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Theoretical Study of the Electrical Behavior of One-Dimensional Metallophthalocyanines and Related Metallomacrocyclic Compounds

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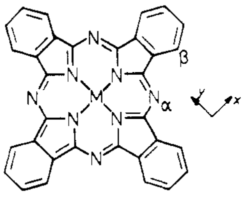
The electronic structures of one-dimensional metallophthalocyanines MPc and MPcL have been studied by means of the tight-binding (LCAO) method. Calculations for the linear (partially oxidized form) and slipped (nonoxidized form) structures of the nonbridged polymers MPc (M = Cr, Mn, Fe, Co, Ni, Cu, H_2) have been carried out. It is shown that the increase in conductivity for these systems upon oxidation is due not only to the existence of a partially filled band but also to the simultaneous increase in the inter-ring overlap associated with the decrease in M–M distance observed for the partially oxidized NiPcI. The differences in the band structures of the metallophthalocyanines produced by changing the central metal atom indicate that the electrical conduction varies from metal-centered to ligand-centered to the right of the first transition-metal series. The analogous behavior of phthalocyanines and porphyrins as well as differences in the experimental gaps between phthalocyanines and porphyrazines is rationalized. The role of mono-, di-, and polyatomic bridging ligands has been considered in the linear MPcL polymers (M = Fe, Co, Ni, L = O, F; M = Si, Fe, L = C_2^{2-}, CN^-; M = Fe, L = pyrazine). For diatomic and polyatomic bridging groups the band structure is determined by the overlap between the metal d_{xz} and d_{yz} orbitals and the π orbitals of the bridging group. When the bridging group is an atom and the central metal in the macrocycle is a non transition metal, the inter-ring spacing determines the band structure. Both overlap and inter-ring spacing are important for atom-bridged polymers with a transition-metal atom in the macrocycle.

Introduction

Phthalocyanine compounds, MPc (**1**), are known to present semiconducting properties.[1,2] Also linear polymer phthalocyanines, MPcL with bridging ligands (**2**) such as F, O, N, C_2^{2-}, CN^-, pyrazine, 4,4′-bipyridine, and 1,4-diisocyanobenzene have been synthesized and found to be semiconductors.[3,4] When metallophthalocyanines or metal-free phthalocyanine are partially oxidized with a halogen (typically I_2), they become conducting while simultaneously adopting a face-to-face stacking (**3**).[5] An increase in electrical conductivity is also observed for ligand-bridged phthalocyanines when they are partially oxidized.[3a,4,6] The closely related mononuclear porphyrins exhibit a similar behavior,[5f,7] although no polymer ligand-bridged porphyrin has been reported to date.



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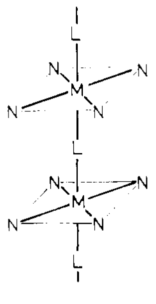

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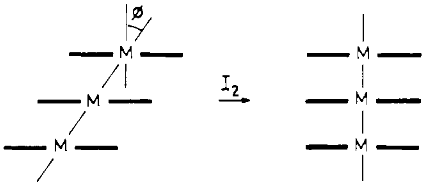

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A vast amount of data is therefore available concerning this family of compounds, and the study of their electronic band structure may help rationalize the experimental data and gain a better insight into the effects that several factors may have

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on their electrical properties: (a) the nature of the central metal atom and its role in the electrical conduction of the doped and undoped metallomacrocycle; (b) the rotation of neighboring rings, producing deviation from the ideal eclipsed stacking; (c) the deviation of the stacking direction away from the molecular symmetry axis; (d) isoelectronic changes in the macrocyclic frame such as the substitution of the four aza nitrogen atoms in phthalocyanines by methine carbon atoms in porphyrins; (e) the existence of a bridging ligand between neighboring rings and its role in the conducting properties of the resulting polymers.

Points a and b have been studied in a recent paper by Whangbo and Stewart,[8] but some comments on point a are still in order. Also, the effect of a monoatomic bridging ligand has been examined by these authors, so we shall restrict our discussion of point e to di- or polyatomic ligands.

Computational Details

The tight-binding method[9,10] of band structure calculation based upon the extended Hückel formalism[11] has been used. Given a set of atomic basis orbitals χ_μ for the atoms of a unit cell, the set of Bloch basis orbitals $\{b_\mu(\mathbf{k})\}$ is formed as

$$b_\mu(\mathbf{k}) = N^{-1/2}\sum_l e^{i\mathbf{k}R_l}\,\chi_\mu(r - \mathbf{R}_l) \qquad (1)$$

where $\mathbf{k}$ is the wave vector and $\mathbf{R}_l = l{\cdot}\mathbf{a}$, $\mathbf{a}$ being the primitive vector. The LCAO crystal orbitals $\psi_n(\mathbf{k})$ can be expressed as

$$\psi_n(\mathbf{k}) = \sum_\mu c_{n\mu}(\mathbf{k})\; b_\mu(\mathbf{k}) \qquad (2)$$

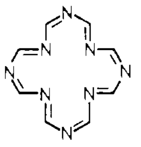
and the eigenvalues $\epsilon_n(\mathbf{k})$ and coefficients $c_{n\mu}(\mathbf{k})$ can be obtained from the secular equation

$$H(\mathbf{k})\;C(\mathbf{k}) = S(\mathbf{k})\;C(\mathbf{k})\;E(\mathbf{k}) \qquad (3)$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k})|H_{\text{eff}}|b_\nu(\mathbf{k})\rangle$ and $S_{\mu\nu} = \langle b_\mu(\mathbf{k})|b_\nu(\mathbf{k})\rangle$.

