

## A Theory of the Optical Properties of Vitamin $B_{12}$ and its Derivatives

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LCAO-MO calculations have been made on the  $\pi$ -electron system of corrin, using both Hückel and Pariser-Parr-Pople methods, with particular emphasis on the way in which the energies of the excited configurations vary with the valence state ionization potentials of the four ligand nitrogen atoms. Configuration interaction between the second and third excited states is particularly sensitive to the effective nuclear charges of these nitrogen atoms, and hence to the covalency of the bond between the metal and the axial ligands. The dipole and rotational strengths calculated by assuming that the molecular conformation in solution is the same as that found in the crystal lead to the conclusion that the wide variations in the absorption and circular dichroism spectra may be due to electronic changes. Low temperature solution spectra of dicyanocobinamide and methylcobalamin are presented and assignments discussed.

Des calculs LCAO-MO des électrons  $\pi$  de la corrine selon les méthodes de Hückel et de Pariser-Parr-Pople ont été effectués avec une insistance particulière sur la manière dont les énergies des configurations excitées varient avec les potentiels d'ionisation des états de valence des quatre atomes d'azote liants. L'interaction de configuration entre le deuxième et le troisième état excité est particulièrement sensible aux charges nucléaires effectives de ces atomes d'azote, et par là au degré de covalence de la liaison entre le métal et les ligands axiaux. Les intensités dipolaires et rotatoires calculées en supposant que la conformation moléculaire en solution est la même que celle trouvée dans le cristal conduit à la conclusion que les grandes variations des spectres d'absorption et de dichroïsme circulaire sont dues à des variations de facteurs électroniques. Les spectres des solution de dicyanocobinamide et de méthylcobalamine à basse température sont présentés et les identifications sont discutées.

HMO und PPP-Rechnungen wurden am Corrin-System durchgeführt. Energieänderungen angeregter Konfigurationen in Abhängigkeit von den Valenzzustands-Ionisationspotentialen der vier äquatorialen N-Atome werden untersucht. Die Konfigurationenwechselwirkung ist empfindlich gegen die effektive Kernladungszahl der N-Atome, und daher abhängig von der Bindung zwischen Zentralatom und den axialen Liganden. Unter der Voraussetzung, daß die Konformation des Moleküls in Lösung die gleiche ist wie im Kristall, ergibt sich, daß die großen Unterschiede der Spektren der Komplexe mit verschiedenen axialen Liganden auf elektronische Unterschiede zurückgeführt werden können. Die Zuordnung der gemessenen Tieftemperatur-Lösungs-Spektren von Dicyanocobinamid und Methylcobalamin wird diskutiert.

### Introduction

Starting from a knowledge of the nuclear coordinates and electron configuration of a molecule, there are a wide variety of methods for calculating its ground state and excited state electronic properties. In this paper we shall use structural information gained from X-ray crystallography as the starting point for some

calculations of the optical properties of corrinoid compounds. In principle, such calculations also yield information about charge densities and bond lengths, but we shall not consider these ground state properties in our subsequent discussion.

Over the last few years, the visible and ultraviolet spectra of very many vitamin  $B_{12}$  derivatives have been published, both from this Laboratory [1, 2] and elsewhere [3, 4, 5, 6], so that there now exists evidence for the effect of numerous different perturbations on the basic chromophore. These include changing one or both of the axial ligands attached to the metal [2—5], changing the metal [6], and changing the substituents bonded to the conjugated chain [7]. There is also a rather limited amount of information about the polarisations of the various electronic transitions [8, 9]. Furthermore, the fact that the conjugated chain is not planar induces a rotational strength in the  $\pi - \pi^*$  transitions, and the circular dichroism spectra [10, 44] will be discussed in the light of the theory to be presented here.

Complexes formed between transition metal ions and conjugated ligands may possess absorption bands of three limiting types: localized transitions on either the metal or the ligand ( $d - d$  and  $\pi - \pi^*$  respectively) or charge transfer transitions from ligand to metal or vice versa. It will be assumed in what follows that the visible and near ultraviolet spectra of corrinoid compounds are entirely of  $\pi - \pi^*$  type, i.e. localized within the conjugated chain of thirteen atoms from  $N(20)$  to  $N(23)$ . (The atom numbering and coordinates are given in Fig. 1). The recently published spectrum of a corrinoid compound which does not contain a metal atom [11] justifies this assumption, since it contains bands which correspond closely to all those occurring in the vitamin  $B_{12}$  spectrum below 35 kK.

One of the most important features of the corrin spectra, which must be emphasised by any theoretical treatment, is the exceptionally wide variation in band energies and intensities brought about by changing the axial ligands. Indeed, the spectra of vitamin  $B_{12}$  and the coenzyme are so different that there was at first serious doubt that they contained the same conjugated chromophore. However, by studying the spectra of ethinyl and vinyl cobalamins, it has recently been established [2] that the  $B_{12}$  and DBC spectra are merely the end members of a sequence. Spectra of dicyanocobinamide (Fig. 1,  $R = R' = \text{CN}^-$ ) and methylcobalamin (Fig. 1,  $R' = \text{benzimidazole}$ ,  $R = \text{CH}_3^-$ ), measured at 77 °K in ethanolic glasses, are shown in Fig. 2 for comparison.

The first quantitative treatment of the vitamin  $B_{12}$  spectrum was that of KUHN [14], who used the free electron model. He has recently extended his calculations [15] to include the perturbation of the periodic potential caused by including nitrogen atoms in place of carbon in the chain. Hückel theory has been applied to vitamin  $B_{12}$  by OFFENHARTZ, as reported briefly at the recent Royal Society Discussion on the chemistry of corrin [16].

