

MO CALCULATION ON THE ABSORPTION SPECTRA OF A MACRO-CYCLIC COMPOUND

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INTRODUCTION

In two previous communications (Basu, 1954, 1955) it has been shown that MO calculations on the absorption spectra of phthalocyanine and tetraphenyl porphine agree fairly closely with the experimental values. In the present paper is reported the result of MO calculation on a macro-cyclic compound which is different from the other two compounds in that two of the pyrrol rings in the porphine nucleus have been replaced by pyridine rings (Fig. 1). The compound has been prepared and its properties studied by Linstead (1953).

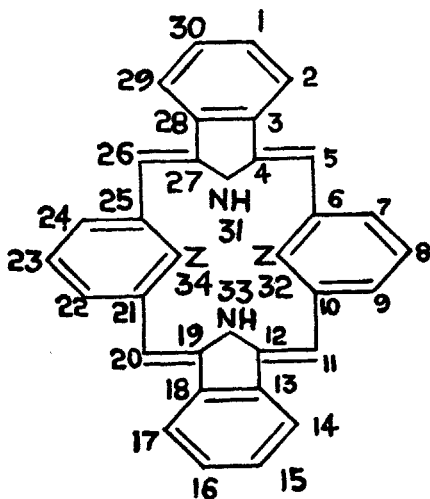


Fig. 1

METHOD OF CALCULATIONS

The mathematical procedure has been described in greater detail in the previous communication (Basu, 1954). The symmetry class to which this compound belongs is, however, different from that of the other two compounds. The group symmetry in this case is D_{2h} and the π -electron MOs belong to group species B_{1u} , B_{2g} , B_{3g} and A_u , shown diagrammatically in Fig. 2. The secular equations for different species are given below :

$$A_u - x^7 - 2x^6 - 4x^5 + 7x^4 + 4x^3 - 4x^2 - 2x = 0.$$

$$B_{3g} - x^9 - 2x^8 - 7x^7 + 13x^6 + 15x^5 - 24x^4 - 11x^3 + 12x^2 + 2x = 0.$$

$$B_{2g} - x^8 + 2x^7 - 6x^6 - 11x^5 + 12x^4 + 20x^3 - 7x^2 - 10x = 0.$$

$$B_{1u} - x^{10} + x^9 - 11x^8 - 19x^7 + 39x^6 + 70x^5 - 51x^4 - 84x^3 + 22x^2 + 32x = 0.$$

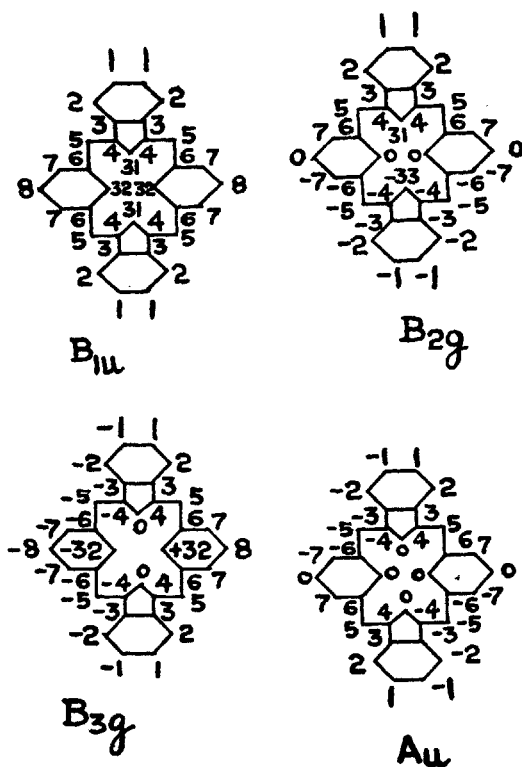


FIG. 2

RESULT

The calculated energy parameters are given in increasing order in Table I. There are 36 π -electrons and 34 available energy levels, out of which 18 will be filled and the absorption spectra will arise out of transition between the highest filled and the lower vacant levels, conditioned by the symmetry requirements of the group species to which the level belongs. The calculated and observed transitions are given in Table II.

TABLE I

Group species and energy parameters

| No. | Group species | Energy parameter | No. | Group species | Energy parameter |
|-----|---------------|------------------|-----|---------------|------------------|
| 1 | B_{1u} | -3.00 | 18 | B_{1u} | 0.00 |
| 2 | B_{2g} | -2.10 | 19 | B_{2g} | 0.00 |
| 3 | B_{2g} | -2.00 | 20 | B_{3g} | 0.00 |
| 4 | B_{3g} | -2.00 | 21 | A_u | 0.00 |
| 5 | A_u | -1.70 | 22 | B_{2g} | 0.90 |
| 6 | B_{1u} | -1.40 | 23 | B_{1u} | 1.00 |
| 7 | B_{3g} | -1.15 | 24 | A_u | 1.00 |
| 8 | B_{3g} | -1.11 | 25 | B_{3g} | 1.00 |
| 9 | B_{2g} | -1.00 | 26 | B_{3g} | 1.11 |
| 10 | B_{1u} | -1.00 | 27 | B_{2g} | 1.50 |
| 11 | B_{1u} | -1.00 | 28 | B_{1u} | 1.60 |
| 12 | B_{1u} | -1.00 | 29 | B_{2g} | 1.70 |
| 13 | B_{1u} | -0.95 | 30 | A_u | 1.90 |
| 14 | A_u | -0.90 | 31 | A_u | 2.00 |
| 15 | B_{2g} | -0.20 | 32 | B_{3g} | 2.00 |
| 16 | A_u | -0.25 | 33 | B_{3g} | 2.25 |
| 17 | B_{3g} | -0.10 | 34 | B_{1u} | 2.90 |

TABLE II

| Transition | Calculated $\lambda(m\mu)$ | Observed |
|-------------------|----------------------------|----------|
| $B_{1u} - A_u$ | 483 | .. |
| $B_{1u} - B_{2g}$ | 435 | .. |
| $B_{1u} - B_{3g}$ | 391 | 354 |
| $B_{1u} - B_{3g}$ | 289 | 301 |

DISCUSSION

Although calculated result indicates too intense absorption in the visible region, in morpholine solution this compound absorbs in the ultraviolet region and there is only end absorption in the visible region. From a consideration of the model of this compound Linstead (1953) has shown that the molecule is not completely planar, and because of this there is a departure from complete conjugation as has been assumed in the calculation. When converted into its zinc salt, the compound shows complex multiband structure with an intense absorption maximum at $440m\mu$ which agrees fairly closely with the calculated value of $435m\mu$. This shows that salt formation and co-ordination of the pyridine nitrogen with the central metal atom forces the system to take up a planar structure. In case of azaporphines, however, salt formation does not affect the absorption spectra, since salt formation does not affect co-planarity of conjugation in the parent compound in any way,

SUMMARY

MO calculation on the absorption spectra of a macro-cyclic compound appears to support Linstead's contention that the parent compound is not co-planar, but salt formation with metals forces the system to take up a co-planar structure.

REFERENCES

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