

Cruciaromaticity in organometallic compounds

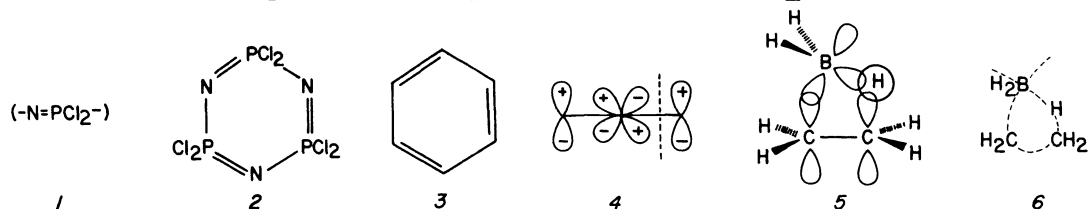
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Abstract - A recent suggestion, that transition metal complexes of unsaturated ligands can be regarded as cruci-conjugated, is explored by studies of various complexes of Fe(II), the aromaticity of the resulting π systems being analyzed in terms of PMO theory. This approach is also applied to porphyrin. The conclusions are supported by preliminary π SCF and MNDO calculations.

INTRODUCTION

The concept underlying cruci-conjugation was first introduced twenty-five years ago by Dewar, Lucken, and Whitehead (ref. 1) in a discussion of the structures of the cyclic polyphosphonitrile chlorides (1).



These had previously been regarded as cyclic conjugated species in view of their apparent analogy to cyclic polyenes; cf. 2 with 3. Craig (ref. 2) indeed had developed a detailed theoretical treatment of them on this basis, assuming them to be planar, with the two relevant d AOs of each phosphorus atom oriented radially and tangentially (4), the radial AOs being neglected. The π system in 1 is thus treated as a cyclic system of $2n$ AOs, formally analogous to that in a cyclic $2n$ polymethine. Craig noted, however, that each d AO introduces a phase dislocation into a π system (see 5). Conjugated rings of this kind consequently fall into two classes, depending on whether the number of d AOs in the ring is odd or even. If it is even, the rules for aromaticity are the same as for cyclic polyenes, i.e. Hückel's rules, while if it is odd, the rules for aromaticity are inverted (refs. 3,4). On this basis, all cyclic phosphonitrile chlorides should be antiaromatic, a conclusion of variance with their observed properties. Antiaromatic compounds are typically unstable, show bond alternation, and absorb visible light, whereas the phosphonitrile chlorides are very stable, have equal PN bond lengths, and absorb only below 220 nm.

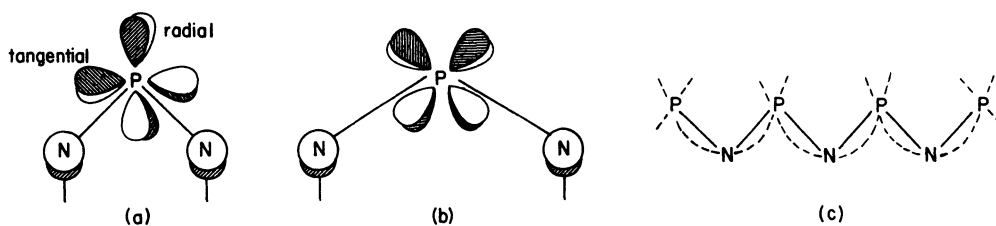
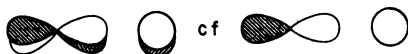


Figure 1. (a) Craig's choice of d AOs in 1; (b) choice giving localized bonds in 1; (c) localized three-center bonds in 1.

As Dewar, Lucken, and Whitehead (ref 1) pointed out, d AOs differ from p AOs in two other significant respects in addition to their introduction of phase dislocations. In the first place, each atom with d AOs has two such AOs that can take part in a conjugated system involving it. And secondly, π bonds formed by a d AO show directional properties analogous to those shown by σ bonds formed by p AOs;



One can therefore select the d AOs of each phosphorus atom in 1 in such a way that each such AO overlaps effectively with the 2p AO of only one adjacent nitrogen atom; see Fig. 1b. Since the resonance integral between two d AOs of a given atom vanishes, the π MOs of 1 consequently break up into essentially non-interacting three-atom segments; see Fig. 1c. Adjacent segments cross at phosphorus without interacting. The π system in 1 is therefore not cyclic. It consists of a number of localized three-center units. A similar situation holds for linear polyphosphonitrile chlorides. This is why there are no significant differences between them and their cyclic counterparts. All such compounds are *nonaromatic*.