Band structures were obtained by performing the above calculation for different values of $\mathbf{k}$. Lattice sums were carried out to first nearest neighbors, and eq 3 was solved at $\mathbf{k} = 0\mathbf{K}, 0.1\mathbf{K}, 0.2\mathbf{K}, 0.3\mathbf{K}, 0.4\mathbf{K}$, and $0.5\mathbf{K}$ ($\mathbf{K} = 2\pi/\mathbf{a}$). The analysis of the band structures was greatly simplified by using the fragment formalism.[12]

In order to reduce the computational effort, several geometrical constraints were assumed. First, the Pc ring in **1** was replaced by the model ring **4**; this model will be referred as Pc′ from now on. In order to study the influence of the conjugation in the ring, some calculations were done with tetraazaporphyrin (tap) as a model for Pc. The changes in the computed band structures as one goes from Pc′ to tap could be easily understood by consideration of the interaction of selected π orbitals of Pc′ with the π and π^* orbitals of adjacent ethylenic groups. So, we did all the calculations with the simplest model Pc′ and assumed that the major differences with the band structure for the real system could be deduced from these calculations and consideration of the interaction of the π orbitals of adjacent benzenes as did Whangbo and Stewart.[8] As pointed out by these authors, it is possible to put this at a more quantitative level by calibrating the results for the MPc′ model (**4**) with the extended Hückel calculations of Schaffer et al.[13] for the complete system MPc (**1**).



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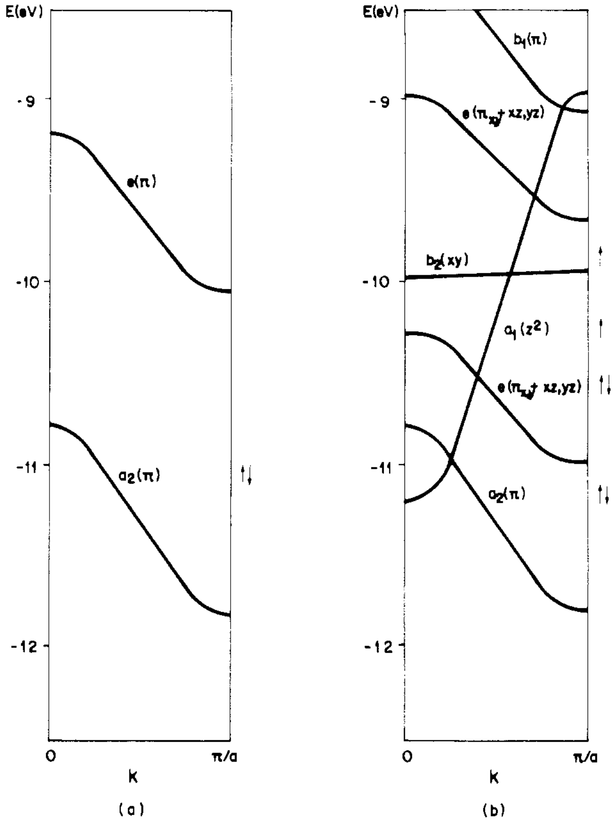

Figure 1. Band structure of the phthalocyaninato dianion (a) and manganese phthalocyanine (b) with an ideal face-to-face stacking. Band occupations shown correspond to the orbital configurations of the real phthalocyanines (β polymorph).

Secondly, although the face-to-face stacked metallomacrocycles do not present an eclipsed configuration, the inter-ring rotation angle is nearly 45°[15] and Whangbo and Stewart have shown that overall inter-ring overlap is not far from that of the eclipsed stacking, so the assumption of an ideal stacking is still valid, greatly reducing computational effort.

Nature of the Central Metal

The electronic bands of stacked phthalocyanines can be interpreted in terms of molecular orbitals of the isolated molecules. These MO's have been previously described by Schaffer et al.[13] and by Tatsumi and Hoffman.[14] The bands can be classified according to the D_{4h} point group at the center and edges of the Brillouin zone, but only according to C_{4v} at all other points in the $\mathbf{k}$ space.

Our calculations on the model metal-free phthalocyaninato dianion (Figure 1a) show that its valence (a_2) and conduction (e) bands are built up from the ring π orbitals a_{1u} (**5**) and the degenerate e_g pair (**6**), respectively, as in the case of MPcX described by Whangbo and Stewart.[8] This calculated band structure explains the metallic conductivity of doped metal-free

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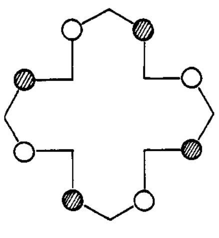

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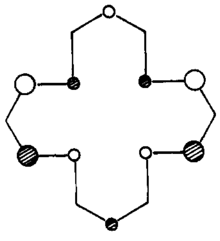

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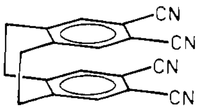
phthalocyanine found by Marks et al.[5a] since the symmetry lowering due to the presence of two hydrogen atoms bound to the pyrrolic nitrogens does not affect the nature of the valence and conduction bands.

