Inorg. Chem. **1993**, *32*, 5637–5639

Porphyrin vs Phthalocyanine Metallomacrocycles Based One-Dimensional "Molecular Metals". Insights from Density Functional Calculations

Angela Rosa

Dipartimento di Chimica, Universitá della Basilicata, Via N.
Sauro, 85, 85100 Potenza, Italy

Evert Jan Baerends*

Scheikunding Laboratorium, Vrije Universiteit, De Boelelaan
1083, 1081 HV Amsterdam, The Netherlands

Received April 15, 1993

Porphyrinic metallomacrocycles are well-known as molecular building blocks of one-dimensional "molecular metals".[1–4] The chemical flexibility inherent in the porphyrin-like metallomacrocycle offers a unique opportunity to elucidate the effects that electronic structure modifications of the metallomacrocycle (metal center or ligand framework) induce in several crucial attributes of the conductive molecular assemblies.

An interesting example of correlation between molecular and solid-state properties is provided in the comparison of systems based on metallomacrocycles having conjugated frameworks of different size. As a matter of fact, the series of large-ring benzoporphyrin based conductors M(Pc)X,[2b,5,6] M(tatbp)X,[3b,4b] M(tbp)X[1e] (M = Ni, X = I_3^-, Br_3^-, PF_6^-, BF_4^-, TCNQ, DDQ) show important behavioral differences when compared to the small-ring porphyrin based series Ni(tmp)X (X = I_3^-,[3b] PF_6^-,[4c] ReO_4^- [4e]). The large-ring metallomacrocycle compounds have remarkably similar properties. They exhibit comparably high electrical conductivities at room temperature, although the details of the temperature dependence of the conductivity and the nature of the charge carriers differ from compound to compound. A single structural motif is retained throughout the series, with metal-over-metal columnar stacks of partially oxidized units surrounded by chains of anions. Successive rings in the stacks assume a staggered conformation with a rotation angle ϕ that is invariably close to 40°. The size and structure of the counterion X have very little effect on the staggering angle of the donor units.

Table I. Energy Terms (eV) for the Formation of $(NiPc)_2$ and $(NiP)_2$ Dimers from Two Superimposed NiPc and NiP Fragments, Respectively, at Different Staggering Angles

		ϕ					
		0°	10°	20°	30°	40°	45°
$\Delta E°$	$(NiPc)_2$	+3.720	+3.249	+2.758	+2.670	+2.283	+2.232
	$(NiP)_2$	+1.590	+1.526	+1.408	+1.316	+1.266	+1.260
ΔE_{oi}	$(NiPc)_2$	−1.550	−1.517	−1.495	−1.418	−1.348	−1.356
	$(NiP)_2$	−0.488	−0.508	−0.520	−0.519	−0.528	−0.530
ΔE_{bond}	$(NiPc)_2$	+2.17	+1.732	+1.263	+1.252	+0.935	+0.876
	$(NiP)_2$	+1.102	+1.018	+0.888	+0.797	+0.738	+0.730

On the contrary, in the series of small-ring based conductors Ni(tmp)I,[3b] $[Ni(tmp)]_2[PF_6]$,[4c] $[Ni(tmp)]_2[ReO_4]$,[4e] there are considerable differences in the structure and stoichiometry of the conductors. The staggering angle is strongly dependent on the size of the counterion, ranging from 37 to 34.7 to 27.5°, respectively. The degree of oxidation, which is $^1/_3$ in Ni(tmp)I, becomes $^1/_2$ in $[Ni(tmp)]_2[PF_6]$ and $[Ni(tmp)]_2[ReO_4]$. The room-temperature conductivities of Ni(tmp) based conductors vary directly with ϕ, changing from metallic to thermally activated types on going from 37 to 27.5°.

