be re-emphasized that the above values of the energy parameter x and the AO coefficients c_r have been calculated on the assumption that the nitrogen atoms and the carbon atoms all have the same Coulomb integral α. With this assumption in mind, let us calculate the electron densities and mobile bond orders for the molecule in its ground state. These are defined by the equations

$$q_r (= \text{electron density in } \phi_r) = 2 \sum c_r^2, \text{ and}$$
$$p_{rs} (= \text{mobile order of bond } rs) = 2 \sum c_r c_s,$$

the summations being taken over the 13 *molecular* orbitals of lowest energy, since the molecule has altogether 26 π electrons. These 13 MO include the 12 MO of positive x (6 of these are non-degenerate, and 3 pairs are doubly degenerate), and the one MO (of species A_{2u}) for which $x = 0$. Summing over these orbitals we obtain for the electron densities and bond orders the values given in Table VI.

It is interesting to note that the π-electron density comes out highest on atoms 21, 22, 23, 24, even though no allowance has been made in the calculations for the greater electron affinity of nitrogen than carbon. This suggests two things. First, that the great stability of porphine is largely due to the presence of nitrogen atoms at points in the skeleton where, for purely *geometrical* reasons, the π-electrons tend to congregate. Secondly, this piling up of the electrons may reduce the effective electron affinity of the nitrogen atoms to a value not very far from that of the carbon atoms; and, if this is so, then it may not be such a bad approximation to set the Coulomb integrals of the nitrogen atoms in porphine equal to those of the carbon atoms.

Table VI also shows that positions 3, 8, 13, and 18 have the lowest π-electron densities. In porphine, therefore, these positions should be the initial points of attack by nucleophilic reagents.

The bond orders call for little comment. The external bond of the five-membered rings appears to have the highest mobile order, but this difference would be
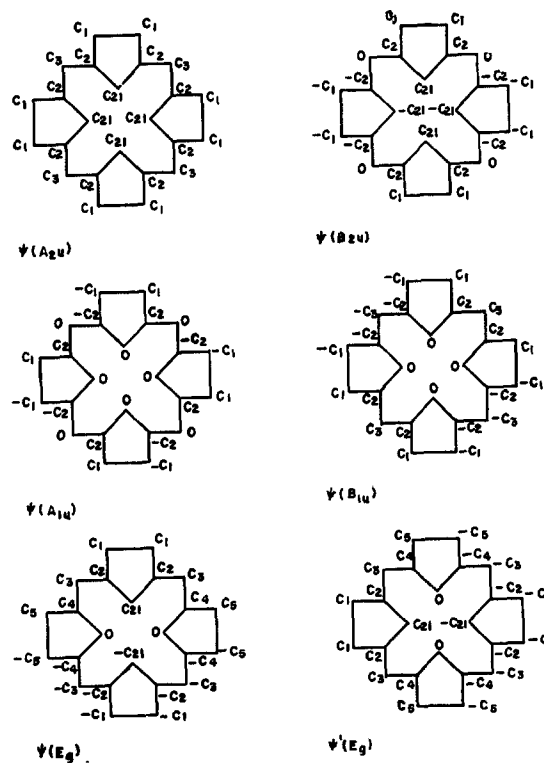

Fig. 2a. Molecular orbital species of porphine.

lessened if one assigned the nitrogen atoms a larger Coulomb integral than the carbon atoms.

MOLECULAR ORBITALS IN TETRAHYDROPORPHINE

The symmetry group of tetrahydroporphine is D_{2h}, and the π MO are of species B_{1u}, B_{2g}, B_{3g}, and A_u. The numbering of the AO is shown in Fig. 1.