When the inter-ring spacing is larger, the valence and conduction bands become narrower. They correspond to highly localized electrons (i.e., flat bands) for large inter-ring distances. Thus, it is clear that increased electrical conductivity in partially oxidized metallophthalocyanines is not merely due to the existence of a partially filled band but also to the short inter-ring spacing giving place to broad bands.

These results suggest that a tuning of the semiconducting properties of phthalocyanines, as well as an improvement in the electrical conductivity of their partially oxidized derivatives, is feasible if one could be able to fix by chemical means the inter-ring distance and force an ideal stacking. Thus, an interesting field of research would be the synthesis of phthalocyanine-like compounds by means of a template reaction in which a cyclophane derivative 7[16,17] is used instead



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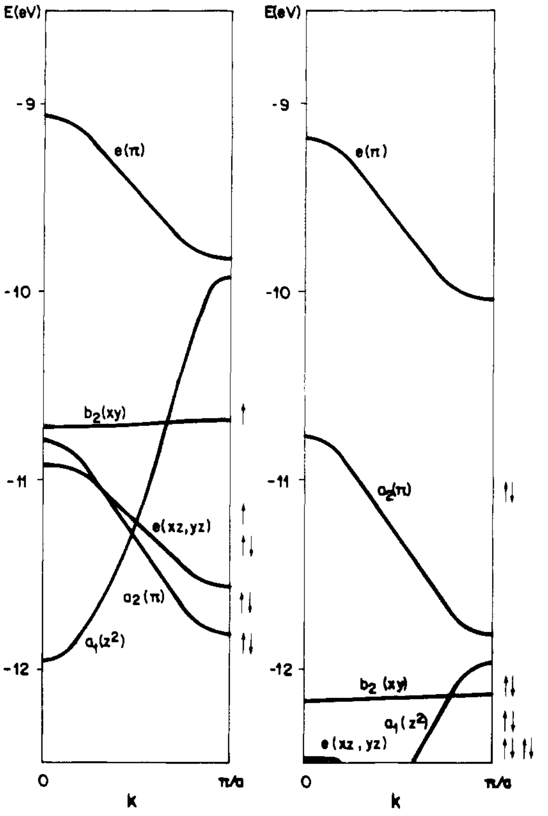
of the usual phthalonitrile or phthalic anhydride. In fact, transannular electron transfer in cyclophanes depends on the inter-ring separation, as evidenced by their basicity toward tetracyanoethylene.[18]

From this band structure, reduction of metal-free phthalocyanine is expected to yield a conducting material provided the inter-ring distance is short enough and a face-to-face stacking is adopted (see below), as happens to NiPc and presumably to other phthalocyanines when they are partially oxidized. This ideal stacking for a partially reduced phthalocyanine is likely because on reduction we are filling the conduction band at the edge ($\mathbf{k} = \pi/\mathbf{a}$) of the Brillouin zone where the band has bonding character between rings.

If the central position of the macrocycle is occupied by a metal ion, the band scheme can be substantially changed by the presence of the metal d orbitals. We have calculated the band structure for different metals using a M–M distance of 3.25 Å; the band schemes for M = Mn, Fe, Ni are shown in Figures 1 and 2. For M = Ni (Figure 2b), the valence and conduction bands are respectively the $a_2(\pi)$ and $e(\pi)$ bands previously discussed; the $b_2(d_{xy})$ band is very narrow and the $e(d_{xz},d_{yz})$ and $a_1(d_{z^2})$ bands are lower in energy. Therefore, the conduction in the doped nickel phthalocyanine must be ligand centered as experimentally found.[5b]

This picture is altered by changing the central metal ion: as we move to the left in the first transition period of the periodic table, raising the energy of the metal d orbitals, the broad a_1 band arising from the $d_{z^2}(A_{1g})$ orbital, which lies lower in energy than the valence band for CuPc and NiPc, may be



(a) (b)

Figure 2. Band structure of iron phthalocyanine (a) and nickel phthalocyanine (b) with an ideal face-to-face stacking. Band occupations shown correspond to the orbital configurations of the real β polymorphs of metallophthalocyanines (see text).

high enough to become the valence band for M = Mn and Fe (Figures 1 and 2). The width of this band decreases to the right of the periodic table due to the contraction of d orbitals. On the other hand, the narrow b_2 band arising from the d_{xy} orbital should also appear at higher energies to the left of the transition series. For M = Mn (Figure 1b), the d_{xz} and d_{yz} orbitals are high enough to mix in with the $e_g(\pi)$ LUMO of the macrocycle. These trends suggest that metal-centered electrical conduction is most probable for the doped phthalocyanines of the early transition elements. Electrochemical studies combined with ESR spectra[19] of MPc are indicative of metal-centered oxidation for M = Cr, Mn, Fe, and Co, ligand or metal oxidation for M = Ni, and ligand oxidation for M = Cu, Zn, H_2. Mössbauer experiments also suggest that for $FePcI_x$ the oxidation is metal centered.[5f,20]

Stacking Direction

The ideal stacking employed so far is a correct model for the partially oxidized phthalocyanines and porphyrins, but undoped compounds present a stacking pattern (**3a**) in which the angle formed between the molecular symmetry axis and the stacking direction, ϕ, is ~26° for the transition-metal phthalocyanines in their α polymorphic form[15] and ~45° for their β polymorphic form.[21] Slipping of neighboring rings

