

MO CALCULATION ON THE ABSORPTION SPECTRA OF TETRAPHENYL PORPHINE

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INTRODUCTION

It has been shown by Basu (1954) that the MO calculation on as complex a molecule as phthalocyanine can be used in predicting the spectral transition for this compound. In view of the insolubility of this compound in common organic solvents, an experimental verification of the calculated results have not been made. Recently Calvin *et al.* (1946) have reported the results of their experimental investigation on the absorption spectra of tetraphenyl porphine (Fig. 1) in alcohol and in chloroform. Since MO calculation can be extended to this compound with equal ease, computation has been made on tetraphenyl porphine and the results have been found to agree fairly closely with the absorption spectra of this compound, as reported in the present paper.

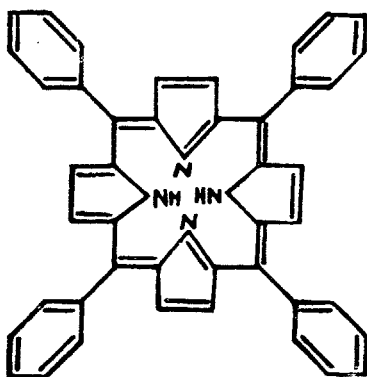


FIG. 1. Tetraphenyl Porphine.

METHOD OF CALCULATION

The method has already been described in detail (Basu, 1954). Only a short account will be given here.

In the LCAO MO method each electron is considered to be in a self-consistent field due to other electrons and atomic nuclei, and the single electron wave function ψ_j is approximated by a linear combination of atomic orbitals ϕ_k , each belonging to one of the nuclei. We treat the problem as a π -electron system, excluding the σ -electrons involved in the formation of single bonds.

$$\psi_j = \sum_k a_{jk} \phi_k$$

The electronic energy E_j of the molecular orbital ψ_j can be obtained as roots $E = E_j$ ($j = 1, 2, 3, \dots, l$) of a secular equation

$$D = | H_{mk} - S_{mk}E | = 0$$

where l denotes the number of π -electron atomic orbitals and H_{mk} and S_{mk} are given by the following equations respectively

$$H_{mk} = \int \phi_m^* H \phi_k d\tau, S_{mk} = \int \phi_m^* \phi_k d\tau$$

For simplicity it is assumed that the atomic orbitals are orthogonal and normalised, viz.,

$$\int \phi_m^* \phi_k d\tau = 1, \text{ if } m = k \\ = 0, \text{ otherwise.}$$

On these assumptions the energy of an electron in ψ is given by

$$(H_{mm} - E)c_m = \sum_{k \neq m} H_{mk}c_k = 0$$

We make further assumption that H_{mm} (E_0) is same for all carbon atoms, $E_0 + 2\beta$ for nitrogen and $H_{mk} = \beta$ for any two neighbouring atoms bounded to each other.

With these assumptions the secular equation takes the form

$$(E - E_0)c_r + \Sigma\beta c_s = 0 \\ \text{or } Wc_r + \Sigma\beta c_s = 0 \\ \text{or } xc_r + \Sigma c_s = 0$$

where $x = (E - E_0)/\beta$ an energy parameter.

There are in all 48 MOs and 50 π -electrons in tetraphenyl porphine. With restrictions that two electrons of opposite spin can be adopted by each orbital, 25 out of 48 orbitals will be occupied. The calculation of absorption frequencies due to electronic transition between the occupied and vacant levels is made with the following prescription:—

- (i) Compute the roots (x) of the simple secular equation.
- (ii) Set $\beta = -23,000 \text{ cm.}^{-1}$ for aromatic C—C bonds.
- (iii) The transition frequencies are given by x (empty) $-x$ (highest filled) and is governed by the symmetry of the corresponding MOs.

