Synthesis and Properties of a New Kind of One-Dimensional Conductors

25. Extended Hückel Calculations on the Energy Band Structure of CN- and N-Bridged Co^{III}-Phthalocyanine

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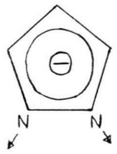
Improvements in the computer program for the extended Hückel calculations of one-dimensional solids allowed the extension to bigger unit cells. So Co^{III}-phthalocyanine (CoPc), $C_{32}H_{16}N_8Co^+$, bridged to stacks over the Co's by CN^- or N^-, respectively, could now be treated although 193 or 189 basis functions in the minimum set had to be used. The iterative (i.e. „SCF" in the framework of IEH) computation yielded energy bands that indicate a gap of 1.15 eV for the CN-, but 0.30 eV for the N-bridged compound. Co-Pc-CN showed an exeedingly (1.15 eV) broad conduction band 1.25 eV above the Fermi level suggesting a good conductivity by reductive n-doping rather than the usual oxidative p-doping by I_2 e.g., and a high photoconductivity of the undoped material.

1. Introduction

In the 24 previous papers of the joint effort to compute and synthesize samples of a new type of one-dimensional conductors we described a number of substances that fit into the general scheme MX_4L, where M is some transition metal (contributing d-orbitals), X_4 is a quadratic array of equal ligands X or a macrocyclic ring system of symmetry D_{4h} like tetrazaporphin (TAP) or phthalocyanine (Pc), and L is a bidentate, non-chelating bridging ligand like $C{\equiv}C^{2-}$, pyrazine etc. (the full list of previous papers by Hanack, Strähle and Seelig, each with coworkers, is given in [1]).

The original scheme was varied by reducing the D_{4h} to D_{2h} symmetry, by introducing the ML_3-concept, where L has now 2 angled coordination positions like in pyrazolate,



thus forming triply bridged complexes, which yielded in the calculation surprisingly narrow energy bands rather than enhancing the conductivity [2].

The first calculations on the type MX_4L [3] were done for Fe^{II}-TAP-C_2^{2-}, but the synthesized materials were Fe^{II} and Co^{II}-Pc-Pyrazine [4] and recently Co^{III}-Pc-CN [5]. A severe drawback of the accompanying calculations up to now was, that despite the use of symmetry adapted basis orbitals the storage limitations of the used time sharing computer (120 K words per user) did not allow to make computations of the experimentally considered phthalocyanines, but only of the somewhat smaller tetraporphin. The main reason for this limitation was that the iterative extended Hückel calculations switched back to the original **C** matrix of the AOs to compute the total electron density of each atom and to correct accordingly the **H** matrix. A thorough inspection revealed that once the blocked matrices in terms of symmetry adapted basis functions had been introduced this form could be preserved during all the iterations without retransformation, thus saving much computer time and at the same time storage space so that bigger elementary cells of the one-dimensional solids could be computed.

2. IEH-Formalism with Symmetry Adapted Basis Functions Throughout

The adapted IEH-procedure was treated in detail in [3] so that only the most important formulas — necessary for definitions of terms needed in the following expansions — have to be repeated here.

Starting from the Bloch functions as crystal orbitals (CO's) for a particular value of k_z, the z-component of the wave vector,

$$\Psi_j(\mathbf{x}, k_z) = \sum_r \varphi_r(\mathbf{x}, k_z)\, C_{rj}(k_z) \tag{1}$$

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with the Bloch basis function

$$\varphi_r(\mathbf{x}, k_z) = \sum_{p=-\infty}^{+\infty} \exp^{i k_z p c} \varphi_{0,r}(\mathbf{x}_p); \tag{2}$$

p being an integer including 0, as index of the cell, c the lattice constant in the z-direction, and $\mathbf{x}_p$ the position vector relative to the p-th cell, we end up with the 1-electron Schrödinger equation in matrix notation

$$\mathbf{H}(k_z)\,\mathbf{C}(k_z) = \mathbf{S}(k_z)\,\mathbf{C}(k_z)\,\mathbf{E}(k_z) \tag{3}$$

with $0 \leqq k_z \leqq \pi/c$ for the first Brillouin zone.