The reason for the difference between this representation and Craig's is the neglect of the axial d AOs in the latter. If these were included, the resulting system of delocalized π bonds could be transformed into the localized one by a typical equivalent orbital transformation. The relationship between these two representations is indeed the same as that between any MO description of a molecule and one in terms of localized bonds (ref. 5). The localized bond model of a molecule, when applicable (ref. 6), is more convenient because it is easily visualized.

This phenomenon, i.e. the crossing of two conjugated systems, without interaction, through use of different AOs by a component atom, is not confined to ones of π type. Furthermore, there is no need for the two systems to be distinct. A single conjugated system may cross itself, giving the illusion of a conjugated ring. These ideas were first used by Dewar and McKee (ref. 7) to explain the ease with which olefins hydroborate, a process which seems at first sight to involve a "forbidden" [2+2] cycloaddition. This is not in fact the case because the boron atom involved has two AOs that can take part in the reaction. The transition state (6) consequently contains a linear system of five AOs, not a cyclic one of four AOs, so it is not antiaromatic. The linear system crosses itself at boron. Dewar and McKee suggested the term *cruciconjugation* for delocalized systems of this kind. Phosphabenzene and thiabenzene can be interpreted in a similar manner, in terms of linear seven-AO cruciconjugated π systems (ref. 7).

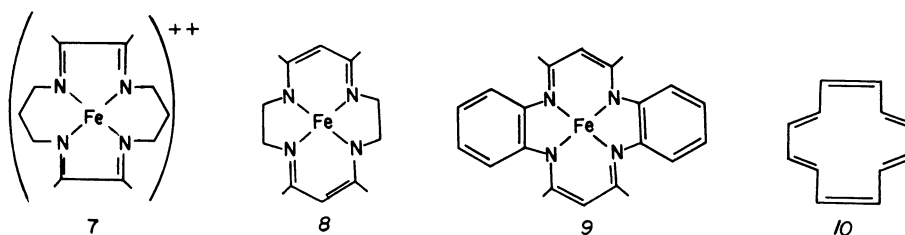
In the cases so far considered, cruciconjugation involves crossing at the terminal AOs of the π systems involved. If a d AO is to occupy a central position in a π system, the latter must be essentially linear at the atom with the d AO. It is also necessary that the energies of the d and p AOs taking part should not differ greatly. As Dewar and McKee (ref. 7) pointed out, these conditions can be met very effectively in square planar or octahedral complexes of transition metals. The metal can π bond to two of the ligands via one AO ($d(xz)$) and to the two others via a second AO ($d(yz)$), the ligands lying on or near the x and y axes.

Complexes of this kind have hitherto been treated as though the orbitals in them were virtually confined to the ligands or to the metal. The metal-ligand interactions have been treated as electrostatic (crystal field theory) or by using perturbation theory. In particular, discussions of the aromaticity of metal porphyrin complexes have centered on the ligand, little attention being paid to the role of the metal. Here we report preliminary studies of some planar complexes of ferrous (Fe(II)) iron with unsaturated ligands, the relevant d AOs of iron combining with the latter to form cruciconjugated systems. The characteristics of the latter are discussed in terms of simple PMO theory (refs. 8,9), which has proved very effective in applications to normal conjugated systems. Those in metal complexes admittedly differ from normal π systems in that the corresponding singlets are often higher in energy than higher spin states, due to the presence of low-lying unoccupied AOs or MOs. In this preliminary study we will consider only singlet states directly, the possible intervention of the higher spin states being inferred from their likely excitation energies.

Fe(II) COMPLEXES OF SIMPLE CONJUGATED LIGANDS

Fe(II) complexes are *high spin* species, four of the d AOs of being singly occupied by electrons with similar spins, unless the ligands have π MOs that can interact with the d(xy), d(xz), and/or d(yz) AOs of iron. The differences in energy between the iron d AOs are therefore less than the gain in correlation energy due to the unpairing electrons. Conjugation may replace the relevant iron d AOs with π MOs of lower energy. These may then fill themselves at the expense of the other d AOs, the loss of correlation energy being outweighed by the decrease in orbital energy. If all the iron electrons become paired in this way, the result is a diamagnetic *low spin* species.