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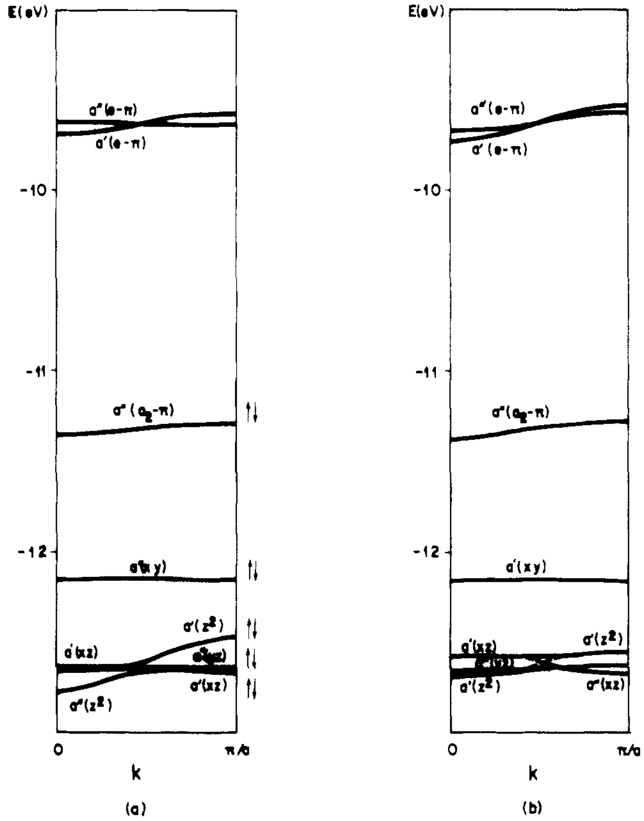
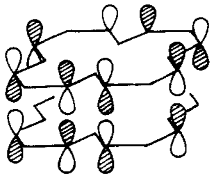


Figure 3. Band structure of (α-phthalocyaninato)– (a) and (β-phthalocyaninato)nickel (b). Bands are labeled according to the C_s point group while C_{4v} labels are shown in parentheses to facilitate comparison.

has the obvious effect of lengthening the M–M distance (3.8 and 4.8 Å for α- and β-CuPc) while maintaining the inter-ring distance nearly constant (3.4 Å for both α- and β-CuPc). The overlap between ring orbitals of neighboring macrocycles also varies on slipping.

The bands for the slipped stacking may be labeled according to the C_s point group for all points in the **k** space. The calculated band structures for α-NiPc ($\phi \cong 26°$) and β-NiPc ($\phi \cong 45°$) (Figure 3) are markedly different from that of the ideally stacked compound discussed above. Besides the expected narrowing of the bands due to the overall decrease of inter-ring overlaps, there is a change in the sign of the slope of both a_2 and e ring-centered bands. A look at **8** and **9**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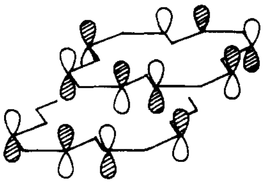
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provides an explanation for this fact: In the case of ideal stacking ($\phi \cong 0°$), the interaction between neighboring $a_{1u}(\pi)$ orbitals is antibonding at the center of the Brillouin zone (**k** = 0) (**8**) and bonding at the edges (**k** = π/**a**) and the resulting band has then a positive slope, while for β-MPc ($\phi \cong 45°$) the interaction is only slightly bonding at **k** = 0 (**9**) and slightly antibonding at **k** = π/**a**, thus producing a band with a small negative slope. Another significative difference is that the symmetry decrease produced by slipping gives place to a mixing (avoided crossing) of the d_{z^2} and d_{xz} band belonging in this case to the same symmetry species (Figure 3).

Table I. Experimental Energy Gaps for Some Metal Phthalocyanines

compd	E_g, eV	ref	compd	E_g, eV	ref
β-MnPc	0.77	21	β-ZnPc	1.70	2a
β-FePc	1.27	4		1.38	21
β-CoPc	1.6	2f		1.44	*a*
	1.66	4	α-H_2Pc	1.42	*a*
α-NiPc	1.20	*a*		0.50	*d*
β-NiPc	1.48	21	β-H_2Pc	1.74	*a*
	1.44	4		1.8	*d*
	1.6	2f		1.4–2.0	2h
	1.90	2a	$FePcI_x$	0.14–0.51	5a
	2.28	*a*	$CoPcI_x$	0.13–0.16	5a
α-CuPc	1.28	4	$NiPcI_x$	0.04–0.07	5a
β-CuPc	1.58	21	$CuPcI_x$	0.04	5a
	1.76	4	H_2PcI_x	0.04	5a
	1.98	2a	Cu(pyPc)[e]	1.17	2m
	1.79	2b	Cu(pzPc)[e]	0.81	2m
	1.8	2g	poly-CuPc	0.95 (0.81)[f]	2b
	1.62 (2.06)[c]	*b*	FePc(pz)	0.80	4
	1.85	2h	FePc(bpy)	1.44	4
α-ZnPc	0.86	*a*	FePc(bpy)I_x	0.72	4

[a] Hamann, C.; Storbeck, I. *Naturwissenschaften* **1963**, *50*, 327. [b] Heilemier, G. H.; Harrison, S. E. *Phys. Rev.* **1963**, *132*, 2010. [c] The two values are for temperatures below and above 373 K, respectively. [d] Wihksne, K.; Newkirk, A. E. *J. Chem. Phys.* **1961**, *34*, 2184. [e] pyPc = tetra-2,3-pyridinoporphyrazine; pzPc = tetra-2,3-pyrazinoporphyrazine. [f] The value in parentheses corresponds to a polymer with a higher degree of polymerization.