In the form in which it is used by KUHN [15], the free electron model cannot easily be extended in an analytic form to deal with variation in the effective

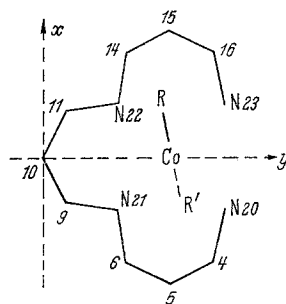


Fig. 1. Coordinates and numbering of the corrin  $\pi$ -system

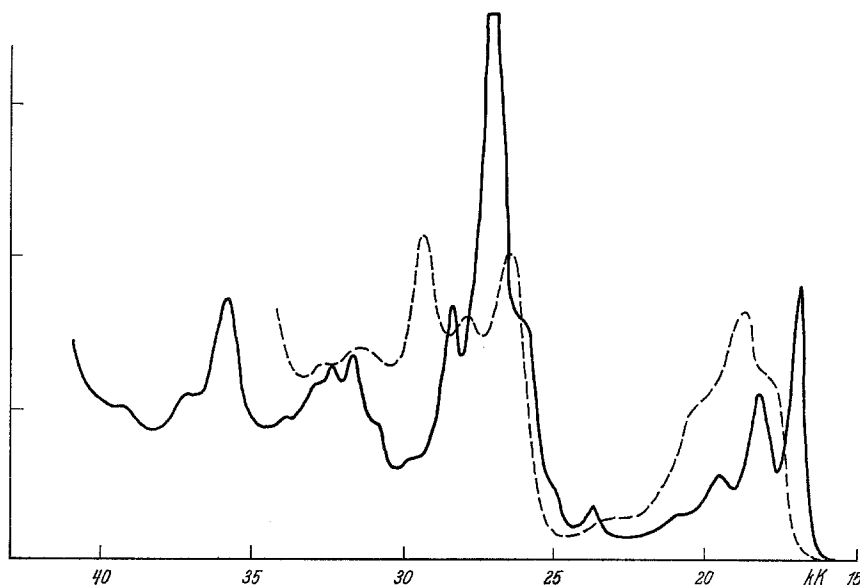


Fig. 2. Absorption spectra of dicyanocobinamide (—) and methylcobalamin (---) in ethanol glass at liquid nitrogen temperature

electronegativity of any atom in the chain. On the other hand, LCAO theory is admirably adapted to the perturbation approach which we shall employ here. Similarly, it is very difficult to introduce electron interaction into the free electron model by any other than a numerical procedure, while in the zero overlap approximation using LCAO basis functions, the molecular Hartree-Fock equation reduces to the analytically simple form first derived by PARISEE and PARR [17] and POPLE [18] and since employed successfully in many molecular calculations.

The Pariser-Parr-Pople (PPP) model has previously been applied with conspicuous success to a number of conjugated ligands related to corrin (such as porphyrin and phthalocyanine). GOUTERMAN [19] used a simplified version, which

Table 1. Energies and oscillator strengths of the corrin chromophore; observed, and calculated with various assumptions

| Transitions | Observed          |                                      | Calculated             |                                           |                                            |
|-------------|-------------------|--------------------------------------|------------------------|-------------------------------------------|--------------------------------------------|
|             | Dicyanocobinamide | Methylcobalamin                      | Hückel ( $h_N = 0.5$ ) | PPP (9 atom chain)<br>$I_\mu^N = -120$ kK | PPP (13 atom chain)<br>$I_\mu^N = -120$ kK |
| I           | 17.0 kK (0.13)    | 17.8 kK (0.16)                       | 17.0 kK (0.29)         | 20.1 kK                                   | 19.00 kK (0.23)                            |
| II          | 23.7 kK (0.01)    | 23.0 kK (0.02)                       | 26.8 kK (0.40)         | 34.0 kK                                   | 23.33 kK (0.01)                            |
| III         | 27.2 kK (0.27)    | 26.1 kK (0.15)<br>28.1 kK<br>29.4 kK | 27.1 kK (0.35)         | 37.9 kK                                   | 29.41 kK (0.51)                            |
| IV          | 32.5 kK (0.13)    | 31.5 kK ( $\sim 0.15$ )              | 42.1 kK (0.18)         | 45.6 kK                                   | 41.25 kK (0.10)                            |

In calculating the observed intensities, all subsidiary bands and shoulders which are clearly vibrational overtones have been included in the main bands to which they relate.

allowed interaction only between configurations arising from the two highest occupied and two lowest empty orbitals, to explain substituent effects in porphyrin spectra, and more recently [20] has justified this simplification by repeating the calculations using up to eighty excited configurations. It was found that the lowest excited states contained over 98% of the four configurations originally assumed. As the present work is much more concerned to gain insight into the electronic and steric factors which determine the broad outline of the absorption and circular dichroism spectra than to reproduce band energies and intensities to the highest accuracy, GOUTERMAN's "four orbital" approximation will be used. GOUTERMAN also assumed that the effect of the central metal atom on the  $\pi$ -system of the ligand could be approximated by changing the valence state ionization potentials of the ligand nitrogen atoms as if the metal were exerting the potential of a point positive charge. We shall likewise suppose that the effect of an axial ligand on the in-plane  $\pi$ -system is derived from the charge it donates to the metal, which is transmitted to the ligand nitrogen atoms.

### One Electron Calculation

To obtain a qualitative picture of the way in which the one electron energy levels of the corrin ligand vary with the effective electronegativity of the nitrogen atoms, we start with the eigenvalues of a linear conjugated chain of  $n$  similar atoms, shown by LENNARD-JONES [21] to be

$$E_r = \alpha + 2\beta \cos(r\pi/n + 1) \quad (1)$$

in the Hückel approximation.