While the majority of Fe(II) complexes fall into one or other of these two categories, having either four, or zero, unpaired electrons, a number of *intermediate spin* ($S=1$) square planar complexes of iron have been discovered in which just two of the electrons are unpaired. The spin states of iron in complexes of this kind are, however, erratic. For example, 7 is a low spin complex (ref. 10) while 8 (ref. 12) and 9 (ref. 13) have intermediate spins. These differences are difficult to explain in terms of current theory.



Square planar iron can form π bonds to adjacent unsaturated groups via its d(xz) and d(yz) AOs, the ligands lying on or near the x and y axes. In 7-9, the ligands provide conjugative paths between these d AOs. The conjugated system in each of these molecules is consequently effectively monocyclic, a cruciconjugated analog of a cyclic polymethine. In the case of 8, the latter is the antiaromatic C(12) cyclic polyene (10) so 8 should also be antiaromatic. There is admittedly a potential difference in that the d AOs in 8 introduce phase dislocations. However, detailed analysis in terms of HMO theory (ref. 3) and PMO theory (refs. 9,11) has confirmed Craig's (ref. 1) conclusion, that cyclic conjugated systems are of two types only, one obeying Hückel's rules and the other the antithesis of those rules, according as the number of phase dislocations in the ring is even or odd. In 8 it is even, so 8 is indeed an antiaromatic analog of 10. Such species form stable dications and dianions, the two NBMOs being either both empty or both doubly occupied. Since the ligands in 8 provide twelve π electrons, iron must provide two, both the "NBMOs" being full. Thus while the d(xz) and d(yz) AOs are both used in the cruciconjugated ring, the resulting bonding and antibonding MOs have room for only two of the iron d electrons.

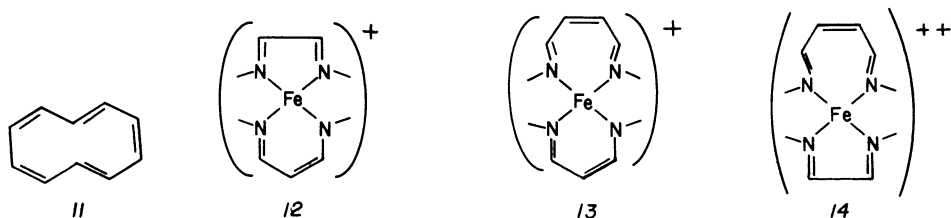
The π orbitals in a cyclic polymethine, apart from the lowest and highest, appear in degenerate pairs. The degeneracies in 10 will be removed in 8 because of the differences in electronegativity between nitrogen, iron, and carbon. An antiaromatic alternant hydrocarbon (AH) has two nonbonding MOs (NBMOs), one confined to starred atoms and one to unstarred ones (refs. 8,9). Since all the nitrogen atoms in 8 occupy starred positions while both d AOs are unstarred, the starred "NBMO" in 8 is lower in energy, and the unstarred one higher, than the NBMOs in 10. It is easily seen (cf. refs. 8,9) that the differences in energy are $(2/3)A(N)$ and $(1/3)A(Fe)$, respectively, $A(N)$ and $A(Fe)$ being the coulomb integrals of N and Fe, relative to carbon. Thus the starred "NBMO" in 8 should be somewhat higher in energy than a nitrogen 2p AO while the unstarred one should be somewhat lower in energy than an iron d AO.

The cruciconjugated system in 8 has $C(2v)$ symmetry. One member of each pair of MOs in 10 consequently has a node at the positions corresponding to the d AOs in 8. It is also easy to see that the positions in 10 corresponding to nitrogen in 8 are close to antinodes in the LUMO with nodes at iron. The corresponding MO in 8 should therefore be much lower in energy than its counterpart in 10.

In 8, two of the electrons from iron occupy the Fe-like "NBMO". Two more should occupy the d(xy) AO which is next in energy, since it is not significantly destabilized by interactions with the ligands. The last two

could occupy the $d(x^2+y^2)$ AO, the $d(z^2)$ AO, or the lower LUMO. While the $d(x^2+y^2)$ AO is high in energy, it seems reasonable that the other two should be close enough together for the ground state to be a triplet, with each of these orbitals singly occupied.

A similar analysis shows that the situation in 9 resembles that in 8, 9 being likewise antiaromatic. It is therefore not surprising that it is also of intermediate spin type ($S=1$).