What is the origin of this different behavior of large-ring (benzoporphyrin) compared to small-ring (porphyrin) based conductors? First, the steric effect of the benzo rings in the benzoporphyrinic systems is an important discriminating factor. We have demonstrated before,[7d] in a density functional investigation of "molecular metals" having metallophthalocyanines as molecular building blocks, that steric hindrance effects drive the staggering angle in those systems to ~40°, where the dispersion of the a_{1u} band and therefore the conductivity is considerable. The steric hindrance can be traced to Pauli repulsion between occupied orbitals mainly located on the benzo rings. The effect of removing the benzo rings can be seen in Table I, where the interaction energy between two NiP monomers as a function of staggering angle ϕ is compared to that of NiPc. The energy decomposition (see refs 7 and 8 for details) shows that the energy

---

(1) (a) Ibers, J. A.; Pace, L. J.; Martinsen, J.; Hoffman, B. M. *Struct. Bonding (Berlin)* **1982**, *50*, 1–55. (b) Ferraro, J. R. *Coord. Chem. Rev.* **1982**, *43*, 205–232. (c) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, *16*, 15–21. (d) Proceedings of the International Conference on the Physics and Chemistry of Low Dimensional Synthetic Metals (ICSM 84). *Mol. Cryst. Liq. Cryst.* **1985**, *120*. (e) Martinsen, J.; Pace, L. J.; Phillips, T. E.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 83–91. (f) Hoffman, B. M.; Martinsen, J.; Pace, L. J.; Ibers, J. A. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, pp 459–549. (g) Palmer, S. M.; Stanton, J. L.; Martinsen, J.; Ogawa, M. Y.; Heuer, W. B.; Van Wallendael, S. E.; Hoffman, B. M.; Ibers, J. A. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 1–11.

(2) (a) Schramm, C. J.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science (Washington, D.C.)* **1978**, *200*, 47–48. (b) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6713. (c) Martinsen, J.; Green, R. L.; Palmer, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 677–678. (d) Martinsen, J.; Palmer, S. M.; Tanaka, J.; Green, R. L.; Hoffman, B. M. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 6269–6276. (e) Palmer, S. M.; Stanton, J. L.; Jaggi, N. K.; Hoffman, B. M.; Ibers, J. A.; Schwartz, L. H. *Inorg. Chem.* **1985**, *24*, 2040–2046. (f) Martinsen, J.; Stanton, J. L.; Green, R. L.; Tanaka, J.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 6915–6920. (g) Ogawa, M. Y.; Martinsen, J.; Palmer, S. M.; Stanton, J. L.; Tanaka, J.; Green, R. L.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1115.

(3) (a) Phillips, T. E.; Scaringe, R. P.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3435–3444. (b) Pace, L. J.; Martinsen, J.; Ulman, A.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2612–2620. (c) Ogawa, M. Y.; Hoffman, B. M.; Lee, S.; Yadkowsky, M.; Halperin, W. P. *Phys. Rev. Lett.* **1986**, *57*, 1177–1180. (d) Liou, O.; Ogawa, M. Y.; Newcomb, T. P.; Quirion, J.; Lee, M.; Poirier, M.; Halperin, W. P.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 3889.

(4) (a) Yakushi, K.; Sakuda, M.; Hamada, I.; Kuroda, H.; Kawamoto, A.; Tanaka, J.; Sugano, T.; Kinoshita, M. *Synth. Met.* **1987**, *19*, 769–774. (b) Almeida, M.; Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J.; Marcy, H. O.; McCarthy, W. J.; Kannewurf, C. R. *Solid State Commun.* **1987**, *63*, 457–461. (c) Newcomb, T. P.; Godfrey, M. R.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 7078–7084. (d) Godfrey, M. R.; Newcomb, T. P.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 7260–7269. (e) Newcomb, T. P.; Godfrey, M. R.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1990**, *29*, 223–228. (f) McGhee, E. M.; Godfrey, M. R.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 803–808. (g) McGhee, E. M.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 2162–2165.

(5) Abbreviation used: pc, phthalocyaninato; tbp, tetrabenzoporphyrinato; tatbp, triazatetrabenzoporphyrinato; tap, tetraoxaporphyrinato; tmp, 5,10,15,20-tetramethylporphyrinato; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane; DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

(6) (a) Inabe, T.; Kannewurf, C. R.; Lyding, J. W.; Moguel, M. K.; Marks, T. J. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 1. (b) Palmer, S. M.; Stanton, J. L.; Hoffman, B. M.; Ibers, J. *Inorg. Chem.* **1986**, *25*, 2296.