COULSON and LONGUET-HIGGINS [22] showed that to second order, the change in energy of orbital  $r$  with respect to changes in  $\alpha$  is

$$\delta E_r = \sum_{\mu=1}^n c_{\mu r}^2 \delta \alpha_{\mu} + \sum_{\mu=1}^n \sum_{i=1}^n \frac{c_{\mu i}^2 c_{i r}^2}{E_i - E_r} \cdot \delta \alpha_{\mu}^2. \quad (2)$$

In the corrin chain, containing thirteen atoms and fourteen  $\pi$ -electrons, we are

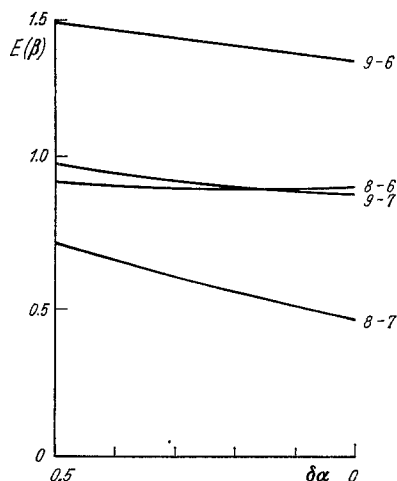


Fig. 3. Excitation energies from the one-electron (Hückel) calculation

interested in orbitals 6, 7, 8 and 9. Fig. 3 shows Eq. (2) plotted as the energy differences between the pairs 7—8, 7—9, 6—8 and 6—9 which, in the Hückel approximation represent the four lowest excited states. Since  $\alpha$  is negative, the right hand side of the plot represents the situation when the nitrogen atoms carry such an excess of negative charge that they have the same electronegativity as the carbons. Two features are at once apparent: the first and fourth excited states become lower in energy and the second and third excited states cross over as negative charge is supplied to the nitrogens. If the bent chain has approximate  $C_{2v}$  symmetry, the four excited states transform respectively as  $A_1, B_1, B_1, A_1$ , and transitions from the  $A_1$  ground state are electric dipole-allowed in the  $y, x, x$  and  $y$  polarisations (see Fig. 1). The one electron LCAO treatment therefore agrees with the polarisation predictions of the free electron model [14]. All transitions are of course predicted as polarised in the plane of the molecule. That the first absorption band at least is so polarised follows from the earliest examination [8] of vitamin  $B_{12}$  crystals under the polarising microscope, taken in conjunction with the subsequently determined structure [36, 37]. KUHN [15] has attempted to discover the polarisations of the higher bands by embedding vitamin  $B_{12}$  in a plastic matrix and stretching it to orient the molecules. The intense  $\gamma$ -band\* at 27.75 kK (see Tab. 1) was thus shown to be differently polarised from the visible band, but the absolute polarisation directions remain unknown.

It is well known that among several sets of cobalamins and cobinamides the lowest energy absorption band (the  $\alpha$ -band) falls in energy along a series of axial ligands that closely parallels the nephelauxetic series [24]. In the light of Fig. 3, this is no surprise, since the nephelauxetic effect is a measure of charge delocalization by covalent bond formation, and in the present example measures the extent to which charge donated by the axial ligand to the cobalt reaches the in-plane ligand. Experimentally, it is also found that the energy of the  $\gamma$ -band falls along the same sequence, but it is not apparent from the Hückel treatment that this should be so. The value of  $\alpha$  giving the best agreement for the first absorption band of a set of symmetrical cyanines is about  $-30$  kK [25], so if we make the usual assumption [26] that the nitrogen coulomb integral  $\alpha_N = \alpha_C + 0.5 \beta_{CC}$ , the Hückel treatment suggests absorption bands as shown in Tab. 1. Corrin  $\alpha$ -bands lie within the region 17—19 kK, in striking agreement with theory, but it is not clear whether the  $\gamma$ -band (which commonly occurs between 27—28 kK) is the  $6 \rightarrow 8$  or  $7 \rightarrow 9$  transition. If it were the latter, Fig. 2 shows that it should fall in energy as the  $\alpha$ -band falls; the  $6 \rightarrow 8$  band has quite a different dependence on the Coulomb integral.

To calculate oscillator strengths for the four one-electron excitations, we make use of MULLIKEN's approximation [27] that in the transition moment integral

$$\mathbf{M}_{rs} = e \langle \psi_r | \sum_{\mu} \mathbf{r}_{\mu} | \psi_s \rangle \quad (3)$$

only diagonal terms are accepted. The molecular orbitals being  $\psi_r = \sum_{\mu} c_{\mu r} \phi_{\mu}$  and

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\* The observed absorption bands of corrins will be labelled according to the scheme proposed by WILLIAMS [23]. The  $\alpha$ - and  $\beta$ -bands are the (0—0) and (0—1) components of the first allowed electronic transition and the  $\gamma$ -band is the first peak on the high energy side of the absorption minimum near 25 kK.

$\psi_s = \sum_{\nu} c_{\nu s} \phi_{\nu}$ , so that

$$\begin{aligned} \mathbf{M}_{rs} &= e \sum_{\mu} \sum_{\nu} c_{\mu r} c_{\nu s} \langle \phi_{\mu} | \mathbf{r} | \phi_{\nu} \rangle \simeq e \sum_{\mu} c_{\mu r} c_{\mu s} \langle \phi_{\mu} | \mathbf{r}_{\mu} | \phi_{\mu} \rangle \\ &= e \sum_{\mu} c_{\mu r} c_{\mu s} (i x_{\mu} + j y_{\mu} + k z_{\mu}), \end{aligned} \quad (4)$$

where  $i, j, k$  are unit vectors and  $x_{\mu}, y_{\mu}, z_{\mu}$  refer to the centre of gravity of the charge cloud on atom  $\mu$ . The oscillator strength is then  $f = 4.703 \cdot 10^{29} \nu_{rs} |\mathbf{M}_{rs}|^2$  [25]. Nuclear coordinates for insertion in Eq. (4) were taken as the average of those in the two most accurate X-ray determinations of the corrin ring, cobyrinic acid [28] and nirin chloride [29]. The calculated oscillator strengths (Tab. 1) show that, in the region of the  $\gamma$ -band, two transitions of roughly equal intensity are expected, each having nearly the same intensity as the  $\alpha$ -band. In the majority of corrinoid compounds this is far from the situation observed. For example in dicyanocobinamide (Fig. 1, R = R' = CN<sup>-</sup>) the second transition is very weak and the third very intense. Only in the compounds containing extremely strong  $\sigma$ -donating axial ligands such as the coenzyme and methylcobalamin are there two bands in the ultraviolet with anything like comparable intensity.

It is clear therefore that although correct in some of its predictions (e.g. direction of movement of the  $\alpha$ -band with changing axial ligand), the one-electron treatment (either Hückel or free-electron) is fundamentally in error and electron interaction must be considered.