The lower homolog (7) of 8, with two five-membered rings, is isoconjugate with the C_{10} cyclic polymethine (11) which is aromatic. Here there is room for ten electrons in bonding MOs. Since the ligands supply eight, iron must again provide two. The situation is therefore similar to that in 8, two of the iron electrons occupying the HOMO, two of the $d(xy)$ AO, and two of the LUMO and/or the $d(z^2)$ AO. The HOMO of 11 is, however, lower in energy than that of 10, their HOMO energies being, respectively $-0.62B$ and $-1.00B$, where B is the carbon-carbon resonance integral. The splitting of the LUMOs on passing from 7 to 11 is moreover similar to that on passing from 8 to 10. The LUMO of 7 should therefore be lower in energy than that of 8. It is not surprising that the difference should be large enough to make 7 a low spin species, two electrons occupying the LUMO while the $d(z^2)$ AO remains empty.

The 5/6 complex (12) is isoconjugate with the C_{11} cyclic polymethine which is stable (aromatic) only as the cation, where there is room for only ten electrons in bonding MOs. Since these are filled by electrons from the ligands and since all the other π MOs are antibonding, there is no room for any from iron. Complexes of this type should therefore be unstable, showing a strong tendency to disproportionate to corresponding analogs of 7 and 8.

The 6/7 complex (13), on the other hand, however, is isoconjugate with the C_{13} cyclic polymethine which is stable (aromatic) as the anion. Seven of the MOs in it should be bonding and six antibonding. Since the ligands contribute twelve electrons, iron needs to contribute two. 13 should therefore be stable, probably of intermediate spin type.

The 5/7 complex (14), like 8, is isoconjugate with the antiaromatic C_{12} cyclic polymethine, which has five bonding MOs and two NBMOs. Here, however, the ligands contribute only ten electrons, i.e. just enough to fill the bonding MOs. Four of the iron d electrons can therefore occupy the "NBMOs" and two the $d(xy)$ AO, so 14 should be a low spin complex. It may, however, be difficult to obtain it free from additional ligands if the $d(z^2)$ AO in it is, as predicted, empty.

No complexes of these (12-14) types seem as yet to have been reported.

The approach indicated above could easily be extended to hexacoordinated systems. It is easily seen that complexes of this kind, derived from conjugated bidentate ligands, also contain single cruciconjugated rings. Studies of this kind are in progress. The same kind of treatment can of course also be applied to metal atoms and ions other than $Fe(II)$. The only requirement is that the relevant d AOs are low enough in energy to interact effectively with the ligand π MOs. Thus the aromatic stabilization of complexes such as 7 is likely to be limited by the fact that iron d AOs are higher in energy than carbon $2p$ AOs. Since the bonding energy of d AOs increases with increasing atomic number, being greater in $Ni(II)$ than $Fe(II)$, nickel complexes analogous to 7 should be correspondingly more stable, as indeed they are.

PORPHYRIN

While porphyrin (15) is generally regarded as a very stable aromatic cyclic conjugated system, no convincing explanation of its aromaticity has as yet been given. The fact that it contains twenty-six π electrons, or that a subunit omitting the NH groups contains twenty-two, is not relevant, because Hückel's rule applies only to monocyclic systems (refs. 8,9). While a more general rule has been formulated (ref. 9) in terms of PMO theory, this applies only to *alternant* molecules, i.e. ones containing only even-numbered conjugated rings. While the PMO approach has been extended (refs. 8,9) to polycyclic systems containing one odd-numbered ring, no extension has yet been reported for molecules containing more than one such ring. Here we will show that porphyrin can be treated by a simple extension of the same techniques, an approach which should moreover be applicable to other analogous systems.