If the effective 1-electron Hamilton operator $\mathscr{H}$ and the basis functions φ_r are given, $\mathbf{H}$ and $\mathbf{S}$ can easily be computed for any k_z by their elements

$$H_{rs} = \int \varphi_r{}^* \mathscr{H} \varphi_s \,\mathrm{d}v\,, \tag{4}$$

$$S_{rs} = \int \varphi_r{}^* \varphi_s \,\mathrm{d}v \tag{5}$$

(from here the argument "k_z" is omitted).

Actually, in the IEH method (5) is used literally, but H_{rs} is computed not from (4) but from the net charge density q_α at atom α, where basis function φ_r comes from, by

$$H_{rr} = A_{\alpha r} q_\alpha{}^2 + B_{\alpha r} q_\alpha + C_{\alpha r} \quad (\text{for } r \in \alpha)\,, \tag{6}$$

where $A_{\alpha r}$, $B_{\alpha r}$ and $C_{\alpha r}$ are typical empirical parameters of the ionization potential for the basis function φ_r at atom α. Then

$$H_{rs} = \tfrac{1}{2}(H_{rr} + H_{ss})\,K\,S_{rs} \tag{7}$$

with $K = 1.75$.

If for each energy band the energy is a monotonous function of k_z, the limits of each band are characterized by $E(0)$ and $E(\pi/c)$, if not so, these values define a lower limit for the band width. The main advantage of the restriction to these values of k_z is that in this case all matrices are real (symmetric) which simplifies the treatment and cuts down the storage need to one half. In the following we confine to this particular case, and the results are gained under this restriction.

It is the unique feature of our treatment that before solving (3) a transformation to symmetry adapted basis functions is performed with the advantage of getting smaller submatrices thus saving storage space (or accordingly the possibility to compute bigger unit cells) and computing time, of getting a higher accuracy and a unique classification of the gained wave functions and energy bands.

The transformation is done by a transformation matrix $\mathbf{T}$ which is orthogonal and constructed according to the symmetry of the problem by hand, but for which a computer program for the automatic construction is underway.

Since from (3)

$$(\mathbf{T}'\mathbf{H}\mathbf{T})\,(\mathbf{T}'\mathbf{C}) = (\mathbf{T}'\mathbf{S}\mathbf{T})\;(\mathbf{T}'\mathbf{C})\,\mathbf{E} \tag{8}$$

we get with the abbreviations

$$\mathbf{H}_\mathrm{B} = \mathbf{T}'\mathbf{H}\mathbf{T}\,, \tag{9}$$

$$\mathbf{S}_\mathrm{B} = \mathbf{T}'\mathbf{S}\mathbf{T}\,, \tag{10}$$

$$\mathbf{C}_\mathrm{B} = \mathbf{T}'\mathbf{C} \tag{11}$$

a form analogous to (3)

$$\mathbf{H}_\mathrm{B}\,\mathbf{C}_\mathrm{B} = \mathbf{S}_\mathrm{B}\,\mathbf{C}_\mathrm{B}\,\mathbf{E}_\mathrm{B}\,. \tag{12}$$

The difference between (12) and (3) is that now $\mathbf{H}_\mathrm{B}$ and $\mathbf{S}_\mathrm{B}$ are in block diagonal form, and $\mathbf{C}_\mathrm{B}$ is composed of blocks of column vectors so that each submatrix which corresponds to a particular irreducible representation Γ of the point group can be treated *separately*. $\mathbf{E}_\mathrm{B}$ of (12) is identical with $\mathbf{E}$ of (3), but is now ordered by symmetry. The further treatment is conventional:

1. find an orthonormal matrix $\mathbf{R}_{\mathrm{B},\Gamma}$ for each Γ such that

   $$\mathbf{R}'_{\mathrm{B},\Gamma}\,\mathbf{S}_{\mathrm{B},\Gamma}\,\mathbf{R}_{\mathrm{B},\Gamma} = \boldsymbol{\lambda}_{\mathrm{B},\Gamma} \tag{13}$$

   where $\boldsymbol{\lambda}_{\mathrm{B},\Gamma}$ is diagonal (first diagonalization)