### Calculations Including Electron Repulsion

To calculate excitation energies in the Pariser-Parr-Pople approximation it is often convenient to take the eigenvectors  $c_{\nu i}$  from a Hückel calculation and make up for the deficiencies of the orbitals by means of configuration interaction. A brief account of this procedure has been given by MURRELL [25].

In the present work we have used the Hückel basis functions of a linear conjugated chain to calculate the bond order matrix and hence the elements of the Fock matrix  $F_{\mu\mu}$  and  $F_{\mu\nu}$  [25]. Despite the fact that non-SCF-basis functions have been used in this calculation, CI between the ground state and excited states has been ignored because of their relatively large energy separation. Excitation energies were calculated from the equation:

$$\begin{aligned} \langle {}^1\Psi_k^r | \mathcal{H} | {}^1\Psi_i^s \rangle - E_0 &= \sum_{\mu} \sum_{\nu} \{ (c_{r\mu} c_{r\nu} - c_{k\mu} c_{k\nu}) F_{\mu\nu} + \\ &+ (2c_{k\mu} c_{r\mu} c_{k\nu} c_{r\nu} - c_{k\mu}^2 c_{r\nu}^2) \gamma_{\mu\nu} \} \end{aligned} \quad (5)$$

and excited states of similar symmetry were then allowed to interact. It is evident from the one-electron calculation that  ${}^1\Psi_7^8$  will interact with  ${}^1\Psi_6^9$  and  ${}^1\Psi_6^8$  with  ${}^1\Psi_7^9$ , the latter pair to a much greater extent since they are nearly degenerate.

The freely chosen *parameters* appearing in this model are the  $I_{\mu}$ ,  $\beta_{\mu\nu}$  and  $\gamma_{\mu\nu}$  (including  $\gamma_{\mu\mu}$ ). Good results have previously been obtained [31] in calculations of the spectra of aromatic heterocycles by using the Hückel orbitals of the parent hydrocarbons as basis functions, and including the heteroatom perturbation by appropriately varying  $I_{\mu}$  and  $\gamma_{\mu\nu}$ . To take advantage of the particularly convenient form of the orbitals in Eq. (1), this procedure was adopted here. A further reduction in arithmetical labour was also achieved by ignoring all  $\gamma_{\mu\nu}$  (and of course  $\beta_{\mu\nu}$ )

Table 2. *Eigenvalues, eigenvectors and oscillator strengths as a function of  $I_\mu^N$* 

| $I_\mu^N$ | Transition | Energy | Oscillator strength | ${}^1\Psi_7^8$ | ${}^1\Psi_7^9$ | ${}^1\Psi_6^8$ | ${}^1\Psi_6^9$ |
|-----------|------------|--------|---------------------|----------------|----------------|----------------|----------------|
| -140 kK   | I          | 22.44  | 0.28                | 0.997          | —              | —              | -0.082         |
|           | II         | 24.48  | 0.07                | —              | 0.391          | -0.919         | —              |
|           | III        | 31.88  | 0.52                | —              | -0.902         | -0.435         | —              |
|           | IV         | 41.43  | 0.08                | -0.077         | —              | —              | -0.998         |
| -120 kK   | I          | 19.09  | 0.23                | 0.998          | —              | —              | -0.056         |
|           | II         | 23.33  | 0.01                | —              | 0.605          | -0.795         | —              |
|           | III        | 29.41  | 0.51                | —              | -0.840         | -0.545         | —              |
|           | IV         | 41.25  | 0.10                | -0.048         | —              | —              | -0.998         |
| -100 kK   | I          | 14.64  | 0.17                | 0.998          | —              | —              | -0.034         |
|           | II         | 21.65  | 0.01                | —              | 0.817          | -0.575         | —              |
|           | III        | 26.56  | 0.48                | —              | -0.579         | -0.813         | —              |
|           | IV         | 41.17  | 0.10                | -0.044         | —              | —              | -0.0998        |
| -90 kK    | I          | 12.71  | 0.15                | 0.999          | —              | —              | -0.027         |
|           | II         | 19.97  | 0.04                | —              | 0.910          | -0.414         | —              |
|           | III        | 25.63  | 0.42                | —              | -0.388         | -0.921         | —              |
|           | IV         | 41.27  | 0.11                | -0.027         | —              | —              | -0.999         |

other than those between nearest neighbours [32]. The numerical values of the various parameters employed were close to those used with similar approximations [33] to give a good account of the spectra of benzene, pyridine and pyridazine:  $I_\mu^C = -90$  kK,  $\beta_{\mu\nu} = -18$  kK,  $\gamma_{\mu\mu}^C = 64$  kK,  $\gamma_{\mu,\mu+1} = 11$  kK. With these values fixed, a set of calculations was performed for  $I_\mu^N$  between  $-140$  and  $-90$  kK and  $\gamma_{\mu\mu}^N$  between  $80$  and  $64$  kK.

It is clear from all the X-ray structures of corrinoid compounds that the bonds at each end of the conjugated chain [N(23)—C(16) and C(4)—N(20)] are nearly pure double bonds, and that the next bonds [C(16)—C(15) and C(5)—C(4)] are almost as long as single bonds. Two extreme approximations to the variation of  $\beta_{\mu\nu}$  with bond length were therefore examined.

At first it was assumed that  $\beta_{\mu\nu}$  was constant for all the bonds from atoms 5 to 15 but zero for C(15)—C(16) and C(4)—C(5), that is, that the conjugation extended over nine atoms and not thirteen. With  $I_\mu^N = -120$  kK, the calculated energies of the four lowest singlet excited states are given in Tab. 1. The effect of the two end bonds may now be included by coupling their transition dipoles with those of the conjugated fragment, but first it is convenient to examine the extent to which they couple with each other.