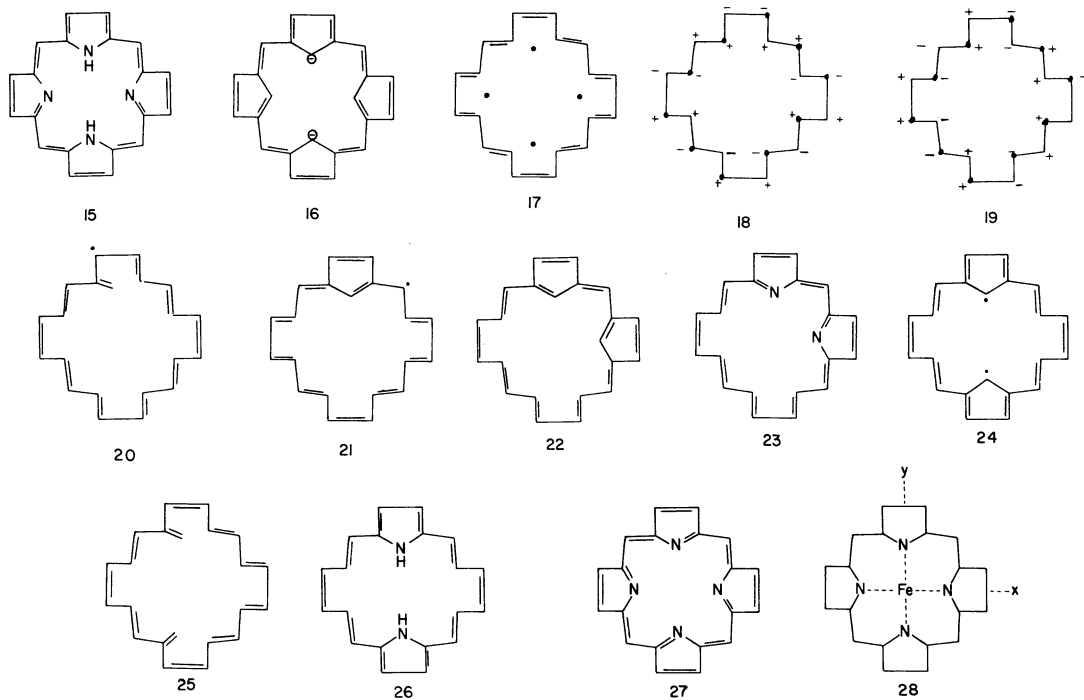
The hydrocarbon analog (16) of 15 can be derived from the C(20) cyclic polyene (17) that forms its perimeter by union (refs. 8,9) with four methyl groups (Me(1-4)), represented by dots inside the ring of 17. Denote their 2p AOs by n_{1-4} . Since 17 is antiaromatic, it has two NBMOs, one (ϕ_O^*) confined to starred atoms and the other (ϕ_O^0) to unstarred atoms, their NBMO coefficients ($+a$; $a = 1/\sqrt{10}$) alternating in sign round the ring; see 18 and 19.

Consider single union of 17 with Me(1) to form the monocyclic hydrocarbon 20. Here n_1 interacts with ϕ_O^* , but not with ϕ_O^0 , the AO coefficient of the latter at the point of attachment vanishing. The interaction between n_1 and ϕ_O^* leads (refs. 8,9) to a bonding-antibonding pair of MOs, with energies $\pm aB$, B being the CC resonance integral. The corresponding energy of union (EU) is thus $2aB$.

The next step is to replace the NBMOs, ϕ_O^* and ϕ_O^0 , by symmetry orbitals ϕ^+ and ϕ^- , given by

$$\begin{aligned}\phi^+ &= (1/\sqrt{2})(\phi_O^* + \phi_O^0) \\ \phi^- &= (1/\sqrt{2})(\phi_O^* - \phi_O^0)\end{aligned}$$

The AO coefficients in ϕ^+ and ϕ^- are $\pm 1/\sqrt{20}$ at each atom, the signs being as indicated in 18 and 19, respectively.



Consider double union of Me(1) with 19 to form 21. The resonance integral between n_1 and ϕ^- vanishes, the AO coefficients at the points of attachment being equal in magnitude and opposite in sign. That between n_1 and ϕ^+ is given by:

$$\int n_1 H \phi^+ d = (1/\sqrt{2})(aB + aB) = aB\sqrt{2}$$

Thus the nonbonding orbitals ϕ^+ and n_1 are again replaced by a bonding-antibonding pair, the corresponding EU being $2aB\sqrt{2}$. 21 is thus aromatic, being more stable than its open chain analog (20) by $2aB(\sqrt{2}-1)$. Consider simultaneous double union of Me(1) and Me(2) with 17 to form 22. Here Me(1) again interacts with ϕ^+ and not with ϕ^- , while Me(2) interacts with ϕ^- but not with ϕ^+ . The corresponding resonance integrals are again $aB\sqrt{2}$. The interactions thus lead to degenerate bonding-antibonding pairs of MOs, with the same splitting as in 21. The EU for formation of 22 from Me(1), Me(3), and 17 is thus double that for formation of 21 from Me(1) and 17. Both five-membered rings in 22 are therefore aromatic. Furthermore, 22 contains no NBMOs. Half the MOs in it are bonding and half antibonding. The additional atoms must therefore each contribute one electron only. The heteroaromatic analog of 22 is thus 23, with two pyrroline rings. Indeed, 22 can be regarded as the aromatic C(18)⁻ cyclic polymethine with two irrelevant localized ethylene bridges added. The bonds involved in the latter are essential single and double bonds (refs. 8,9) and would therefore be expected to be localized.