2. construct

   $$\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2} = \mathbf{R}_{\mathrm{B},\Gamma}\,\boldsymbol{\lambda}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{R}'_{\mathrm{B},\Gamma} \tag{14}$$

   which is orthogonal and symmetric, so that

   $$\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{S}_{\mathrm{B},\Gamma}^{1/2} = \mathbf{S}_{\mathrm{B},\Gamma}^{1/2}\,\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2} = \mathbf{I}$$

   and

   $$\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{S}_{\mathrm{B},\Gamma}\,\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2} = \mathbf{I} \tag{15}$$

   ($\mathbf{S}_{\mathrm{B},\Gamma}^{1/2}$ is defined in a similar way like $\mathbf{S}_\mathrm{B}^{-1/2}$, but not really needed for actual computations!)

3. construct

   $$\mathbf{H}_{\mathrm{u},\Gamma} = \mathbf{S}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{H}_{\mathrm{B},\Gamma}\,\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2} \tag{16}$$

   since from (12) for each Γ

   $$\begin{aligned}(\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{H}_{\mathrm{B},\Gamma}\,\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2})\,(\mathbf{S}_{\mathrm{B},\Gamma}^{1/2}\,\mathbf{C}_{\mathrm{B},\Gamma}) \\ = (\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2}\,\mathbf{S}_{\mathrm{B},\Gamma}\,\mathbf{S}_{\mathrm{B},\Gamma}^{-1/2})\,(\mathbf{S}_{\mathrm{B},\Gamma}^{1/2}\,\mathbf{C}_{\mathrm{B},\Gamma})\,\mathbf{E}_{\mathrm{B},\Gamma}\end{aligned} \tag{17}$$

or

$$\mathbf{H}_{\mathrm{u},\Gamma}\mathbf{C}_{\mathrm{u},\Gamma} = \mathbf{C}_{\mathrm{u},\Gamma}\mathbf{E}_{\mathrm{B},\Gamma} \tag{18}$$

with

$$\mathbf{C}_{\mathrm{u},\Gamma} = \mathbf{S}^{1/2}_{\mathrm{B},\Gamma}\mathbf{C}_{\mathrm{B},\Gamma}\,. \tag{19}$$

4. find the orthogonal matrices $\mathbf{C}_{\mathrm{u},\Gamma}$ as the matrices of eigenvectors according to

$$\mathbf{C}'_{\mathrm{u},\Gamma},\mathbf{H}_{\mathrm{u},\Gamma}\mathbf{C}_{\mathrm{u},\Gamma} = \mathbf{E}_{\mathrm{B},\Gamma} \tag{20}$$

(second diagonalization), yielding $\mathbf{E}_{\mathrm{B},\Gamma}$ and thus the complete $\mathbf{E}$ of eigenvalues.

5. transform

$$\mathbf{C}_{\mathrm{B},\Gamma} = \mathbf{S}^{-1/2}_{\mathrm{B},\Gamma}\mathbf{C}_{\mathrm{u},\Gamma} \tag{21}$$

yielding the matrices of eigenvectors in the basis of symmetry adapted eigenfunctions.

In [3] the set of $\mathbf{C}_{\mathrm{B},\Gamma}$ was transformed to the very matrix of eigenvectors $\mathbf{C}$ by

$$\mathbf{C} = \mathbf{T}\mathbf{C}_{\mathrm{B}}\,, \tag{22}$$

because the net charge density at each atom α which is needed for the iterative process is defined in terms of $\mathbf{C}$ by

$$q_\alpha = n_{v,\alpha} - \sum_{r\in\alpha} q_{rr}\,, \tag{23}$$

$$\mathfrak{q} = \mathbf{S}\mathbf{C}\mathbf{n}\mathbf{C}'\,, \tag{24}$$

where $n_{v,\alpha}$ is the (integer) number of valence electrons of atom α, $\mathfrak{q}$ is the diagonal matrix of valence electron population density, and $\mathbf{n}$ is the ad hoc introduced diagonal matrix of occupation numbers whose elements are 2 for fully occupied and O for empty COs and has the marginal value of 1 for simply occupied orbitals in case of degenerate half filled highest occupied COs. The necessity of computing $\mathbf{C}$ would mean that the use of $\mathbf{C}_{\mathrm{B}}$ is only transient for the sake of some, but modest computational advantages. But a thourough inspection shows that a switching back to $\mathbf{C}$ is not necessary so that $\mathbf{C}_{\mathrm{B}}$ is a final result and a drastic simplification is achieved.