A sizable energy gap appears between the valence and conduction bands. This calculated gap is not significantly different for both polymorphic forms of NiPc, as a result of the severe decrease in the inter-ring overlap. Similar trends are found for other transition metals. Comparison with experimental results is difficult due to the great dispersion of reported gaps (Table I).

Emptying the very narrow valence band by means of partial oxidation would not now produce an improvement of the electrical conductivity if simultaneous change of the stacking pattern toward the ideal face-to-face assembly were not produced. For NiPcI, the change toward the face-to-face stacking pattern upon partial oxidation can be easily explained from the calculated band structures shown in Figures 2b and 3. The only change in the band structure produced by this geometrical change is the broadening of some bands. As all the bands up to $a_2(\pi)$ are completely filled, this geometrical change will not be stabilizing unless the upper (antibonding) part of the valence band is emptied by means of partial oxidation.

Isoelectronic Changes in the Macrocyclic Frame

The relevant bands discussed so far are almost insensitive to the change of the four α-nitrogen atoms in MPc for C–H groups in metal porphyrins as calculated for the model MPor′ analogous to MPc′ (**4**). This result can be explained by considering that the important bands are either metal-centered or ligand-centered bands built from orbitals **5** and **6**, which have no contribution (**5**) or little contribution (**6**) from the substituted atoms. Only slight differences in the band gap are therefore expected between a metal phthalocyanine and the corresponding porphyrin as a consequence of a small variation in the energy of the conduction e band.

Furthermore, ligand-centered oxidation is to be expected for nickel porphyrins, as is found for octaethylporphyrin and octamethyltetrabenzoporphyrin.[7b,c] In our calculations there is apparently no reason for the different behavior reported for a tetrabenzoporphyrin.[7a]

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(21) (a) Brown, C. J. *J. Chem. Soc. A* **1968**, 2488. (b) Barrett, P. A.; Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1936**, 219. (c) Robertson, J. M.; Woodward, I. *Ibid.* **1937**, 219. (d) Kirner, J. F.; Dow, W.; Scheidt, W. R. *Inorg. Chem.* **1976**, *15*, 1685. (e) Scheidt, W. R.; Dow, W. *J. Am. Chem. Soc.* **1977**, *99*, 1101. (f) Mason, R.; Williams, G. A.; Fielding, P. E. *J. Chem. Soc., Dalton Trans.* **1979**, 676.

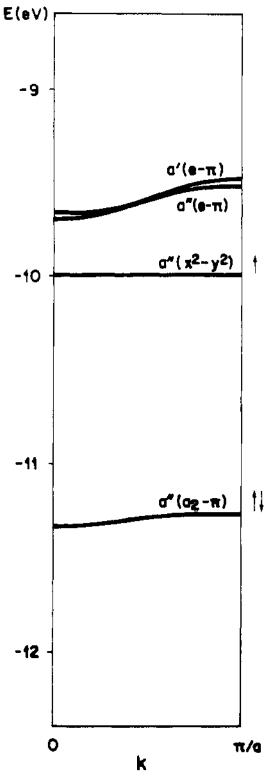

Figure 4. Band structure of (β-phthalocyaninato)copper. Bands are labeled according to the C_s point group while C_{4v} labels are shown in parentheses to facilitate comparison.

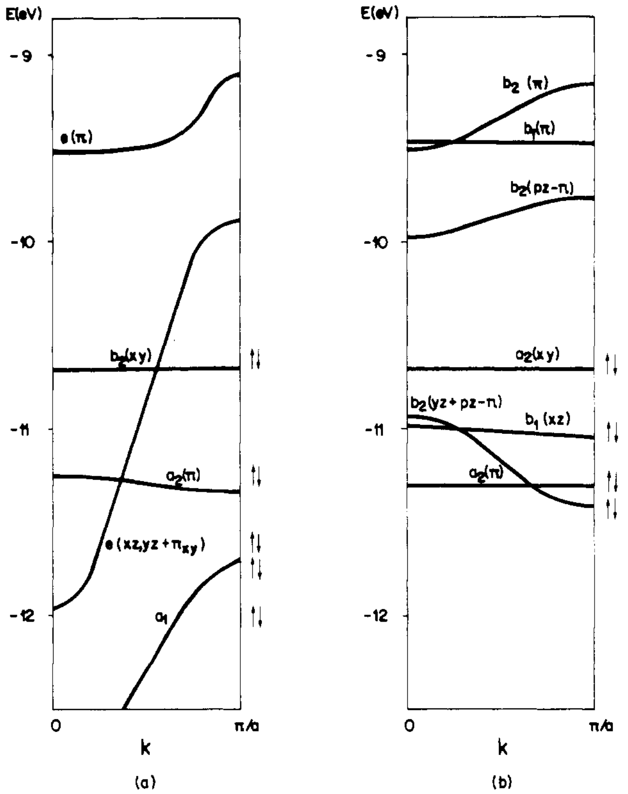

Figure 5. Band structures of FePcC$_2^{2-}$ (a) and FePc(pz) (b). Symmetry labels in the second case are for the C_{2v} point group.