The interaction energy of two dipoles  $\mathbf{M}$  lying along the same axis is  $-2 |\mathbf{M}|^2 / r^3$  where  $r$  is the distance between them, here taken as  $3.9 \text{ \AA}$ , the approximate distance between the centres of bonds C(4)—N(20) and C(16)—N(23). As a rough approximation we take  $\mathbf{M}$  from the observed oscillator strength (0.3) and energy (56 kK) of the lowest  $\pi - \pi^*$  transition of an isolated C=C double bond. Then the interaction energy is 0.48 kK and the previously degenerate transitions of the N C bonds are split by 0.96 kK into an allowed ( ${}^1A_1$ ) and a forbidden ( ${}^1B_1$ ) combination, the latter at the higher energy. Since the  ${}^1B_1$  combination of the coupled

C N transitions has approximately zero transition dipole moment, it cannot couple with the  ${}^1B_1$  of the nine atom fragment. To get a rough idea of how much the  ${}^1A_1$  interact, we can use the same dipole-dipole approximation, together with the observed energies and oscillator strengths of the first and fourth bands of corrin.

In this way it is found that the lowest energy corrin  ${}^1A_1$  is lowered by only 0.2 kK, and the next by 0.5 kK, leaving the predicted transition energies very far from those observed. In particular the second and third transitions are at least 10 kK from any observed bands of appropriate intensity. Therefore no further calculations were performed with this approximation.

The other extreme view that could be taken of the variation of  $\beta_{\mu\nu}$  with bond length is to ignore the effect altogether and employ Eq. (1) with  $n = 13$  to yield the basis functions. A calculation for  $I_\mu^N = -120$  kK gave the excitation energies and oscillator strengths listed in Tab. 1. If transition I is identified with the  $\alpha$ -band and transition III with the  $\gamma$ -band, the agreement with the spectra of corrins such as vitamin  $B_{12}$  and dicyanocobinamide is very striking. Fig. 4 shows the variation in energy of the pure configurations  ${}^1\Psi_7^8$ ,  ${}^1\Psi_7^9$ ,  ${}^1\Psi_6^8$  and  ${}^1\Psi_6^9$  and the excitation energies after configuration interaction as a function of the valence state ionization potentials of the four ligand nitrogen atoms. In Tab. 1 are given the eigenvectors of the pure configurations and the eigenvalues for four values of  $I_\mu^N$ , together with the oscillator strengths calculated from Eq. (4). It is interesting that in his recent very extensive calculations on porphyrins, GOUTERMAN [19] also found that a rather shallow dependence of  $\beta_{\mu\nu}$  on bond length gave better results.

In outline Fig. 4 bears a marked resemblance to Fig. 3, and like the one-electron treatment, the Pariser-Parr-Pople model predicts that the  $\alpha$ -band moves to lower energy with increasing donor power of the axial ligands. However, we

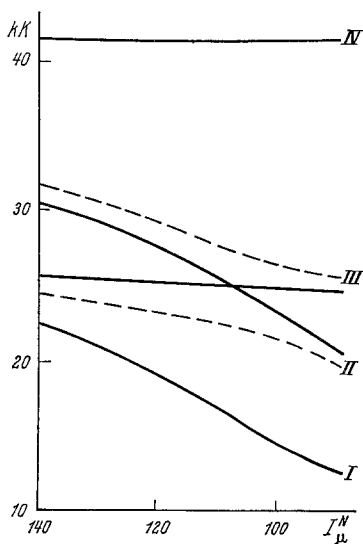


Fig. 4. Singlet excited states from the PPP calculation



now have a similarly clear prediction for the movement of the  $\gamma$ -band, now identified with the in-phase linear combination of  ${}^1\Psi_7^9$  and  ${}^1\Psi_8^8$ . A most important new feature of Fig. 4 is the manner in which interaction between the latter singly excited states also depends on the donor power of the axial ligands, since this provides the key to the wide variations in energy and intensity of the  $\gamma$ -band. An example will illustrate the point.

In the spectra of both dicyanocobinamide (Fig. 1,  $R = R' = \text{CN}^-$ ) and methylcobalamin (Fig. 1,  $R = \text{CH}_3^-$ ,  $R' = \text{benzimidazole}$ ) at 77 °K (Fig. 2 and Tab. 1) there is a band in the region of 31.0 kK with very similar vibrational structure (the  $\delta$ -band) which we take to be band IV. That its energy varies so little with the axial ligand is in agreement with Fig. 4, though the predicted energy is very badly wrong probably because CI with  ${}^1\Psi_8^8$  and  ${}^1\Psi_7^{10}$  has been ignored. Now between this band and the  $\alpha$ -band in dicyanocobinamide lies the intense sharp  $\gamma$ -band at 27.0 kK and two very weak bands in the 24–25 kK region. In contrast, methylcobalamin exhibits three bands of comparable intensity in this region, none of which is more than half the intensity of the dicyanocobinamide  $\gamma$ -band. Methylcobalamin also has a single weak band at 23.6 kK before the onset of the vibrational fine structure of the  $\alpha$ -band. Fig. 4 and Tab. 1 predict that as more charge is placed on the ligand nitrogen atoms, interaction between  ${}^1\Psi_7^9$  and  ${}^1\Psi_8^8$  decreases until in the complete absence of configuration interaction we would expect to observe two bands of comparable intensity in the  $\gamma$ -band region in place of the very strong and very weak bands predicted when configuration interaction is almost complete. The latter situation appears to be realized in the cobalamins with ligands such as  $\text{CN}^-$ ,  $\text{H}_2\text{O}$ , pyridine, imidazole and halogens except  $I^-$ , except that although the  $\gamma$ -band is clearly transition III of Fig. 4, it is not so certain that the weak bands between 23 and 25 kK represent transition II. (The sign of the matrix element  $\langle {}^1\Psi_7^9 | \mathcal{H} | {}^1\Psi_8^8 \rangle$  requires that the out-of-phase combination of  ${}^1\Psi_8^8$  and  ${}^1\Psi_7^9$  has the lower energy.)

In methylcobalamin and the coenzyme, for example, we might choose to assign two of the three ultraviolet bands as the almost pure  ${}^1\Psi_8^8$  and  ${}^1\Psi_7^9$ , but there remains the problem of the very weak band at 23.6 kK, which appears to be related to the weak bands in dicyanocobinamide in that region. That the weak bands are not  $d-d$  transitions is proved by their presence in Toohey's metal-free corrin [11]. Nor do they appear to be  $\pi - \pi^*$  triplets, since addition of ethyl iodide, a well-known triplet enhancing substance [34], causes no change in their intensity.