Defining analogously to (9) and (10)

$$\mathfrak{q}_{\mathrm{B}} = \mathbf{T}'\mathfrak{q}\mathbf{T} \tag{25}$$

and using (11) and correspondingly

$$\mathbf{C}_{\mathrm{B}}' = \mathbf{C}'\mathbf{T} \tag{26}$$

we get from (24) and (25)

$$\begin{aligned}\mathfrak{q}_{\mathrm{B}} &= \mathbf{T}'\mathfrak{q}\mathbf{T} = \mathbf{T}'\mathbf{S}\mathbf{C}\mathbf{n}\mathbf{C}'\mathbf{T}\\ &= (\mathbf{T}'\mathbf{S}\mathbf{T})(\mathbf{T}'\mathbf{C})\mathbf{n}(\mathbf{C}'\mathbf{T}) = \mathbf{S}_{\mathrm{B}}\mathbf{C}_{\mathrm{B}}\mathbf{n}\mathbf{C}_{\mathrm{B}}'\end{aligned} \tag{27}$$

which means that $\mathfrak{q}_{\mathrm{B}}$ can be computed directly from $\mathbf{S}_{\mathrm{B}}$ and $\mathbf{C}_{\mathrm{B}}$ without the detour over $\mathbf{C}$.

By the backtransformation (from (25))

$$\mathfrak{q} = \mathbf{T}\mathfrak{q}_{\mathrm{B}}\mathbf{T}' \tag{28}$$

we get $\mathfrak{q}$ and can compute the net charge density q_α for each atom α which is needed to compute the new $\mathbf{H}$ according to (6).

Up to now not much would have been gained, if really a computation of $\mathbf{H}$ rather that $\mathbf{H}_{\mathrm{B}}$ were necessary. Since $\mathbf{H}_{\mathrm{B}} = \mathbf{T}'\mathbf{H}\mathbf{T}$ involves offdiagonal elements of $\mathbf{H}$ which are gained by a nonlinear operation according to (7) everything seems to be lost. But $\mathbf{T}$ is a sparse matrix in which the symmetry transformation operates only on equal types of orbitals of equivalent atoms which have exactly the same q_α and thus the same ionization potential.

So for some H_{rs} involved in (9) by (7) H_{rr} and H_{ss} are equal and can be extracted as a common factor outside the transformation of $\mathbf{S}$ to $\mathbf{S}_{\mathrm{B}}$ according to (10). So $\mathbf{H}_{\mathrm{B}}$ can be computed directly from $\mathfrak{q}$ and $\mathbf{S}_{\mathrm{B}}$.

Finally it is claimed that whatever the application may be, never a backtransformation to $\mathbf{C}$ is necessary.

Wavefunctions are not interesting by themselves, but are only needed to compute expectation values of some physical observable A represented by an operator $\mathcal{A}$ according to

$$A_{pq} = \int \Psi_p{}^* \mathcal{A}\, \Psi_q \,\mathrm{d}v\,. \tag{29}$$

Since each Ψ_p is expressed as a linear combination of basis functions according to

$$\Psi_p = \sum_r \varphi_r C_{rp} \tag{30}$$

or better according to the somewhat more complicated (1),

$$\begin{aligned}A_{pq} &= \int \Big(\sum_r \varphi_r^* C_{rp}^*\Big)\mathcal{A}\Big(\sum_s \varphi_s C_{sq}\Big)\,\mathrm{d}v\\ &= \sum_{r,s} C_{rp}^* a_{rs} C_{sq}\end{aligned} \tag{31}$$

with

$$a_{rs} = \int \varphi_r^* \mathcal{A}\, \varphi_s \,\mathrm{d}v\,. \tag{32}$$

So the full matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \mathbf{C}^{+}\mathbf{a}\,\mathbf{C} \tag{33}$$