(7) (a) Canadell, E.; Alvarez, S. *Inorg. Chem.* **1984**, *23*, 573. (b) Bohm, M. C. One-dimensional organometallic materials. *Lecture Notes in Chemistry*; Springer Verlag: Berlin, 1987. (c) Kutzler, F. W.; Ellis, D. E. *J. Chem. Phys.* **1986**, *84* (2), 1033. (d) Rosa, A.; Baerends, E. J. *Inorg. Chem.* **1992**, *31*, 4717.

(8) All calculations were carried out using the Amsterdam DF package.[9] The LSD exchange-correlation potential was employed,[10] using the Vosko-Wilk-Nusair[11] parametrization of electron gas data with a correction of Stoll.[12] Bond energies included Becke's nonlocal correction[13] to the local exchange expression and Stoll's correction to the electron gas expression for the correlation energy. The molecular orbitals were expanded in an uncontracted double-ζ STO basis set for all atoms with the exception of the Ni 3d orbital, for which we used a triple-ζ STO basis set. As polarization functions, one 4p was used for nickel. The cores (Ni, 1s-2p; C, 1s) have been kept frozen.

(9) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 42. (b) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 51. (c) Baerends, E. J.; Ros, P. *Int. J. Quantum Chem.* **1978**, *S12*, 169. (d) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87. (e) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

0020-1669/93/1332-5637$04.00/0

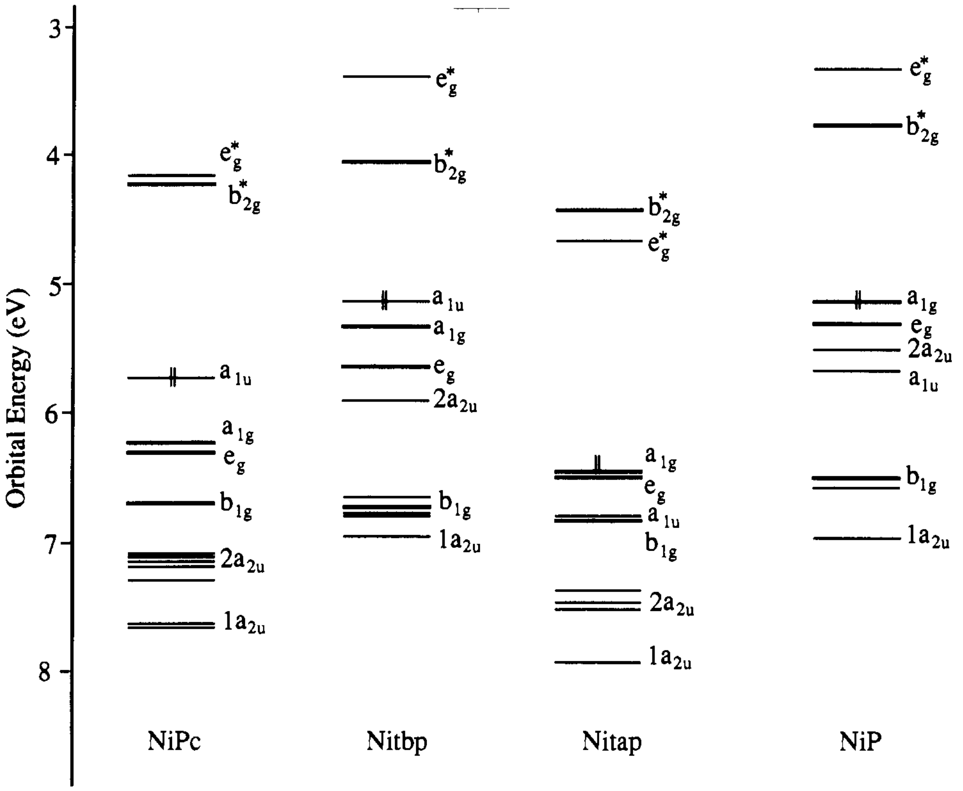

Figure 1. Energy level schemes for NiPc, Ni(tbp), Ni(tap), and NiP. The labeled orbitals (heavy lines) are predominantly of metal character.

terms have very little angle dependence. The theoretical bond energy has a very shallow minimum toward 45°. The steric repulsion $\Delta E°$ has its maximum at the eclipsed situation at 0°, which however is only 0.3 eV above the minimum, much less than the 1.5 eV in the $(NiPc)_2$ case. Although the 0.3-eV rise is sufficient to make the eclipsed conformation unfavorable, the steric term hardly prevents rotation in the range 30–45°, unlike in large-ring based conductors. The fine tuning of the staggering angle observed in Ni(tmp) based conductors, in the range 37–27.5° is therefore only dictated by external factors (crystal packing and structure and size of the counterions).