Species B_{1u}

The MO of this species have the form

$$\psi(B_{1u}) = c_1(\phi_1+\phi_9+\phi_{10}+\phi_{18})+c_2(\phi_2+\phi_8+\phi_{11}+\phi_{17})$$
$$+c_3(\phi_3+\phi_7+\phi_{12}+\phi_{16})+c_4(\phi_4+\phi_6+\phi_{13}+\phi_{15})$$
$$+c_5(\phi_5+\phi_{14})+c_{19}(\phi_{19}+\phi_{20}).$$

The AO coefficients and energies in these MO are found to be:

Species B_{2g}

The orbitals of this species have nodes through atoms 5 and 14. They are of the general form:

$$\psi(B_{2g}) = c_1(\phi_1-\phi_9-\phi_{10}+\phi_{18})+c_2(\phi_2-\phi_8-\phi_{11}+\phi_{17})$$
$$+c_3(\phi_3-\phi_7-\phi_{12}+\phi_{16})+c_4(\phi_4-\phi_6-\phi_{13}+\phi_{15})$$
$$+c_{19}(\phi_{19}-\phi_{20}).$$

The AO coefficients and energy parameters are:

Species B_{3g} and A_u

These MO are of the forms

$$\psi(B_{3g}) = c_1(\phi_1+\phi_9-\phi_{10}-\phi_{18})+c_2(\phi_2+\phi_8-\phi_{11}-\phi_{17})$$
$$+c_3(\phi_3+\phi_7-\phi_{12}-\phi_{16})+c_4(\phi_4+\phi_6-\phi_{13}-\phi_{15})$$
$$+c_5(\phi_5-\phi_{14}).$$
$$\psi(A_u) = c_1(\phi_1-\phi_9+\phi_{10}-\phi_{18})+c_2(\phi_2-\phi_8+\phi_{11}-\phi_{17})$$
$$+c_3(\phi_3-\phi_7+\phi_{12}-\phi_{16})+c_4(\phi_4-\phi_6+\phi_{13}-\phi_{15}).$$

The MO of both these species have nodal planes through

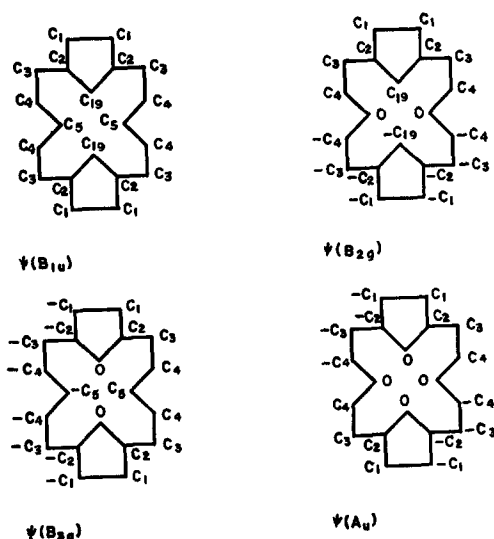$\psi(B_{1u})$ $\psi(B_{2g})$ $\psi(B_{3g})$ $\psi(A_u)$

Fig. 2b. Molecular orbital species of tetrahydroporphine.

TABLE VII. B_{1u} orbitals in tetrahydroporphine

x	2.28618	1.63047	0.68163	0 00000	−1.50203	−2.09625
c_1	0 23801	−0.17437	0.38333	0.00000	−0 08515	0.09356
c_2	0.30612	−0 10994	−0.12205	0.00000	0.21305	−0.28969
c_3	0 19404	0.12997	−0.10843	−0 35355	0 04883	0.23731
c_4	0.13748	0 32185	0.04814	0 00000	−0.28640	−0 20777
c_5	0.12027	0.39480	0 14124	0.35355	0.38134	0.19823
c_{19}	0.26780	−0 13485	−0 35809	0.35355	−0.28369	0 27639

TABLE VIII. B_{2g} orbitals in tetrahydroporphine.

x	2.24698	1.00000	0.55496	−0.80194	−2.00000
c_1	0.25838	−0.28868	0.28747	0.06668	−0.11323
c_2	0.32220	0.00000	−0 12794	−0.12015	0.33968
c_3	0.17881	0.28868	0.10259	−0.26998	−0.22646
c_4	0.07958	0.28868	0.18487	0.33665	0.11323
c_{19}	0.28678	0.00000	−0 46106	0.29965	−0.33968

atoms 19 and 20. They therefore satisfy the secular equations for a closed 18-membered ring, and the values of x and c_r are readily obtained. The solutions are given in Table IX.