The substitution of one or two nitrogen atoms for carbon atoms in β positions (1) in the phenyl rings, as in copper tetra-2,3-pyridinoporphyrazine, Cu(pyPc), and copper tetra-2,3-pyrazinoporphyrazine, Cu(pzPc), should not affect the position of the metal-centered valence band a″(d$_{x^2-y^2}$) (Figure 4) but must produce a lowering of the conduction band a″(ligand-centered) due to the contribution of those atoms to the e(π) ring orbital that gives place to this band. This prediction is in excellent agreement with the experimental results[2m] (Table I).

Role of the Bridging Ligand

The band structure of stacked metallophthalocyanines can be deeply altered by the presence of bridging groups between the macrocyclic rings 2. In principle, atoms, diatomic ligands like N_2 or CN^- or molecules as big as 4,4′-bipyridine can be used as bridging groups. The single-atom-bridged metal phthalocyanine polymers, MPcX, have been studied by Whangbo and Stewart[8] and will not be discussed here. Hanack, Seelig, and Strähle[22] have recently proposed that metal phthalocyanine polymers with diatomic and polyatomic bridging groups have a π system positioned in such a way as to permit the formation of a linear chain perpendicular to the plane of the macrocycle are potential conductors. Some of these polymers have been obtained by these workers.[3a,c]

With acetylide as the bridging group (L = C_2^{2-}) and Fe(II) as the metal ion, Seelig[22b] proposed, on the basis of extended Hückel band structure calculations, a metallic behavior. To date, the only reported polymeric material with such a bridging group is SiPcC$_2$.[3c] This polymer shows a very low conductivity ($\sim 10^{-12}$ Ω^{-1} cm^{-1}). The bands for these systems can be classified according to the D_{4h} group at the edges and center of the Brillouin zone but only according to the C_{4v} group at all other points in the **k** space. The band structure for SiPcC$_2$ is very similar to that of SiPcO reported by Whangbo and Stewart[8] and to that previously found for metal-free phthalocyanine (Figure 1a): The valence (a_2) band is composed only of the a_{1u} π orbitals (5) of the Pc ring, and the conduction band (e) is built up from the LUMO's e_g π orbitals of the Pc ring. The mean values of these bands must be separated by 1.6 eV after calibration with the results of Schaffer et al.[13] and the widths are determined by the inter-ring separation. By symmetry, no orbital of the bridging group can mix into the a_2 band. Due to the lack of e orbitals in Si and the poor direct overlap with the macrocycle e orbitals, no orbital of the bridging group can mix into the e band. The σ band lies lower in energy. As the inter-ring distance is now relatively great, the a_2 and e bands are very narrow. So, at variance with the case of SiPcO we do not expect an increase in conductivity on doping. The same considerations apply to the other polymers reported by Mitulla and Hanack.[3c]

With d orbitals on M this picture presents an important change. The two π systems of acetylide strongly interact with the ideally oriented d_{xz} and d_{yz} orbitals of M, and the associated bands should have a strong structure. This expected trend was not apparent from the band structure reported by Seelig[22] for Fe(tap)C$_2^{2-}$. The predicted metallic behavior of this material was attributed to a very broad and partially filled band built up from the Fe d_{z^2} orbital and the σ orbitals of the bridging group. This seems unlikely in view of the octahedral local field at Fe,[23,24] which highly destabilizes the $d_z{}^2$ orbital, the corresponding band being therefore an empty one. Our calculated band structure for FePcC$_2^{2-}$ is very different (Figure 5a). The a_2 and b_2 narrow bands are composed of the a_{1u} Pc ring orbitals and the Fe d_{xy} orbitals, respectively. The form of the e bands is the result of a strong mixing between the Pc, acetylide, and Fe orbitals. The lowest pair of e bands are mainly ($d_{xz} + \pi^*_L$) and ($d_{yz} + \pi^*_L$) at **k** = 0 as schematically shown in **10**. There is also a sizable contribution of a pair of e_g Pc orbitals not

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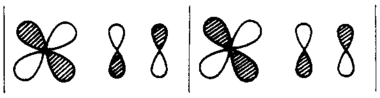
(22) (a) Hanack, M.; Seelig, F. F.; Strähle, J. *Z. Naturforsch., A* **1979**, *34A*, 983. (b) Seelig, F. F. *Ibid.* **1979**, *34A*, 986.

(23) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(24) Albright, T. *Tetrahedron* **1982**, *38*, 1339.



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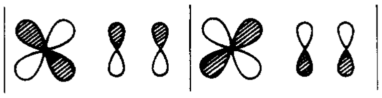

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shown for simplicity. By symmetry, the d_{xz} orbital can only mix with the π^* orbital of the bridging ligand at $\mathbf{k} = 0$ (**10**) but only with the π orbital at $\mathbf{k} = \pi/\mathbf{a}$ (**11**). Consequently, the energy raises strongly from the center to the edges of the Brillouin zone. At higher energy appears a pair of very flat e bands composed of the e_g LUMO's of the Pc ring. As both pairs of bands are of the same symmetry, they repel each other, an avoided crossing appears, and as a result the top of the valence band is strongly ligand centered while the metal and bridging-group orbitals appear in the conduction band at the edges. As the a_2, b_2, and lowest e bands are fully occupied, this polymer will be a semiconductor with a small gap.