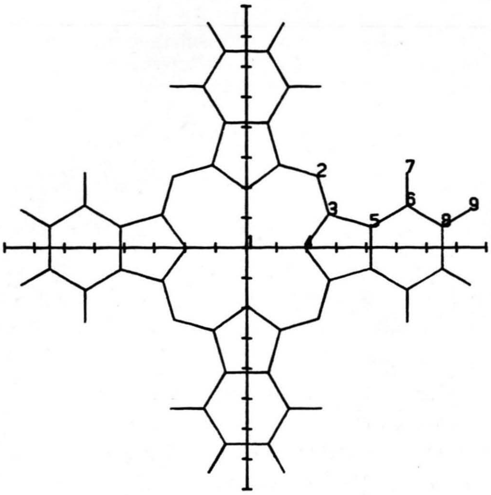

Fig. 1. Structure and designation of atoms of Co^{III}-Pc.

or for the case of real operators and wavefunctions

$$\mathbf{A} = \mathbf{C}' \mathbf{a} \mathbf{C} . \tag{34}$$

Then

$$\mathbf{A} = (\mathbf{C}' \mathbf{T}) (\mathbf{T}' \mathbf{a} \mathbf{T}) (\mathbf{T}' \mathbf{C}) = \mathbf{C}_B' \mathbf{a}_B \mathbf{C}_B \tag{35}$$

i.e. only $\mathbf{C}_B$ (blockwise) and not $\mathbf{C}$ itself is needed to compute $\mathbf{A}$. Another advantage of this formulation besides its compactness is that expection values and their matrices $\mathbf{A}$ are governed by selection rules expressed in terms of symmetry and that the eigenvectors of $\mathbf{C}_B$ are just ordered by symmetry.

3. Computations for Co^{III}-Pc-CN and Co^{III}-Pc-N

According to the results of the preceding section the purely real version (for $k_z = 0$ and π/c) of the IEH program was altered in such a way that instead of working with 3 big matrices of dimension 174 × 174 each, that were used for various purposes,