An alternative assignment of the methylcobalamin spectrum could be made by assuming that the lowest in energy of the three ultraviolet bands is transition III and the weak band at 23.6 kK is transition II, configuration interaction remaining quite strong. This leaves the other two ultraviolet bands unassigned.

An analysis of the vibrational fine structure at very low temperatures might be helpful in clarifying the band assignments, but meanwhile, the 77° spectra reveal at least four vibrational components of the  $\alpha$ -band, at intervals of  $1.30 \pm \pm 0.05$  kK. The (0 – 0) band is the most intense, in agreement with the view that the transition is from an orbital which would be non-bonding in the absence of the heteroatom perturbation. No doubt the vibrational interval is related to the aromatic C C stretching frequency, and the close resemblance between the corrin

$\alpha$ -band and the lowest transitions of cyanine dyes [35] is worth noting. In dicyanocobinamide, the  $\delta$ -band is also resolved into four components at  $77^\circ$ , but they are closer than those of the  $\alpha$ -band (about 0.7 kK) and (0 — 1) is the most intense. This can be rationalized from the Hückel calculation, which shows that the fractional decrease in bond order accompanying the transition  $7 \rightarrow 8$  is 19%, while for  $6 \rightarrow 9$  it is 48%. In an attempt to obtain further theoretical evidence for all these assignments, some calculations were made about the probable form of the circular dichroism curves for the cobalamins.

### Circular Dichroism Calculations

In all the compounds in which it has so far been examined, the corrin conjugated chain shows marked deviations from planarity. These appear to be broadly divisible into two types, depending on whether the nucleotide is attached or not. In the nucleotide-free compounds cobyrinic acid [28], hexacarboxylic acid [36] and "nirrin" chloride [29], C(5) and C(15) are on opposite sides of the plane containing the metal atom and the four ligand nitrogen atoms, while in wet and dry [38] vitamin  $B_{12}$  and the coenzyme [39] they are on the same side of the plane. The two conformations may be nicknamed, respectively, "wavy" ( $w$ ) and "seagull" ( $s$ ). The widest range of circular dichroism results [10] is for compounds with the nucleotide attached, and so calculations were performed for the  $s$ -conformation only.

Electronic transitions take on a rotational strength  $R$  in addition to their dipole strength when their electric and magnetic dipole transition moments are either parallel or antiparallel:

$$R_{rs} = Im \{ \mathbf{M}_{rs} \cdot \boldsymbol{\mu}_{sr} \} \quad (6)$$

where  $\mathbf{M}_{rs}$  is the electric dipole transition moment Eq. (3) and  $\boldsymbol{\mu}_{sr}$  is the magnetic dipole transition moment. Now an electron rotating about an axis produces a magnetic moment  $\boldsymbol{\mu}$  along the axis given by

$$\boldsymbol{\mu} = (e/2mc) (\mathbf{r} \times \mathbf{p}) = (e/2mc) (\mathbf{l}) \quad (7)$$

where  $\mathbf{r}$  is the vector distance of the electron from the centre of rotation,  $\mathbf{p}$  is its linear and  $\mathbf{l}$  its angular momentum. The latter is related [40] to the electric dipole moment of a transition between two states  $r$  and  $s$  by

$$\mathbf{p}_{rs} = - (2\pi im/e) v_{rs} \mathbf{M}_{rs} \quad (8)$$

so that

$$\boldsymbol{\mu} = - \pi v_{rs} (\mathbf{r} \times \mathbf{M}_{rs}). \quad (9)$$

When performing calculations of rotational strengths using approximate wave functions, it is advisable [41] to use the dipole-velocity rather than the dipole-length matrix element in Eq. (6), because Eq. (8) is only valid for exact eigenfunctions, and otherwise the vector matrix elements of linear momentum and electric moment will not be parallel. In that case the scalar product  $\mathbf{M} \cdot \mathbf{l}$  depends on the choice of origin for  $\mathbf{l}$ . We therefore re-write Eq. (6) as

$$R_{rs} = (2\beta_M^2/\pi v_{rs}) \langle \Psi_r | \nabla | \Psi_s \rangle \langle \Psi_r | \mathbf{r} \times \nabla | \Psi_s \rangle, \quad (10)$$

where  $\beta_M$  is the Bohr magneton  $eh/4\pi mc$ , and  $\nabla = -i(\partial/\partial x) - j(\partial/\partial y) - k(\partial/\partial z)$ . An analogous expression to Eq. (3) is

$$\mathbf{M}^{v_{rs}} = \sqrt{2}(\beta_M/\pi v_{rs}) |\langle \Psi_r | \nabla | \Psi_s \rangle|^2 \quad (11)$$

where the superscript  $v$  acknowledges the new basis for calculation. All these matrix elements over molecular orbitals reduce to matrix elements over atomic orbitals:

$$\langle \Psi_r | \nabla | \Psi_s \rangle = \sum_{\mu} \sum_{\nu} c_{\mu r} c_{\nu s} \langle \phi_{\mu} | \nabla | \phi_{\nu} \rangle \cong \sum_{\mu} \sum_{\nu} (c_{\mu r} c_{\nu s} - c_{\mu s} c_{\nu r}) \nabla_{\mu\nu} \quad (12)$$

adjacent

(Note that  $\nabla_{\mu\nu} = -\nabla_{\nu\mu}$ ). Dipole velocity matrix elements over the bonds  $\mu\nu$  are conveniently resolved along the Cartesian coordinates in terms of the absolute value of  $\nabla_{\mu\nu}$ , denoted  $\langle\nabla_{\mu\nu}\rangle$ :

$$\nabla_{\mu\nu} = (\mathbf{i} \cos x_{\mu\nu} + \mathbf{j} \cos y_{\mu\nu} + \mathbf{k} \cos z_{\mu\nu}) \langle\nabla_{\mu\nu}\rangle. \quad (13)$$