In the second place, differences in electronic structure between Pc and P will affect the properties of the molecular metals. It is well-known[7] that the highest occupied π ligand orbital, a_{1u}, forms the conduction band in the NiPc based conductors (see Figure 1). The a_{1u} molecular orbitals of adjacent rings have zero overlap at $\phi \sim 20°$ and maximum overlap at $\phi = 0$ or 45°, hence the large conductivity at the prevalent staggering angle of ca. 40°. For the related porphyrin based systems Ni(tmp)X, Newcomb et al.[4e] suggest the a_{1u} orbital to be also the main actor in the conductivity. The suggestion of these authors is based on the observation that the gradual change from metallic to thermally activated behavior in going from 37 to 34.7 to 27.5° for the porphyrin series agrees with a conductivity dominated by an a_{1u} band whose bandwidth is decreasing. However, in simple porphyrins the highest occupied ring orbitals are the nearly degenerate a_{1u} and $2a_{2u}$ set (see Figures 1 and 2). The overlap between porphyrin a_{1u} molecular orbitals on adjacent rings behaves analogously to that between Pc a_{1u} orbitals, from a positive maximum at $\phi = 0°$ to an almost equally large negative minimum at $\phi = 45°$ (see Figure 3). This behavior can be easily deduced from the orbital plots in Figure 2, as can the different behavior of the overlap between adjacent $2a_{2u}$ orbitals, which is largest near $\phi = 0°$ and decreases to a small negative minimum as ϕ approaches 45°. In view of the consequences of the difference in electronic structure between the Pc and P type building blocks for the conductivity of the stack, we inspect more closely the Pc/P difference for the ground-state one-electron levels as shown in Figure 1 for the series NiPc, Ni(tbp), Ni(tap), NiP. The outstanding difference between NiP and NiPc molecules is the destabilization of the occupied a_{1g} (d_{z^2}) and e_g (d_π) metal levels and notably the ring $2a_{2u}$ level with respect to the ring a_{1u} level. The different effects that the introduction of aza bridges and benzo rings have on the a_{1u} and $2a_{2u}$ levels of P may be understood from the orbital plots in Figure 2. The Ni(tap) level scheme in Figure 1 shows that the effect of introducing aza bridges in P stabilizes all the levels due to the higher nuclear charge of N, but preferentially $2a_{2u}$, which ends up considerably below a_{1u} in Ni(tap). Note that the preferential stabilization of $2a_{2u}$ compared to a_{1u} agrees with $2a_{2u}$ having a high amplitude and a_{1u} having nodes on the aza bridges. As a matter of fact, the plots of Figure 2 demonstrate that in NiPc it is even the lower lying $1a_{2u}$ rather than the $2a_{2u}$ orbital that correlates with the P $2a_{2u}$ orbital. On the other hand, the introduction of benzo groups to give Ni(tbp) has relatively little effect on the a_{2u} levels but preferentially destabilizes a_{1u}, which ends up above a_{2u} and all metal levels in Ni(tbp). The pushing-up effect of the benzo rings is in accordance with the antibonding, visible in the plot of the NiPc a_{1u} orbital in Figure 2, between the porphyrinic part of the ring system and the benzo part. The benzo rings also have some pushing-up effect on the lower a_{2u} level ($1a_{2u}$ in NiP) that (with some $2a_{2u}$ admixture) correlates with $2a_{2u}$ in NiPc. Note that the benzo rings in Pc not only have the steric effect pointed out before[7d] but also have the important electronic structure effect of driving a_{1u} on top.

Given the importance of the HOMO a_{1u} of the Pc ring for the conductivity, one wonders how the near degeneracy of a_{1u} and $2a_{2u}$ orbitals and the relatively high position of metal levels in NiP influence the electronic structure of the dimeric units and therefore the properties of Ni(tmp) based "molecular metals". Our calculations on $(NiP)_2$ dimers at different staggering angles indicate that, due to the large dispersion, the a_{1g} (d_{z^2}) metallic

---

(10) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(11) Vosko, S. H.; Wilk, L.; Nusair, M. *J. Can. J. Phys.* **1980**, *58*, 1200.
(12) Stoll, H.; Golka, E.; Preuss, E. *Theor. Chim. Acta* **1980**, *29*, 55.
(13) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.