ELECTRON DENSITIES AND BOND ORDERS IN TETRAHYDROPORPHINE

From the above values of the coefficients, we can calculate, as for porphine itself, the values that the electron densities and bond orders would have if the nitrogen and carbon atoms had equal Coulomb integrals.

There are 22 π-electrons, and so in the ground state the 10 MO of positive x will contain 2 electrons each, and there will also be two electrons in the MO for which $x=0$. Summation of $2c_r^2$ and $2c_rc_s$ over these MO leads to the following values for the electron densities and bond orders (see Table XI).

As in porphine itself, the calculated electron densities are highest on atoms 19 and 20, though no allowance has been made in the calculation for the fact that these are nitrogen and not carbon atoms. The bond orders show a trend similar to that in porphine, but here again the calculated difference in mobile order between the external bonds are probably too large.

MO ENERGIES IN PORPHINE AND TETRAHYDROPORPHINE

Up to this point, no account has been taken in the theory of the difference in the Coulomb integral of nitrogen and of carbon. We shall now examine how this difference affects the calculated MO energies.

Coulson and Longuet-Higgins[1] showed that if the Coulomb integral of atom r is altered by a small amount $\delta\alpha_r$, then the change in energy of any MO involving that atom is given by

$$\delta\epsilon = c_r^2 \delta\alpha_r, \tag{9}$$

where c_r is the coefficient of ϕ_r in the MO under discussion. Now $\alpha_n - \alpha_c$ is of the order of β;[4] and although β

[4] H. C Longuet-Higgins, J. Chem. Phys. 18, 275 (1950).

TABLE IX. B_{3g} orbitals in tetrahydroporphine.

x	1.87939	1.00000	−0.34730	−1 53209	−2 00000
c_1	0 05788	−0.16667	0.25535	−0 31323	0.23570
c_2	0.16667	−0.33333	0.16667	0.16667	−0.23570
c_3	0.25535	−0 16667	−0.31323	0 05788	0.23570
c_4	0 31323	0.16667	−0.05788	−0.25535	−0.23570
c_5	0.33333	0.33333	0.33333	0.33333	0.23570

TABLE X. A_u orbitals in tetrahydroporphine.

x	1 53209	0.34730	−1 00000	−1.87939
c_1	0.11401	−0.21726	0.00000	−0.32827
c_2	0.28868	−0.28868	0 00000	0 28868
c_3	0 32827	0.11401	−0.35535	−0.21726
c_4	0 21726	0.32827	0.35355	0.11401

TABLE XI. Electron densities and bond orders caused by π-electrons in tetrahydroporphine

$q_1 = 1.1135$	$p_{1,2} = 0.5034$
$q_2 = 1.0928$	$p_{2,3} = 0.5256$
$q_3 = 1.0617$	$p_{3,4} = 0.6796$
$q_4 = 1.0564$	$p_{4,5} = 0.6207$
$q_5 = 1.0750$	$p_{1,18} = 0.7534$
$q_{19} = 1.2759$	$p_{2,19} = 0.5838$

is not small Eq. (9) will at least give a rough idea how the MO energies are modified by the nitrogen atoms. Denoting by x' the modified values of x, we have the following approximate relations:

(for porphyrin) $x' = x + c_{21}^2 + c_{22}^2 + c_{23}^2 + c_{24}^2,$
(for tetrahydroporphyrin) $x' = x + c_{19}^2 + c_{20}^2.$

The values of x, and the corresponding values of x', are listed in Table XII, and presented graphically in Fig. 3.