Similarly, the matrix element  $\langle\Psi_r | \mathbf{r} \times \nabla | \Psi_s\rangle$  may be expressed as sums of atomic  $\langle\phi_\mu | \mathbf{r} \times \nabla | \phi_\nu\rangle$ , which are clearly equal to the vector product of the  $\nabla_{\mu\nu}$  and the radius vector from the origin of coordinates to the midpoint of bond  $\mu\nu$ . Thus in sum:

$$\begin{aligned} \langle\Psi_r | \mathbf{r} \times \nabla | \Psi_s\rangle = \sum_{\mu} \sum_{\nu}^{adjacent} (c_{\mu r} c_{\nu s} - c_{\mu s} c_{\nu r}) \{ \mathbf{i} (\bar{y}_{\mu\nu} \cos z_{\mu\nu} - \bar{z}_{\mu\nu} \cos y_{\mu\nu}) + \\ + \mathbf{j} (\bar{z}_{\mu\nu} \cos x_{\mu\nu} - \bar{x}_{\mu\nu} \cos z_{\mu\nu}) + \mathbf{k} (\bar{x}_{\mu\nu} \cos y_{\mu\nu} - \bar{y}_{\mu\nu} \cos x_{\mu\nu}) \} \langle\nabla_{\mu\nu}\rangle \end{aligned} \quad (14)$$

$\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$  are the Cartesian coordinates of the midpoints of each bond.

The experimental values for the atomic coordinates required to evaluate Eqs. (13) and (14) were obtained from the X-ray data, the  $z_\mu$  by averaging the results for wet [37] and dry [38] vitamin  $B_{12}$ , and the  $x_\mu$ ,  $y_\mu$  by averaging the coordinates of cobyric acid [28] and nirrin chloride [28] as before. This procedure was adopted because the X-ray determinations of cobyric acid and nirrin chloride have the lowest reliability indices among all the corrinoid structures (15.9% and 16.0% respectively), but have the *w*- rather than *s*-conformation. The average *z*-coordinates of both conformations are sufficiently small compared with *x*- and *y*-, that a conformational change is not expected to lead to significant bond length differences. The eigenfunctions used in the calculation were again those of a linear conjugated chain of carbon atoms, and configuration interaction was included.  $\langle\nabla_{\mu\nu}\rangle$ , which acts as a scaling parameter for the dipole and rotational strengths, was calculated for two carbon  $2p\pi$  Slater orbitals separated by the average bond length in the corrin chain, 1.38 Å. The formula employed was that derived by EHRENSON and PHILLIPSON [42] in terms of the C-integrals defined by RUEDENBERG et al. [43], and the value obtained was  $4.50 \cdot 10^7 \text{ cm}^{-1}$ . The results in Tab. 3 cover the same range of  $I_\mu^N$ , as Fig. 4. Dipole and rotational strengths measured in solution refer to spherical averages, which are tabulated in the last two columns in the form of oscillator strengths and the predicted areas under the circular dichroism curves of each transition. The oscillator strengths of Tab. 3 are very much smaller than those in Tab. 2, in agreement with Wolfsberg's comparison of dipole length and velocity matrix elements of approximate wave functions, but the relative magnitudes are in excellent agreement. There are a number of factors, however, that might invalidate comparisons between the calculated and observed rotational strengths. First, we have no guarantee that the conformation in solution is the same as that revealed by the X-ray examination of the crystal, where such factors as intermolecular hydrogen bonding and molecular packing might be important. Second, the accuracy of the atomic parameters in the crystal is not very high compared with the small deviations from planarity that we are considering. A further reason for caution is the very approximate wave functions employed.

Nevertheless, with these factors in mind, Tab. 3 does offer an explanation for some of the major, and previously rather puzzling, features of the cobalamin circular dichroism spectra. First of all, there is little rotational strength associated with the  $\alpha$ -band absorption [10]. Without placing too much weight on the precise numerical reliability of Tab. 3, we see that the two major contributions to the

Table 3. Dipole and rotational integrals. To convert to cm units, multiply by  $\langle \nabla_{12} \rangle \cdot 10^{-8} \approx 0.45$ 

| $I_{\mu}^N$ | Transition | $ \langle \Psi_r   \nabla   \Psi_s \rangle ^2$ |        |       | $\langle \Psi_r   \nabla   \Psi_s \rangle \langle \Psi_r   \mathbf{r} \times \nabla   \Psi_s \rangle$ |        |        | $f$   | $\int \Delta \epsilon d\nu \times 10^{-1}$ |
|-------------|------------|------------------------------------------------|--------|-------|-------------------------------------------------------------------------------------------------------|--------|--------|-------|--------------------------------------------|
|             |            | $i$                                            | $j$    | $k$   | $i$                                                                                                   | $j$    | $k$    |       |                                            |
|             | 7 → 8      | .1572                                          | .0000  | .0001 | +.0302                                                                                                | +.0001 | -.0147 |       |                                            |
|             | 7 → 9      | .0000                                          | .4485  | .0012 | -.0010                                                                                                | -.0331 | -.0012 |       |                                            |
|             | 6 → 8      | .0001                                          | .5757  | .0017 | -.0030                                                                                                | -.0259 | -.0019 |       |                                            |
|             | 6 → 9      | .3637                                          | .0000  | .0078 | -.1206                                                                                                | +.0004 | +.0785 |       |                                            |
| -140 kK     | I          | .1980                                          | .0000  | .0001 | +.0267                                                                                                | .0000  | -.0151 | 0.050 | + 188                                      |
|             | II         | .0000                                          | .1900  | .0006 | -.0012                                                                                                | -.0052 | -.0007 | 0.043 | - 116                                      |
|             | III        | .0000                                          | .8722  | .0025 | -.0029                                                                                                | -.0554 | -.0025 | 0.153 | -1454                                      |
|             | IV         | .3265                                          | .0000  | .0007 | -.1146                                                                                                | +.0004 | +.0794 | 0.044 | - 560                                      |
| -120 kK     | I          | .1845                                          | .0000  | .0001 | +.0279                                                                                                | .0000  | -.0151 | 0.054 | + 208                                      |
|             | II         | .0000                                          | .0394  | .0001 | -.0003                                                                                                | +.0005 | -.0002 | 0.009 | 0                                          |
|             | III        | .0001                                          | .9495  | .0027 | -.0034                                                                                                | -.0586 | -.0028 | 0.181 | -1053                                      |
|             | IV         | .3399                                          | .0000  | .0007 | -.1186                                                                                                | +.0004 | +.0785 | 0.046 | - 638                                      |
| -100 kK     | I          | .1731                                          | .0000  | .0001 | +.0287                                                                                                | .0000  | -.0149 | 0.066 | + 222                                      |
|             | II         | .0000                                          | .0123  | .0000 | +.0002                                                                                                | -.0023 | .0000  | 0.003 | - 34                                       |
|             | III        | .0001                                          | 1.0100 | .0030 | -.0042                                                                                                | -.0567 | -.0031 | 0.213 | -1028                                      |
|             | IV         | .3417                                          | .0000  | .0007 | -.1187                                                                                                | +.0004 | +.0790 | 0.046 | - 632                                      |
| -90 kK      | I          | .1696                                          | .0000  | .0001 | +.0290                                                                                                | .0000  | -.0150 | 0.075 | + 227                                      |
|             | II         | .0000                                          | .0874  | .0002 | +.0001                                                                                                | -.0091 | -.0002 | 0.025 | - 145                                      |
|             | III        | .0001                                          | .9203  | .0027 | -.0041                                                                                                | -.0486 | -.0029 | 0.201 | - 894                                      |
|             | IV         | .3495                                          | .0000  | .0008 | -.1194                                                                                                | +.0004 | +.0789 | 0.047 | - 648                                      |