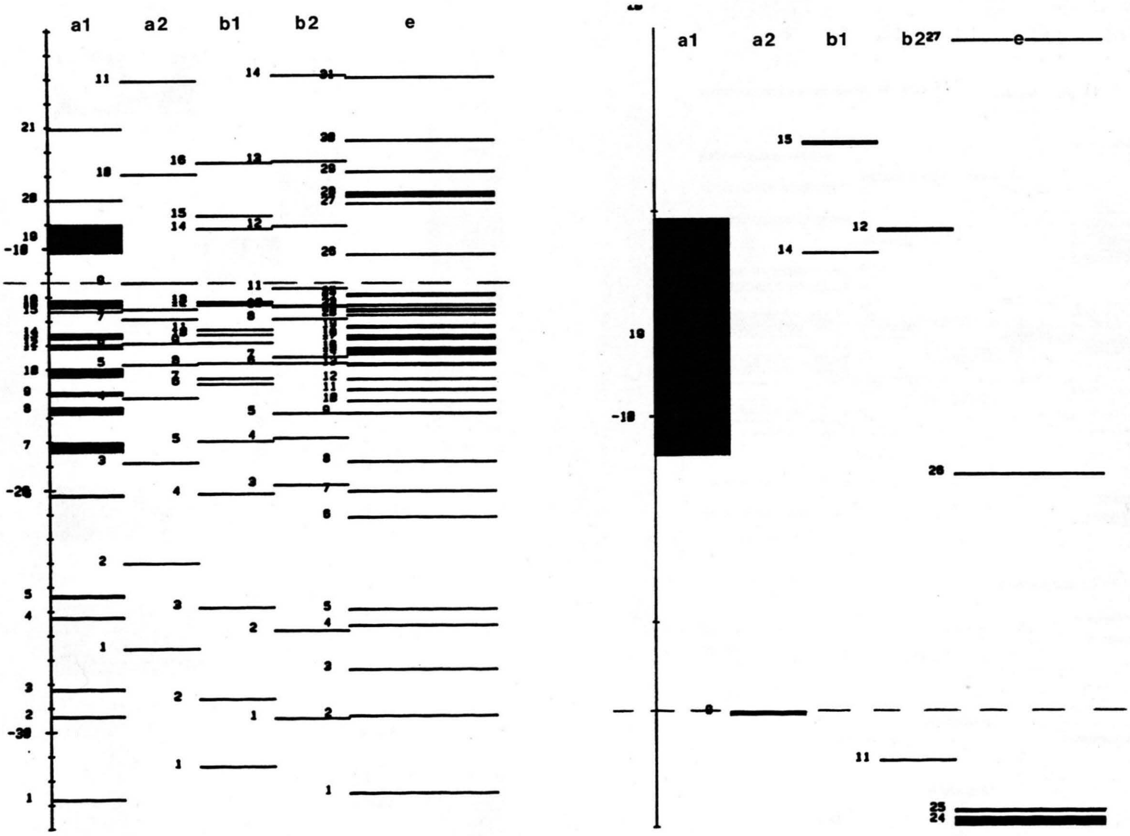

Fig. 2. a) complete, (between −30 and −1 eV), b) detailed (between −12 and −8 eV) energy band scheme of Co^{III}-Pc-CN; — — — = Fermi level.

Table I. x-y-coordinates of atoms in Co^{III}-Pc (in Å, for all atoms $z = 0$).

Position	Atom	x	y
1	Co	0	0
2	N	2.376	2.376
3	C	2.745	1.100
4	N	1.935	0
5	C	4.142	0.701
6	C	5.337	1.407
7	H	5.337	2.487
8	C	6.523	0.709
9	H	7.458	1.249

only one even bigger matrix of size 200 × 200 was established in which $\mathbf{S}(k_z)$ was generated. Since $\mathbf{S}$ has to be constructed by addition of several matrices of equal size for the overlap matrices of the considered elementary cell with neighbor cells which would have needed at least one more big matrix in storage, column vectors were computed and stored on disc and read later on.

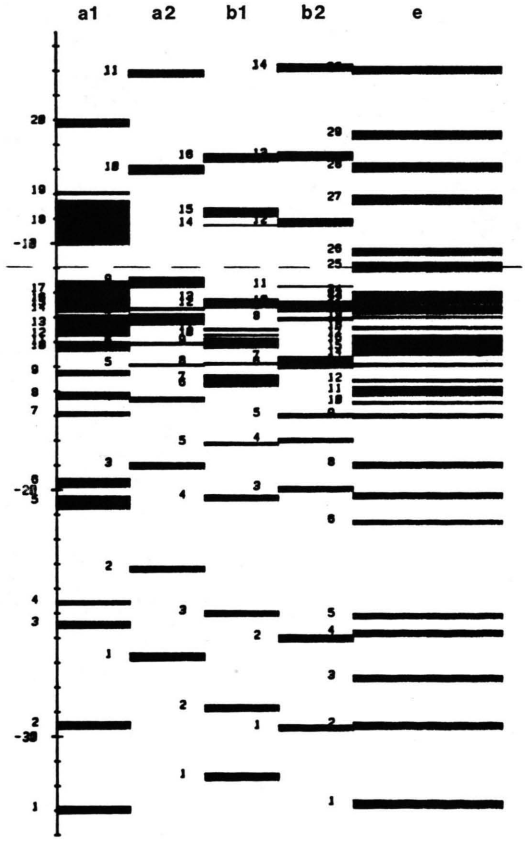

Fig. 3. Energy band scheme of Co^{III}-Pc-N, c = 3.8 Å.

Table II. z-coordinates of the axial ligands (in Å, for all atoms $x = y = 0$) and elementary cell constant (the second case of Co^{III}-Pc-N corresponds to the approximate van-der-Waals-distance of the planes of two Pc's).

Case	Co	C	N	c
Co^{III}-Pc-CN	0	1.950	3.110	5.300
Co^{III}-Pc-N	0	—	1.900	3.800
Co^{III}-Pc-N	0	—	1.700	3.400

This procedure is more complicated and time-consuming, but since it has to be performed only once, the advantage of being able to compute bigger samples overrides this small disadvantage. $\mathbf{S}$ was transformed to block form via (10) and these blocks were stored and treated further separately. From here on no reactivation of $\mathbf{S}(k_z)$ itself is necessary; only the eigenvalues (orbital energies) of the different blocks are combined in order to be able to construct the energy level scheme in an ordered way and to determine the occupation with electrons, the matrix $\mathbf{n}$.