COMPARISON WITH OBSERVED SPECTRA: PORPHINE

In another paper[5] it is shown how fairly accurate spectroscopic predictions can be obtained from LCAO orbital energies for a whole series of molecules. We may apply this procedure to porphine and tetrahydroporphine. First, the orbital energies, x and x', are corrected for overlap, using $S = 0.25$.[5, 6] The corrected energies, y and y', in units of β are given in Table XIII and the highest filled and lowest unfilled levels are shown with corrected energies in Fig. 4. This figure also indicates the lowest allowed transitions in the two molecules, with their polarizations. Using $\beta = -23,000$ cm^{-1} these transition energies then should give the approximate location of the centers of gravity of singlet-triplet pairs in the spectrum.

The observed singlet energy states of the molecules[3] and the computed centers-of-gravity are compared in Table XIV and in Fig. 5. When we consider how accu-

rate the number, sequence, and position of energy levels is predicted in other molecules by this method,[5] it becomes quite probable that the 6000A transition of porphine is doubly degenerate in the approximation used here, and that the 4000A transition or "Soret band" is also doubly degenerate. These general conclusions hold whether we adopt the set of levels y or y'. A choice between the two sets is not possible because each fits the data about as well as do other predictions made by this method. M. Kasha has independently arrived at the conclusion that the 6000A bands involve at least two electronic transitions,[7] from the variable appearance of their envelopes under different substitutions[3] in the porphyrines, which are porphine derivatives. This probably means that the degeneracy is removed and the two component transitions are separated different amounts by the different substitutions. Conceivably the degeneracy is removed even in porphine itself by the presence of the two central hydrogens, since they must slightly distort the D_{4h} symmetry of the conjugated system. These bands may also be in different positions, as Simpson supposes,[2] in the two tautomers in which these central hydrogens are located (a) on opposed, or (b) on adjacent nitrogens.

The 6000A bands of porphine are relatively weak, even though they represent a formally allowed transition in the simple LCAO scheme used here. This means that there must be configuration interaction between the upper state of these bands and the upper state of the Soret bands. Porphine is thus another typical in-
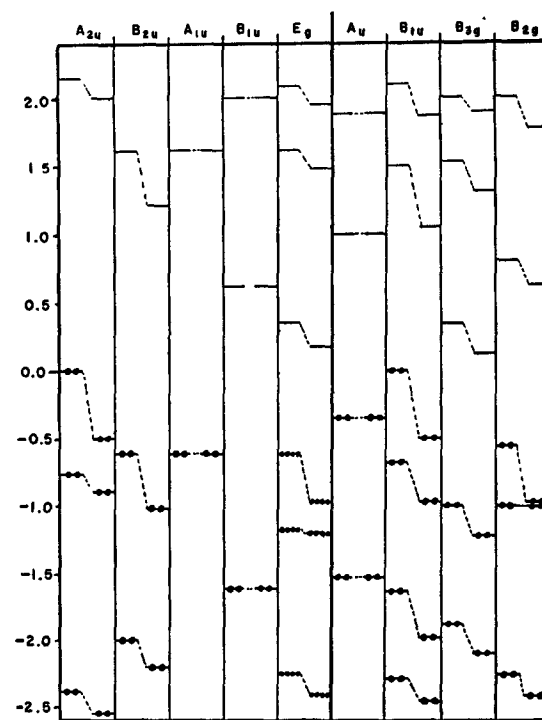
FIG. 3. MO energies in porphine and tetrahydroporphine.

[5] John R. Platt, J. Chem. Phys. 18, 1168 (1950).
[6] G. W. Wheland, J. Am. Chem. Soc. 63, 2025 (1941)

[7] M. Kasha, private communication.

stance of the "round-field" type of spectra[1] found in benzene, triphenylene, and coronene. The configuration interaction does not seem to alter the LCAO-predicted positions of bands as much as it alters their intensities.