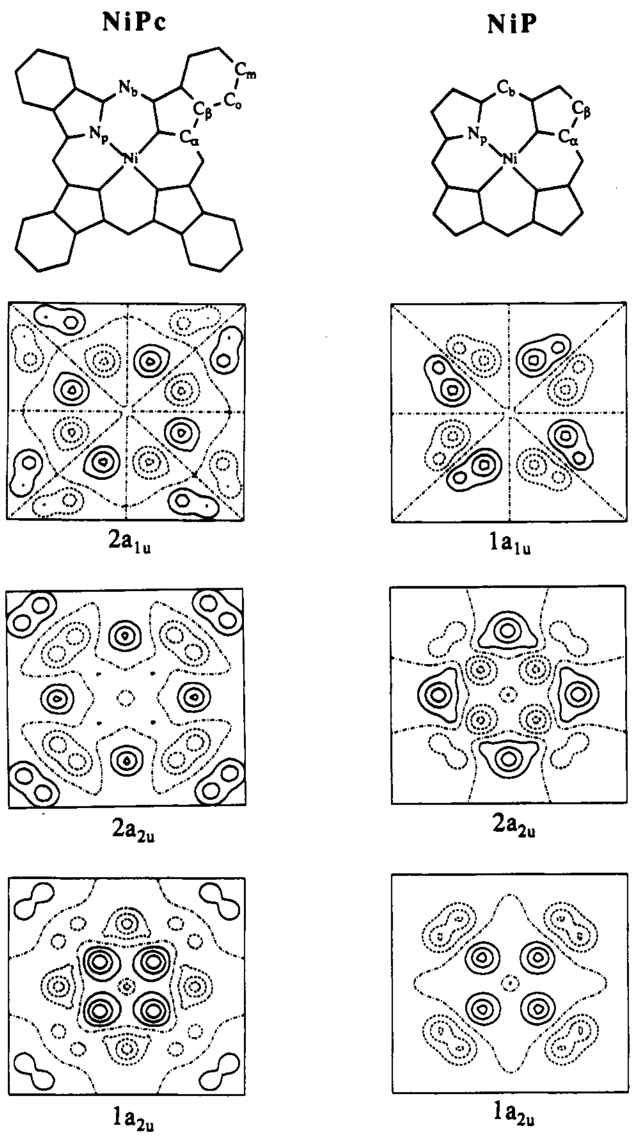

Figure 2. Atom-labeling schemes and contour plots of a_{1u} and a_{2u} orbitals for NiPc and NiP. The plane of drawing is 0.7 bohr above the molecular plane. Contour values: 0.0, ±0.02, ±0.05, ±0.1, ±0.2, ±0.5 $(e/bohr^3)^{1/2}$.

band is the highest occupied at all angles. When the interacting monomers are in the D_4 staggered conformations, i.e. $\phi \neq 0, 45°$, the nearly degenerate a_{1u} and $2a_{2u}$ orbitals mix and form one band. As shown in the plot of Figure 3, the a_{1u}/a_{2u} overlap causing a_{1u}/a_{2u} mixing is large when ϕ is in the range 15–35°. The a_{1u} and a_{2u} set approaches a_{1g} from below closely enough that the a_{1u}/a_{2u} derived band overlaps the bottom of the broad d_{z^2} band. Although the Fermi level coincides with the top of d_{z^2} band, differential relaxation effects cause the a_{1u}/a_{2u} ligand-ionized state to be computed about 0.3 eV more stable than the metal-ionized one. This implies that the oxidation would partially empty the a_{1u}/a_{2u} band, in agreement with ESR measurements[3b,4c,e] that indicate the porphyrin ligand to be the site of oxidation. The conductivity should then occur through this band. This conclusion is supported by the angle dependence of the conductivity, since no angle dependency would be expected for conductivity through an a_{1g} (d_{z^2}) band. As can be seen in Figure 3, the overlap of a_{2u} and notably a_{1u} orbitals on adjacent rings decreases and hence the dispersion of the a_{1u}/a_{2u} overlapping bands will drop upon going from 40 to 27° (at ~32° $S_{a_{2u}}$ is zero). This accounts for the decrease of conductivity along the series Ni(tmp)I, $[Ni(tmp)]_2[PF_6]$, $[Ni(tmp)]_2[ReO_4]$. The decrease may actually be somewhat counteracted by the increasing a_{1u}/a_{2u} overlap.