RESULTS

Like phthalocyanine the group symmetry in tetraphenyl porphine is D_{4h} and π -electron MOs belong to group species A_{2u} , B_{2u} , A_{1u} , B_{1u} , and E_g . The last species exist in doubly degenerate pairs. The energy equations for these species are as follows:—

$$A_{2u}: x^8 + x^7 - 10x^6 - 9x^5 + 27x^4 + 22x^3 - 16x^2 - 12x = 0$$

$$B_{2u}: x^7 - x^6 - 8x^5 + 7x^4 + 18x^3 - 13x^2 - 9x + 4 = 0$$

$$A_{1u}: x^4 - x^3 - 2x^2 + x + 1 = 0$$

$$B_{1u}: x^5 - 4x^3 + 5x - 2 = 0$$

$$E_g: x^{10} - 12x^8 + x^7 + 36x^6 + 10x^5 - 41x^4 - 44x^3 + 32x^2 + 23x - 4 = 0$$

All these equations are solved by method of successive approximation correct up to first decimal place. The values of x (the energy parameter) for different species are listed in Table I in increasing order.

TABLE I
Energy parameter for tetraphenyl porphine

No.	Group species	α	No.	Group species	α
1	E_g	-3.25	23	B_{1u}	0.48
2	E_g	-3.25	24	A_{2u}	0.80
3	E_g	-2.70	25	E_g	0.95
4	E_g	-2.70	26	E_g	0.95
5	A_{2u}	-2.33	27	B_{2u}	0.98
6	B_{2u}	-2.00	28	E_g	1.00
7	B_{1u}	-1.98	29	E_g	1.00
8	B_{2u}	-1.80	30	E_g	1.00
9	B_{1u}	-1.18	31	E_g	1.00
10	E_g	-1.00	32	A_{1u}	1.00
11	E_g	-1.00	33	B_{1u}	1.00
12	A_{2u}	-1.00	34	E_g	1.10
13	E_g	-0.75	35	E_g	1.10
14	E_g	-0.75	36	E_g	1.20
15	A_{2u}	-0.61	37	E_g	1.20
16	B_{2u}	-0.60	38	A_{1u}	1.61
17	E_g	-0.55	39	B_{1u}	1.65
18	E_g	-0.55	40	B_{2u}	1.71
19	A_{2u}	0.00	41	A_{2u}	2.00
20	E_g	0.31	42	A_{2u}	2.13
21	E_g	0.31	43	B_{2u}	2.25
22	B_{2u}	0.40			

Only 43 energy levels have been listed in the table since calculated transition extends up to that level.

Lowest 25 of these levels are filled. The electron transition between the highest filled level and the vacant levels are controlled by the requirements that there can be no transition between levels belonging to the same group species, i.e. there can be no transition between E_g and E_g or between B_{1u} and B_{1u} and so on. With this restriction the first allowed transition is between the levels 25 (E_g) and 27 (B_{2u}), the second between 25 and 32 (A_{1u}), and so on. But it may be noted that the energy difference between these states are extremely small, so there will be strong configurational interaction and the levels will mix, as discussed in the previous communication (Basu, 1954). These transitions will give absorption in the infra-red region, the exact position of which will be rather uncertain. Transition accompanied with appreciable energy difference so as to give absorption in the visible and near ultraviolet region are listed in Table II along with the calculated and observed wavelength.

TABLE II
Calculated and observed absorption maxima for tetraphenyl porphine

Levels	Group species	Degeneracy	Wavelength (Å)	
			Calculated	Observed
25-38	$A_{1u}-E_g$	Double	6521	6500
25-39	$B_{1u}-E_g$..	6210	6100
25-40	$B_{2u}-E_g$..	5434	5500
25-41	$A_{2u}-E_g$..	4223	5200
25-43	$B_{2u}-E_g$..	3344	..

It may be observed that the agreement between the calculated and observed wavelength at maximum absorption is fairly close. A better agreement is not expected in view of the approximations used in solving the secular determinant and the neglect of configurational interactions for these high energy transitions.

SUMMARY

Calculation of energy levels in tetraphenyl porphine has been made by LCAO MO method and the result has been correlated with the observed spectral transition.

REFERENCE

- Basu, S. (1954). Molecular Orbital calculation on phthalocyanine. *Indian Jour. Phys.*, **28**, 511.
- Calvin, M., Ball, R. H., and Dorough, G. D. (1946). A further study of the Porphine-like products of the reaction of benzaldehyde and pyrrole. *J. Amer. Chem. Soc.*, **68**, 2278.

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