This interpretation of the porphine bands is substantially equivalent to that given by Simpson.[2] However, he used an oversimplified model for the conjugated system, a closed 18-atom ring, neglecting two double bonds in the molecule and the effect of the two amino nitrogens. On considering electron interaction, he then obtained a weak doubly degenerate low transition and a strong higher one, just as here. But the oversimplification is dangerous, since it is hard to know in advance when it will be justified; and it is unnecessary, since the low frequency bands will be weak in any "round-field" molecule,[5] such as porphine or coronene, regardless of whether we can draw a closed ring through most of the conjugated atoms or not. Kuhn[8] has made a qualitative interpretation similar to Simpson's, but says he has a more accurate discussion in press. Neither author gives such detailed predictions of the different bands as are given by the present method.

COMPARISON WITH OSBSERVED SPECTRA: TETRAHYDROPORPHINE

In tetrahydroporphine, the situation is less clear than in porphine. If the nitrogen Coulomb integral is about equal to that of carbon (MO energies, y), a perpendicularly polarized transition is lowest in the LCAO scheme; otherwise (y'), a parallel transition. Furthermore, in either case, crossovers could occur, as they do in the polyacenes,[5,9] between the predicted center-of-gravity
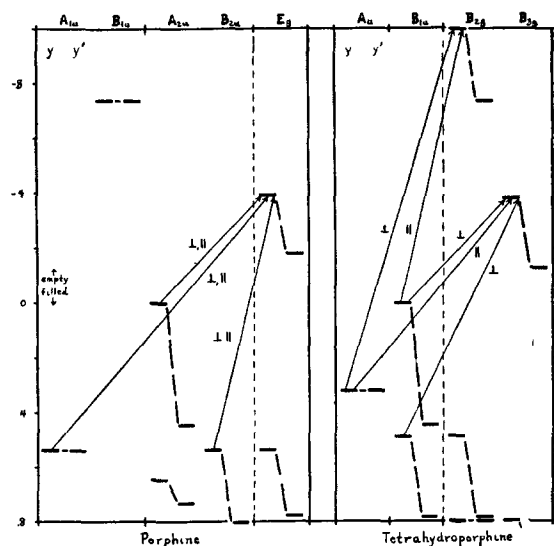
Table XII. MO energies in porphine and tetrahydroporphine, uncorrected (x) and corrected (x').

	Porphine			Tetrahydroporphine	
	x	x'		x	x'
A_{2u}	−2.16425	−2.01457	B_{1u}	−2 09625	−1.86508
	0.00000	0 50000		−1.50203	−1 05023
	0.77287	0 89651		0 00000	0.50000
	2 39138	2 54919		0.68163	0 97798
				1.63047	1.97857
B_{2u}	−1 61803	−1.21803		2 28618	2.45853
	0.61803	1.01803	B_{2g}	−2 00000	−1.76923
	2 00000	2 20000		−0.80194	−0 62236
A_{1u}	−1 61803	−1 61803		0 55496	0.98011
	0.61803	0 61803		1.00000	1 00000
				2 24698	2.41147
B_{1u}	−2.00000	−2 00000	B_{3g}	−2 00000	−1.88889
	−0.61803	−0.61803		−1.53209	−1.30987
	1.61803	1 61803		−0 34730	−0 12508
E_g	−2 08963	−1.95387		1 00000	1.22222
	−1.61803	−1.47952		1 87939	2.10161
	−0.35650	−0.17509	A_u	−1.87939	−1 87939
	0.61803	0.97984		−1.00000	−1.00000
	1 18994	1.20020		0 34730	0 34730
	2.25619	2.41653		1 53209	1.53209

sequence and the observed sequence of singlets, because of different singlet-triplet separations in the two low states.