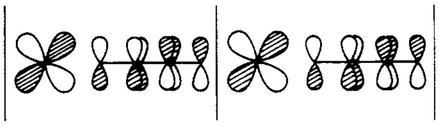
Let us recall that the calculations have been done with the Pc′ model for the macrocyclic ring. An extension of the conjugation would only change the position of the a_2 band and the highest e band near $\mathbf{k} = 0$ but would leave the b_2 band, the highest e pair of bands at the edges, and the lowest e pair of bands at the center unaltered. We have verified these qualitative changes by doing a calculation for Fe(tap)C_2^{2-}. The band structure for the real polymer FePcC_2^{2-} has therefore been obtained by the calibration mentioned (Figure 5a).

The band gap could be tuned with other diatomic ligands (e.g., CN^-, N_2), but the essential trends of the band structure would remain, as has been verified in a calculation for FePc′CN^-. Moving to the left/right of the first transition series would raise/lower the narrow $b_2(d_{xy})$ band and the broad e band near the zone center. The avoided crossing between the e bands would be sooner/later (or eventually disappear), but the global topology of the band structure diagram would not be changed. So, conducting polymers with and without doping could probably be obtained by appropriately changing the electron count. Recently, Metz and Hanack have reported the synthesis and conductivity measurements of CoPc(CN);[3g] this polymer has a room-temperature powder conductivity of $\sim 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which could correspond to a semiconductor with a small band gap as is predicted for FePcC_2^{2-} with the same electron count (Figure 5a).

The difference with the single-atom-bridged polymers is clear: the bridging atom has no orbitals of the appropriate symmetry to be mixed with the d_{xz} and d_{yz} bands at $\mathbf{k} = 0$. At the same time, the difference in electronegativity between the bridging atom and the metal will strongly reduce the mixing of the p_x and p_y orbitals of the bridging atom into the lower e bands at $\mathbf{k}$ near $\pi/\mathbf{a}$, relieving the antibonding metal–bridging-atom interaction. Both effects contribute toward a severe narrowing of the lower e band, which will not be far from the a_2 band, now substantially broadened as are the higher pair of e bands due to the smaller inter-ring separation. Assuming electron localization for the b_2 and e bands,[8] the b_2 narrow band will be the highest occupied one for CrPcF, but the b_2, a_2, and e bands will overlap for more electronegative metals like Fe. With this band structure, the electrical and magnetic behaviors for different electron counts are not easy to predict.

It is interesting to see how the band structure of Figure 5a is changed by substitution of the bridging ligand for other molecules with a π system like pyrazine or bipyridine. The calculated band structure for FePcpz (pz = pyrazine) is shown in Figure 5b. The appropriate symmetry to classify the bands is now D_{2h} at the center and edges but only C_{2v} at all other points in the $\mathbf{k}$ space. The e bands become $b_1 + b_2$, and the b_2 bands become a_2.

As can be seen in Figure 5b, the formerly b_2 and a_2 bands previously found in Figure 5a remain unaltered. A new band (b_2) appears at −10.0 eV, which at $\mathbf{k} = 0$ is composed exclusively of the pyrazine LUMO. The b_1 bands coming from the e bands of Figure 5a are narrow because there are no appropriate orbitals of the pyrazine to interact with. The b_2 band originated from the lowest pair of e bands has completely changed its slope. The reason is that the bridging ligand orbital that is allowed by symmetry to mix into the $b_2(d_{yz})$ band is not a high-energy empty orbital but an occupied π orbital of pyrazine that destabilizes the metal orbitals (**12**). At the same time, the orbital d_{yz} mixes at $\mathbf{k} = \pi/\mathbf{a}$ with the LUMO of pyrazine and is therefore stabilized (**13**), resulting in a positive slope of the band. The other b_2 bands can be analyzed in a similar way. A band gap of ~0.7 eV results, and semiconductor behavior is expected. This gap is largely determined by the difference in energies between the bridging ligand LUMO and the metal d_{xy} orbital.[28] As the highest occupied band for FePc(pz) is the very narrow $a_2(d_{xy})$ band, it is not expected that an increase in the conductivity will be found on doping. Schneider and Hanack[3a] have reported an increase of $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ on doping with iodine, but recent results[4] for the same polymer show only a slight increase. Other bridging ligands such as bipyridine or *p*-diisocyanobenzene have LUMO's and occupied π orbitals with the appropriate symmetry to interact with the metal d_{yz} orbital in the same way described for pyrazine, and the conductivity of these polymers will depend only slightly on the length of the bridging ligand as found by Schneider and Hanack.[3a]



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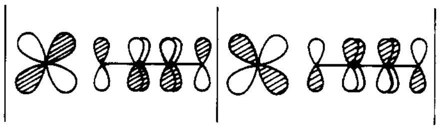

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While the a_2 and b_1 bands will always be very narrow, the width of the b_2 bands could be changed by systematic replacement of the bridging ligand and the metal. With an appropriate electron count good conductors could be obtained. Further work in this field would be worthwhile to pursue.