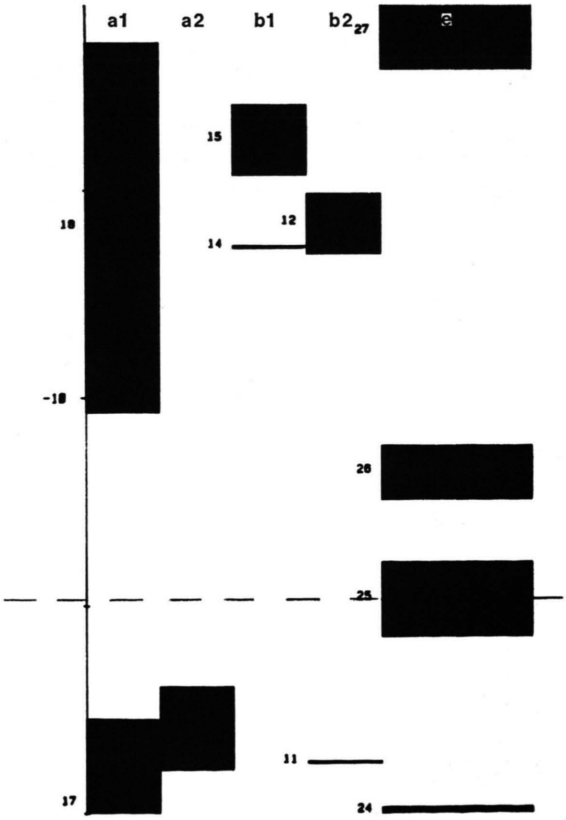

Table III. Parameters A, B, C (eV) and φ (atomic units) for s-, p- (and for Co) d-orbitals of the valence shell.

Atom	A_s	B_s	C_s	A_p	B_p	C_p	$\zeta_{s,p}$	A_d	B_d	C_d	ζ_d
Co	− 0.9113	− 9.057	− 8.468	− 0.9051	− 7.166	− 4.996	1.5	− 1.711	− 12.58	− 8.679	3.0
C	− 3.471	− 17.51	− 21.20	− 3.475	− 13.88	− 10.77	1.625	—	—	—	—
N	− 3.478	− 20.25	− 28.02	− 3.721	− 14.13	− 16.04	1.950	—	—	—	—
H	− 13.62	− 27.18	− 13.60	—	—	—	1.0	—	—	—	—

The used coordinates of phthalocyanine whose structure is depicted in Fig. 1, were the same as those of a single molecule IEH treatment by Schaffer, Gouterman and Davidson [6], because X-ray data are not yet available. The complete list of coordinates of Pc is given in Table I, the list of coordinates and unit cell constants for the different axial ligands CN^- and N^-, the latter in two different distances from Co, is given in Table II, and the list of parameters A, B, C of (6) and exponents ζ of the STO as basis functions is compiled in Table III. These were taken from [7] and [8]; the ζ_s were modified in some cases. The resulting schemes of energy bands for the 3 cases is given in Figs. 2, 3, and 4, each as a survey of all valence and the lowest conduction bands and as a detailed view of the bands near the Fermi level.

4. Discussion

In good agreement with the results of [3] for $Fe^{II}-TAP-C_2^{2\ominus}$ very narrow energy bands for the irreducible representations a_2, b_1, and b_2 are found in $Co^{III}-Pc-CN$, broader bands for e, even broader bands for a_1. Counting of bands yields $8a_2$ to be the highest valence band followed by 26e as