Next consider the alternative mode of union of two methyl groups with 17, i.e. that of Me(1) and Me(3) to form 24. Here it is convenient to replace the methyl AOs, n_1 and n_3 , by corresponding symmetry orbitals θ^+ and θ^- , given by:

$$\theta^+ = (1/\sqrt{2})(n_1 + n_3); \quad \theta^- = (1/\sqrt{2})(n_1 - n_3)$$

Here neither θ^+ nor θ^- interacts with ϕ^- . The latter therefore survives as a NBMO. Furthermore, θ^+ fails to interact with ϕ^+ , the sum of the products of AO coefficients at the points of attachment vanishing, through symmetry. Thus θ^+ also survives as a NBMO. The interaction between ϕ^+ and θ^- leads to a bonding-antibonding pair, the splitting being given by:

$$\int \theta^- H \phi^+ d_{\tau} = 2aB$$

The corresponding EU is thus $4aB$, just double the EU for formation of 22. Indeed, since first order perturbations are additive, it is also the EU for simultaneous single union of both Me(1) and Me(3) with 19 to form the open chain analog (25) of 24. Thus 24 is less stable than its isomer, 22. It is indeed a typical antiaromatic hydrocarbon, being relatively unstable and possessing two NBMOs. It should therefore form a very stable (aromatic) dianion, isoconjugate with the bispyrrole derivative 26. The latter should therefore be a stable aromatic compound and it should moreover strongly resist loss of electrons to form the corresponding (antiaromatic) bispyrroline.

Consider now quadruple union of Me(1-4) with 17 to form porphyrane, (16), the hydrocarbon analog of porphyrin. Here again it is convenient to replace the methyl AOs with symmetry orbitals θ_{1-4} , given by:

$$\begin{aligned} \theta_1 &= 0.5(n_1+n_2+n_3+n_4) & \theta_2 &= 0.5(n_1-n_2+n_3-n_4) \\ \theta_3 &= (1/\sqrt{2})(n_1-n_3) & \theta_4 &= (1/\sqrt{2})(n_2-n_4) \end{aligned}$$

Here θ_1 and θ_2 have, respectively, A and B type symmetry in the D(4h) point group, while θ_3 and θ_4 correspond to an (inherently degenerate) E-type pair. ϕ^+ and ϕ^- are also of E type, so neither θ_1 nor θ_2 can interact with the methyl AOs. Both therefore survive in 16 as NBMOs. The other interactions lead to an E-type pair of bonding MOs and an E-type pair of antibonding ones, one derived from ϕ^+ and θ_4 and the other from ϕ^- and θ_3 , the corresponding

resonance integrals each being equal to $aB\sqrt{2}$. The EU for formation of 16 is thus $4aB\sqrt{2}$, i.e. exactly the same as that for formation of 22. The two extra carbon atoms in 16 thus contribute *nothing* to its π energy. Since 16 also contains two NBMOs, it is clearly another antiaromatic system, like 23, and as such should form a very stable dianion (as indicated in 16). The latter is isoconjugate with porphyrin (15), two of the five-membered rings being of pyrrole type and two of pyrroline type. Oxidation of 15 to 27 would involve loss of electrons from an aromatic system to form an antiaromatic one. This is why such reactions are not observed. The stability of 15 to oxidation is difficult to explain in terms of resonance theory, given that classical structures for 27 each contain one more bond than corresponding structures for 15.