rotational strength of the  $\alpha$ -band, along  $x$ - and  $z$ -directions, have opposite signs, and might therefore be expected to cancel to a large degree. Neither will the difference between these contributions be very sensitive to the axial ligands, since the amount of configuration interaction between  ${}^1\Psi_7^8$  and  ${}^1\Psi_8^9$  is always very small.

In contrast, there is only one major contribution to the rotational strength of both  ${}^1\Psi_7^9$  and  ${}^1\Psi_8^8$ , so that the rotational strengths of the pure configurations are both large and of equal sign. The circular dichroism spectrum of Vitamin B<sub>12</sub> and dicyanocobalamin [10, 44] contains a negative peak in the region of the  $\gamma$ -band absorption and a positive peak of nearly equal intensity in the region of the weak absorption bands near 25 kK. In aquo-, hydroxo-, pyridino- and amino-cobalamins, however, the pattern is inverted and the circular dichroism peak under the  $\gamma$ -band is positive. LEGRAND and VIENNET [44], who first measured the circular dichroism spectra of cobalamins, interpreted this inversion as resulting from positional isomerism of the ligands about the cobalt, but the present calculations show that it could be due to electronic rather than steric factors. We have already noticed that the extent of interaction between  ${}^1\Psi_6^9$  and  ${}^1\Psi_6^8$  is very sensitive to  $I_{\mu}^N$ , such that when the axial ligand is a very strong donor, II is a transition to a state consisting mainly of  ${}^1\Psi_7^9$ , and III to a state that consists mainly of  ${}^1\Psi_6^8$ . Thus not only will the rotational strengths of these two transitions vary strongly with the axial ligand, but if the rotational strengths of the two pure configurations are sufficiently different, the resulting rotational strengths may even have opposite signs. Furthermore, with changing configurational admixture, the rotational

strengths of bands II and III might very well change sign. In fact, the calculated  $R$  values of Tab. 3 do not change sign, but a small adjustment of either the wave functions or the geometry could easily cause them to do so.

The rotational strength of transition IV is predicted to be always negative, in agreement with observation if this transition is identified with the  $\delta$ -band at 32 kK. Furthermore, the energy of the circular dichroism and absorption peaks at 32 kK is very insensitive to the axial ligand, as is the energy of transition IV in Fig. 4. As far as they can be compared with the strongly overlapping circular dichroism peaks [10, 44], the calculated rotational strengths are of the right magnitudes.

### Conclusions

The experimental dipole and rotational strengths of the  $\alpha$ - and  $\delta$ -bands are in excellent agreement with their assignment as transitions I and IV of Fig. 4, though the calculated energy of IV is a good deal too high (see p. 336). The assignment of transitions II and III is at once more problematic and more interesting. In the cobalamins in which configuration interaction between  ${}^1\Psi_6^8$  and  ${}^1\Psi_7^9$  is at its strongest, there is little doubt that the  $\gamma$ -band is transition III, but transition II may be assigned either as one of the weak bands near 25 kK or as a hidden satellite of the  $\gamma$ -band. In the cobalamins with the strongest donors as axial ligands, where configuration interaction is expected to be much weaker, it is not even possible to assign transition III with any certainty. Nevertheless, the theory developed in this paper offers a clear explanation for the following observations:

1. The most intense absorption bands of a wide range of cobalamins and cobinamides lie near 19 kK ( $\alpha$ -band) and 28 kK ( $\gamma$ -band).

2. Among the cobalamins in which configuration interaction between  ${}^1\Psi_6^8$  and  ${}^1\Psi_7^9$  is strongest, the  $\alpha$ -band decreases in energy with increasing donor power of the axial ligands. If the two ligands are different, their total effect on the  $\alpha$ -band energy is related to the sum of their donor powers.

3. Among the same compounds as in (2), the  $\gamma$ -band energy changes in the same direction as the  $\alpha$ -band but over a smaller range. As the  $\gamma$ -band energy decreases, its intensity passes through a maximum and then decreases [45].

4. The energy and the dipole and rotational strengths of the  $\delta$ -band are very insensitive to changes in the axial ligands.

5. The rotational strength of the  $\alpha$ -band is small, while that of the  $\gamma$ -band is much larger. Changes in the axial ligands which produce relatively minor shifts in the absorption spectrum (e.g.  $\text{CN}^-$  to  $\text{H}_2\text{O}$ ) may have a pronounced effect on the circular dichroism by altering the degree of configuration interaction between  ${}^1\Psi_6^8$  and  ${}^1\Psi_7^9$ , without necessarily affecting the conformation of the ring.

These conclusions are stated in general terms, both because certain experimental exceptions can be quoted and because the theory employed is a very approximate one. The present work nevertheless provides a theoretical framework into which we hope to build experimental data obtained with higher resolution at low temperatures and which will be a starting point for improved calculations.

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