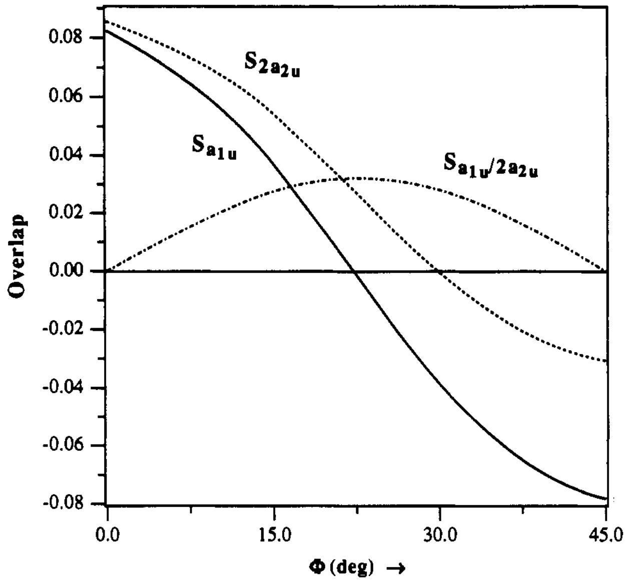

Figure 3. Overlaps between orbitals on adjacent porphyrin rings as a function of the staggering angle. $S_{a_{1u}} = \langle a_{1u}|a_{1u}\rangle$, $S_{2a_{2u}} = \langle 2a_{2u}|2a_{2u}\rangle$, $S_{a_{1u}}/2a_{2u} = \langle a_{1u}|2a_{2u}\rangle$.

Table II. Percentage Contributions of Individual Atoms to a_{1u} and a_{2u} Orbitals (Based on Mulliken Population Analysis per MO) of NiPc, Ni(tbp), Ni(tap), and NiP[a]

		ϵ (eV)	Ni	N_p	C_α	C_β	$N(C)_b$	C_o	C_m
a_{1u}	NiPc	–5.73	0.0	0.0	59.1	1.4	0.0	26.5	13.0
	Ni(tbp)	–5.15	0.0	0.0	63.6	4.2	0.0	19.8	12.4
	Ni(tap)	–6.78	0.0	0.0	79.0	21.0	0.0		
	NiP	–5.67	0.0	0.0	77.0	23.0	0.0		
$2a_{2u}$	NiPc	–7.15	0.0	0.0	0.0	37.6	22.6	0.0	39.8
	Ni(tbp)	–5.89	1.3 (p_z)	29.1	3.9	4.9	58.3	0.0	2.5
	Ni(tap)	–7.49	0.0	5.0	0.0	52.8	42.2		
	NiP	–5.51	1.3 (p_z)	24.3	3.2	9.2	62.0		
$1a_{2u}$	NiPc	–7.63	2.2 (p_z)	48.4	1.6	4.8	32.3	0.0	10.7
	Ni(tbp)	–6.97	0.0	18.0	0.0	38.0	0.0	0.0	44.0
	Ni(tap)	–7.93	2.5 (p_z)	50.2	0.0	32.7	14.6		
	NiP	–6.97	1.4 (p_z)	30.4	0.0	68.2	0.0		

[a] On nitrogen and carbon the contributing AO's are $2p_z$.

We conclude that the different behavior of porphyrin based conductors compared to Pc based ones is primarily due to the lack of a steric hindrance force that strongly opposes lowering of the staggering angle toward 30° in the case of Pc. We have also identified electronic structure effects of the aza bridges and benzo rings in Pc. They give the HOMO a_{1u} in Pc its privileged role and put $2a_{2u}$ out of business. In NiP the highest occupied states have metal character, but nevertheless the a_{1u} and a_{2u} orbitals are together involved in the conductivity.