In this situation, empirical analogies may help us to infer the probable polarization. Tetrahydroporphine is a C_{18} conjugated loop with two carbons replaced by aza-nitrogens and with two amine substituents. The spectrum of a simple C_{18} conjugated loop is not known. The closest known approximation may be the spectrum of the C_{18} ring system, tetracene, which has cross links.[9] The tetrahydroporphine spectrum may therefore be related to the tetracene spectrum somewhat as the amino and diamino-acridine spectra studied by Craig and Short[10] are related to the spectrum of their parent C_{14} hydrocarbon, anthracene (Fig. 6).

Aza substitution in ring systems slightly modifies the π-electron spectra in intensity and position, and no doubt adds weak bands of extinctions 1000 or less, though these seem to be hidden by the strong π-bands in acridine. But these changes are small compared with those introduced by amino substitution. This has the effect of mixing the π-electron intensities, producing strong red-shifts, and adding a strong new band to the spectrum as seen in Fig. 6. Probably a second band is added in the diamino case, but is blended with the first or with one of the other bands.

This is indeed also the general description of changes in going from the tetracene spectrum to that of tetrahydroporphine.

These changes with amino substitution seem to be less profound with increasing size of the substituted molecule and might be expected to become negligible for very large molecules. Consequently it is tempting to

Fig. 4. Lowest allowed transitions in porphine and tetrahydroporphine. (The symbol ⊥, ‖ indicates double degeneracy. The symbols ⊥ and ‖ indicate polarization, with respect to the longest axis of the conjugated system in tetrahydroporphine.)

[8] H. Kuhn, Zeits. f. Elektrochimie **53**, 165 (1949); an English translation has appeared in J. Chem. Phys. **17**, 1198 (1949).
[9] John R. Platt, J. Chem. Phys. **17**, 484 (1949).
[10] D. P. Craig and L. N. Short, J Chem. Soc., 419 (1945).

TABLE XIII *MO energies from Table XII corrected for overlap* $(S=0.25)$.

	Porphine			Tetrahydroporphine	
	y	y'		y	y'
A_{1u}	−2.71714	−2.71714	A_u	−3.54501	−3.54501
	0.53531	0.53531		−1.33333	−1.33333
				0.31955	0.31955
B_{1u}	−4.00000	−4.00000		1.10778	1.10778
	−0.73097	−0.73097			
	1.15202	1.15202	B_{1u}	−4.40444	−3.49442
				−2.40521	−1.42415
A_{2u}	−4.71575	−4.05868		0.00000	0.44444
	0.00000	0.44444		0.58238	0.78584
	0.64771	0.73236		1.15831	1.32377
	1.49663	1.55694		1.45473	1.52265
B_{2u}	−2.71714	−1.75132	B_{2g}	−4.00000	−3.17242
	0.53531	0.81149		−1.00302	−0.73703
	1.33333	1.41935		0.48734	0.78721
				0.80000	0.80000
E_g	−4.37536	−3.81973		1.43876	1.50447
	−2.71714	−2.34803			
	−0.39137	−0.18310	B_{3g}	−4.00000	−3.57893
	0.53531	0.78704		−2.48321	−1.94767
	0.91711	0.92287		−0.38031	−0.12911
	1.44253	1.50644		0.80000	0.93617
				1.27862	1.37774