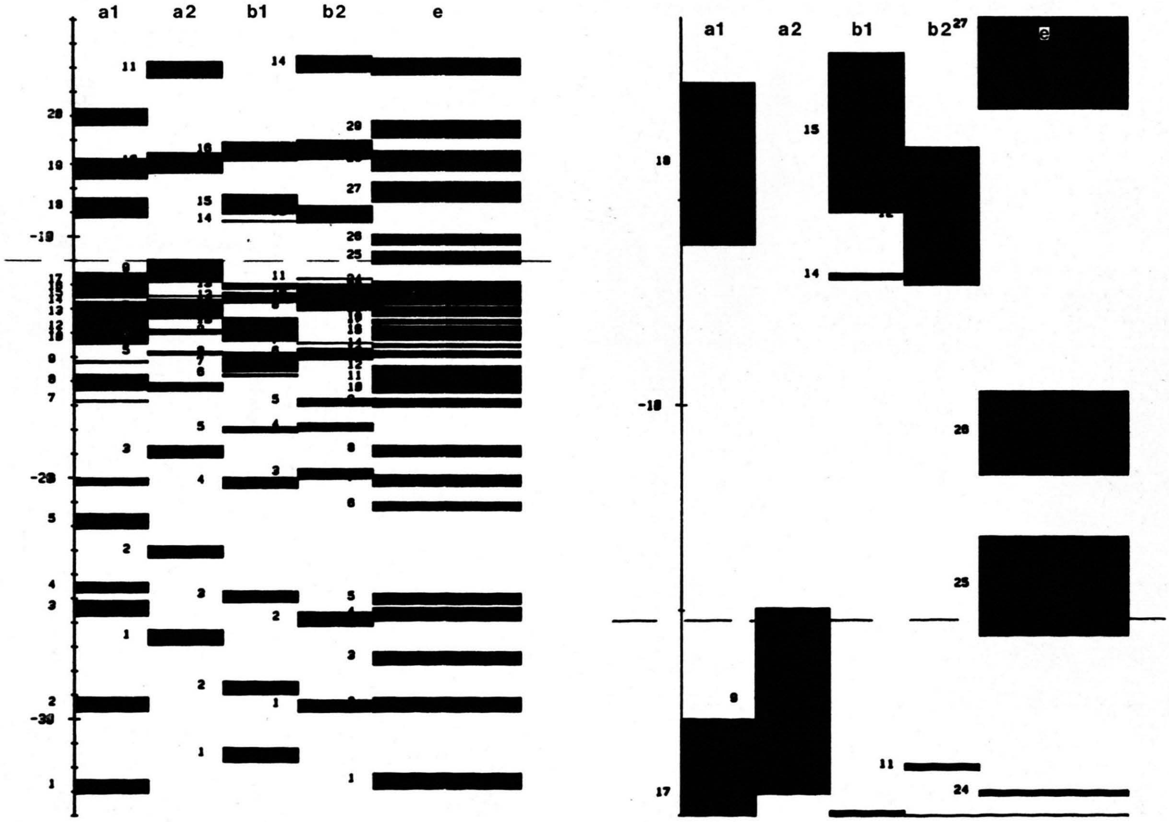

Fig. 4. Energy band scheme of Co^{III}-Pc-N, $c = 3.4$ Å.

the first conduction band with an energy gap of 1.15 eV. But very close up (1.25 eV above the Fermi level) follows another very broad conduction band, namely 19a_1, which has a width of 1.15 eV. Since for a good electrical conductivity partially filled bands are needed which should qualitatively be as broad as possible, good conductivity can be expected if the material is n-doped by reduction rather than p-doped by oxidation (usually by I_2 or SbF_5).

Whereas the calculations on $Co^{III}-Pc-CN$ referred to a synthesized material, $Co^{III}-Pc-N$ is a mere speculation up to now. Therefore two different Co-N-distances were assumed which represent the approximate van-der-Waals distance of two adjucent Pc's (3.4 Å) and in the other calculation a slightly greater value (3.8 Å). Again the results correspond to those of the appropriate TAP compound: for the small distances all CO's have a relatively strong interaction between neighboring Pc's and all bands are comparably broad. In the case of the longer distance a_2, b_1 and b_2 become narrower and now one particular a_1 band (18a_1) broadens considerably. For $c = 3.4$ Å a true overlap of different bands (8a_2 with 25e) occurs at the Fermi level so that a metallic conductivity can be expected even without doping. This property is lost for $c = 3.8$ Å.

Acknowledgements

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