Concluding Remarks

The qualitative trends of the electrical conductivity of metallomacrocyclic compounds are well described by tight-binding extended Hückel band calculations. These calculations for the cases of metallophthalocyanines and metalloporphyrins are in good accordance with the rules developed by Brown et al.[25] for the design of a molecular metal.

According to the present study, the increase in electrical conductivity of doped polymer phthalocyanines is the result of both the existence of partially filled bands and the decrease

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(25) Brown, D. B.; Carneiro, K.; Day, P.; Hoffman, B.; Keller, H. J.; Little, W. A.; Underhill, A. E. In "Molecular Metals"; Hatfield, W. E., Ed.; Plenum Press: New York, 1979; p 527.

Table II. Atomic Parameters[a, b]

	χ_μ	ζ_μ	ζ_μ'	$H_{\mu\mu}$, eV
Cr	4s	1.70		−7.76
	4p	1.70		−4.49
	3d	4.95 (0.4968)	1.70 (0.6689)	−9.72
Mn	4s	1.80		−8.06
	4p	1.80		−4.62
	3d	5.15 (0.5241)	1.80 (0.6689)	−10.60
Fe[c]	4s	1.90		−8.39
	4p	1.90		−4.74
	3d	5.35 (0.5366)	1.80 (0.6678)	−11.46
Co	4s	2.00		−8.68
	4p	2.00		−4.74
	3d	5.55 (0.5606)	2.00 (0.6267)	−12.32
Ni	4s	2.10		−8.93
	4p	2.10		−4.96
	3d	5.75 (0.5683)	2.00 (0.6292)	−13.11
Cu	4s	2.20		−9.30
	4p	2.20		−5.00
	3d	5.95 (0.5878)	2.20 (0.5928)	−14.10

[a] The metal d functions are of a double-ζ type. The numbers in parentheses are the coefficients of the corresponding Slater orbitals. [b] The atomic parameters of H, C, N, O, and F are the standard values. [c] Reference 14.

of the M–M distance afforded by the change in the stacking pattern. The electrical conduction for the doped polymers changes from metal centered to ligand centered by increasing the electronegativity of the metal atom along the first transition series.

No major differences are expected by changing the phthalocyanine ring for porphyrin ring. On the other hand, observed differences between phthalocyanines and porphyrazines can be easily explained.

The band structures for the bridged polymers are determined by the overlap between the metal d_{xz} and d_{yz} orbitals with the π orbitals of the bridging diatomic or polyatomic ligand. For atom-bridged polymers both the inter-ring spacing and overlap determine the band structure if the central atom in the macrocyclic ring has d orbitals but only the inter-ring spacing determines the structure for atom-bridged polymers with non-transition-metal atoms.

Acknowledgment. We thank Professor R. Hoffmann for permission to use the extended Hückel band structure programs, Professor M.-H. Whangbo for preprints and for his comments on the manuscript, and Professors M. Hanack, J. Strähle, and F. F. Seelig for reprints and preprints of their work. We are also grateful to Professors M. Kertész and O. Eisenstein for clarifying suggestions. E.C. thanks the University of Michigan for hospitality during the summer of 1982 and for allocation of computer time. S.A. is indebted to the Comissió Interdepartamental per a la Recerca i la Innovació Tecnològica for a grant.

Appendix

Calculations were done for Pc'^{2-}, MPc′ (M = Cr, Mn, Fe, Co, Ni, Cu), FePor′, α-MPc′, and β-MPc′ (M = Mn, Fe, Co, Ni, Cu), Fe(tap), MPc′X (M = Fe, Co, Ni; X = N, O, F), MPc′L (M = Fe, Co, Ni; L = C_2^{2-}, CN^-, pz), and $Fe(tap)C_2^{2-}$. The exponents and parameters used in these calculations were those of Table II. A modified Wolfsberg–Helmholtz formula was used.[26] The geometry of the model rings Pc′ and tap was based on the experimental data for NiPcI.[5b] The inter-ring separation was 3.25 Å for MPc′ systems (this distance was varied between 3.20 and 4.4 Å for FePc′), 3.4 Å for α-MPc′ and β-MPc′, 4.46 Å for the polymers with C_2^{2-} and CN^- bridging groups, and 6.81 Å when the bridging group was pyrazine. In the last case, the metal–pyrazine distance was 2.00 Å, according to experimental data for similar systems.[27]

Registry No. 1 (M = Mn), 14325-24-7; 1 (M = Fe), 132-16-1; 1 (M = Ni), 14055-02-8; Cu(pyPc), 16049-07-3; Cu(pzPc), 26603-03-2; $FePcC_2^{2-}$, 88412-34-4.

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(26) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(27) Kubel, F.; Strähle, J., submitted for publication. Kobayashi, T.; Kurokawa, F.; Ushida, T.; Yeda, W. A. U.; Suito, E. *J. Chem. Soc. D* **1971**, 1631.

(28) A report (Schneider, O.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 784) of the tetrazine-bridged polymer of FePc with a higher conductivity (0.1 Ω^{-1} cm^{-1} for pressed powder at room temperature) than that of the analogue pyrazine-bridged polymer provides interesting proof of the predictions exposed here: by substituting two nitrogen atoms for two carbon atoms in the bridging ligand, the energy of the LUMO is lowered and the energy gap consequently decreased.