TABLE XIV. *Comparison of calculated centers of gravity with observed singlets.*

Molecule	Trans. type	Pol	Calculated trans. energy[a] β	Calculated trans. energy[a] cm⁻¹	Observed singlets[b] cm⁻¹	Correction
Porphine	$A_{2u}-E_g$	⊥, ‖ doub. degen	0.391 (0.627)	9000 (14,500)	16,000	+7000
	$A_{1u}-E_g$	⊥, ‖ doub. degen	0.927 (0.718)	21,300 (16,500)	23,200	+2000
	$B_{2u}-E_g$	⊥, ‖ doub degen.	0.927 (0.994)	21,300 (23,000)	?	?
Tetra-hydro-porphine	$B_{1u}-B_{3g}$	⊥	0.380 (0.573)	8700 (13,200)	13,000	+4000
	A_u-B_{3g}	‖	0.700 (0.449)	16,100 (10,300)	16,300	0
	$B_{1u}-B_{3g}$	⊥	0.963 (0.915)	22,200 (21,000)	19,000(?)	−3000
	$B_{1u}-B_{2g}$	‖	1.003 (1.181)	23,000 (27,200)	24,000	+1000
	A_u-B_{2g}	⊥	1.322 (1.056)	30,400 (24,300)	?	?

[a] Predicted energies in brackets are between orbitals y' of Table XIII and Fig. 4. The others are between orbitals y.
[b] See reference 3.

relate the 19,000 and 34,000 cm⁻¹ bands of 2,6-diamino-acridine to the 26,000 and 39,000 cm⁻¹ bands of anthracene respectively. It is even more tempting, because the symmetry is preserved, to relate the 12,000 and 24,000 cm⁻¹ bands of tetrahydroporphine to the 21,000 and 36,000 cm⁻¹ bands of tetracene, and to say that they are polarized ⊥ and ‖ to the longer axis of the system respectively, as the latter bands are believed to be.[9]

Some other arguments support this assignment. One is that the position of the Soret band (24,000 cm⁻¹) is but little changed in going from porphine to the dihydro compound (chlorins[3]) and then to the tetrahydro compound. This suggests the band is polarized ‖, along the unchanged, or long, axis of the latter system. If this is the case, it seems improbable that the 12,000 cm⁻¹ band in the tetrahydro system would have so much intensity unless it had the opposite, or transverse (⊥), polarization.

Another argument is that the 12,000 cm⁻¹ band may be related to the low bands in dihydroporphine (chlorins), which are stronger than in porphines and so are probably polarized in this same ⊥ direction (transverse to the long axis, or parallel to the C_{2v} axis in dihydroporphine); because a permanent dipole in this direction is created in going from porphine to the chlorins.

The two strong bands in tetrahydroporphine are therefore assigned as indicated in Fig. 5. The remaining bands are tentatively assigned to the nearest remaining predicted levels. Tetrahydroporphine appears to give a typical and even an extreme example of the "long-field" type of spectrum, in which the lowest transition is very strong.[5]

The dihydroporphine bands are intermediate in position and intensity between those in porphine and in the

tetrahydro compound,[3] as seems reasonable. No doubt they have a sequence of assignments and polarizations similar to that in the latter compound, but simply
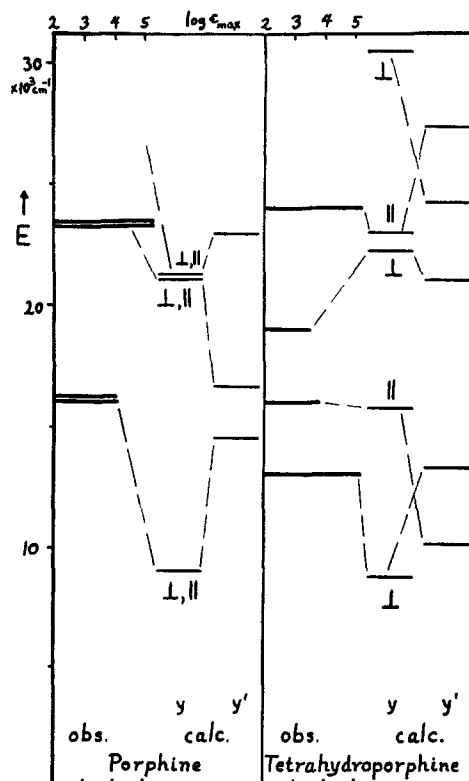