IRON [Fe(II)] PORPHYRIN

Fe(II) porphyrin (28) can be analyzed in a similar way, by considering its formation through union of the perimeter polyene (17) with the four nitrogen atoms and the iron atom. The orbitals in question are the NBMOs (ϕ^+ and ϕ^-) of 17, the four nitrogen symmetry orbitals θ_{1-4} and the $d(xz)$ and $d(yz)$ AOs of iron. The latter interact only with θ_4 , and θ_3 , respectively, interactions between them and the other nitrogen combinations vanishing. Thus θ_1 and θ_2 again survive unchanged in 28 effectively as nitrogen AOs, while θ_3 interacts with ϕ^- and $d(xz)$ and θ_4 with ϕ^+ and $d(yz)$. Each of the latter three-orbital interactions leads (cf the p MOs of allyl) to a bonding MO, an antibonding MO, and a HOMO. Four of the twenty-six p MOs of 28 are therefore nonbonding, while eleven are bonding and eleven antibonding. Since porphyrin contains twenty-six p electrons, there is room for four d electrons from iron in the NBMOs derived from ϕ^+ , θ_4 , and $d(yz)$, and from ϕ^- , θ_3 , and $d(xz)$. Since the $d(xy)$ AO can accommodate the other two, 28 should be a low spin ($S=0$) species, all the iron d electrons being paired.

However, derivatives of 28 are in fact of intermediate spin ($S=1$) type. The reason for this is that they are not planar, the iron atom being apparently too large to fit into the porphyrin. Moving iron out of the plane of the ring reduces the repulsive σ interactions between the in-plane nitrogen lone pair AOs and the $d(z^2)$ AO, thus lowering the energy of the latter to a point where the energy required to excite an electron from $d(xy)$ to $d(z^2)$ is outweighed by the exchange energy in the corresponding triplet. Indeed, the stabilization achieved in this way may be partly responsible for moving iron out of the plane of the porphyrin ring.

Since the $d(z^2)$ AO in Fe(II) porphyrins is thus singly occupied, such species react rapidly and irreversibly with oxygen to form peroxy radicals, (FeP)OO., which can undergo various secondary reactions. In order to make addition of oxygen reversible, the Fe-O₂ must be weakened. This is achieved in haemoglobin, and haem models, by attaching an additional axial ligand, the interaction between its donor AO and the $d(x^2)$ AO of iron leading to a bonding MO, which is filled with electrons from the ligand, and an antibonding MO, which is much higher in energy than $d(xy)$. Complexes of this type are consequently of low spin type, the $d(xy)$ AO being doubly occupied. In order to bond oxygen, an electron has to be transferred from the $d(xy)$ AO to the $D(z^2)$ AO. The heat of reaction for addition of oxygen is thus reduced by the necessary promotion energy.

THEORETICAL CALCULATIONS

The only calculations so far reported for complexes of the kind considered above have been for certain iron porphyrins, using procedures (EH; INDO) that are known (ref.14) to give very poor estimates of molecular energies. The most satisfactory approach would be to use one of the semiempirical treatments developed here, i.e MINDO/3 (ref. 15), MNDO (ref. 16), or AM1 (ref. 17); unfortunately, parameters are not yet available for iron. We have, however, recently developed what appear to be reasonably satisfactory MNDO parameters for chromium (ref. 18) and we have accordingly been using these to study Cr(0) analogs of the complexes discussed above. The results (which will

be reported in detail elsewhere) are in very good qualitative agreement with the conclusions given by our PMO analysis of the corresponding Fe(II) complexes. In particular, the $d(xz)$ and $d(yz)$ AOs of chromium are very extensively delocalized, in spite of the large difference in electronegativity between Cr(0) and carbon.

We have also developed a treatment of cruciconjugated metal complexes, based on the Pople SCF approximation (ref. 19) as parametrized by Dewar and de Llano (ref. 20). The latter has given remarkably good estimates of the geometries and heats of formation of a wide range of conjugated hydrocarbons (refs. 20,21) and heteroconjugated molecules (ref. 22). In this approach, resonance integrals are included only between atoms linked by bonds and the atoms so linked are specified in the input to a calculation. In our extension of this treatment, the metal is simulated by a pair of coincident heteroatoms, one linked to one pair of ligands and the other to the other two. Since the electron repulsion integrals between different AOs in the conjugated system are estimated (ref. 20) by a Pariser-Parr-type approach, the repulsion between the AOs of the coincident atoms automatically reproduces the metal one-center integral. The phase dislocations due to the d AOs can of course also be simulated by reversing the sign of the resonance integral between each "metal AO" and one of the ligands. Preliminary applications to the complexes discussed above look very promising, even though no attempt has yet been made to optimize the parameters for iron. The results agree qualitatively with the MNDO calculations for the isoelectronic Cr(0) complexes, again supporting the representation of such species as cruciconjugated. Full details of this work will be reported elsewhere in due course.

ACKNOWLEDGEMENT

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