FIG. 5. Comparison of calculated with observed electronic energy states. (Vibrational structure omitted for simplicity. Length of the horizontal lines in the "observed" column indicates approximate intensity of transition from the ground state. Double lines indicate presumed double degeneracy.)

represent an intermediate type of field. This interpretation would relate the longest wave-length bands in the three compounds to each other, in contradiction to Rabinowitch's interpretation[3] which seeks to relate

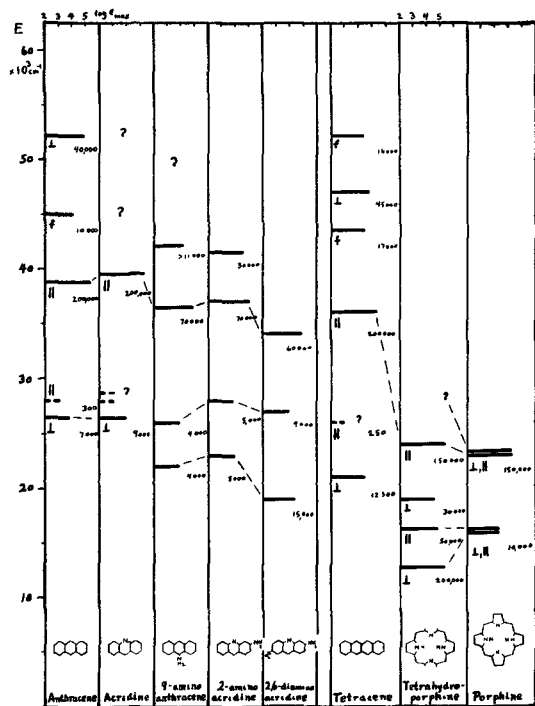FIG. 7. Blue shifts produced by adding conjugated atoms to the sides of a long conjugated system.

FIG. 6. Effect of aza and amino substitution on spectra of ring systems (See note under Fig. 5. Numbers near horizontal lines indicate ϵ_{max}.)

bands which have nearly the same position and intensity in the three compounds.

It has occasioned some surprise that there should be a *blue* shift of the long wave bands in adding conjugated
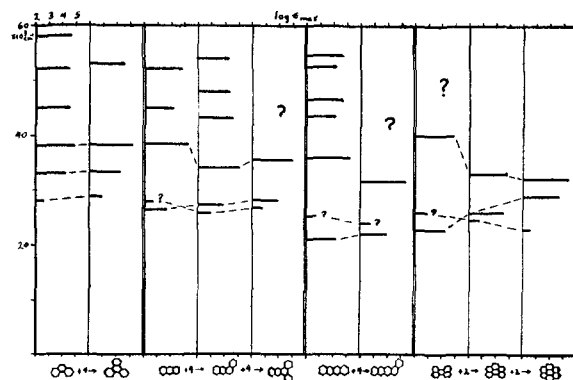
atoms to a conjugated system, as in going from tetrahydroporphine to porphine itself.[3] However, such blue shifts are fairly common when the additional atoms are at the sides of an initially elongated system, as is shown by several examples in Fig. 7.[11] They seem to be associated, as here, with the change from a "long-field" to a "round-field" type of spectrum, and are more prominent in larger molecules where the normal red shift associated with the simple increase of molecular size from the additional atoms is not so important.

The qualitative parallel between the spectral changes in the porphine→dihydroporphine→tetrahydroporphine sequence and those in the coronene→dihydrocoronene→ tetrahydrocoronene (perylene) sequence shown in Fig. 7 is especially remarkable.

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[11] The data in Fig. 7 are principally from: E. Clar, *Aromatische Kohlenwasserstoffe* (Verlag. Julius Springer, Berlin, 1941), with some additional spectra from Fromberg, Thaler, and Wolf, Zeits. f. Elektrochemie **49**, 387 (1943), (coronene); H. B. Klevens and J. R. Platt, J. Chem. Phys. **17**, 470 (1949), (short wave-length cata-condensed spectra).