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(10) Products were shown to be homogeneous on silica gel thin layer chromatography. ^1H and ^{13}C NMR spectroscopy of metal-free porphyrin and iron(III) imidazole derivatives was consistent with expected structures.
(11) Resonance assignments are readily made based on earlier literature studies of high-spin and low-spin iron(III) porphyrins.[12]
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Harold Goff

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received October 22, 1979

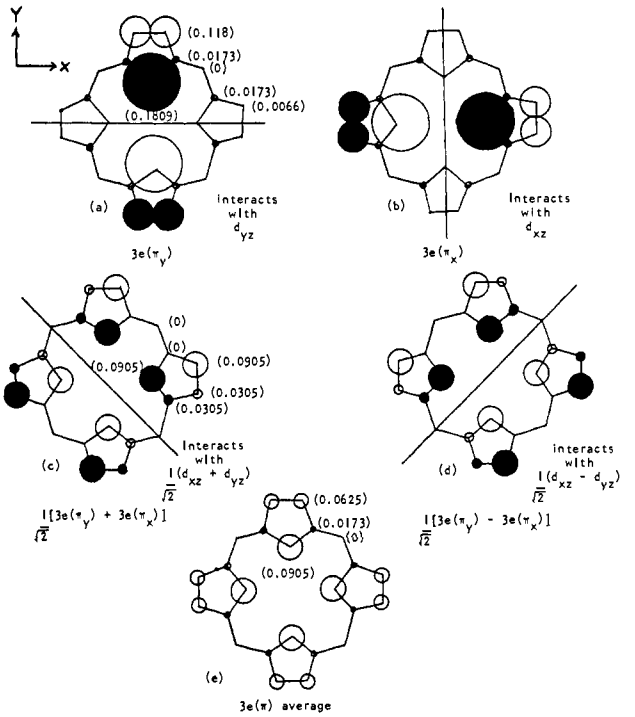

Figure 1. (a, b) Electron density and nodal properties of porphine $3e(\pi)$ orbitals,[10] which interact with the d_{xz} and d_{yz} orbitals of low-spin Fe(III), respectively. (c, d) Linear combinations of these orbitals, appropriate for interaction with meso-bonded planar ligands. (e) Average electron density distribution if the $3e(\pi)$ orbitals remain degenerate. The light and dark shades depict orbital symmetry properties, and the numbers in parentheses give the square of the atomic orbital mixing coefficients, c_i^2, for each position. These c_i^2 values are proportional to the unpaired electron density, ρ_i, expected at the carbon i. The size of the circles depicts the relative size of c_i^2.

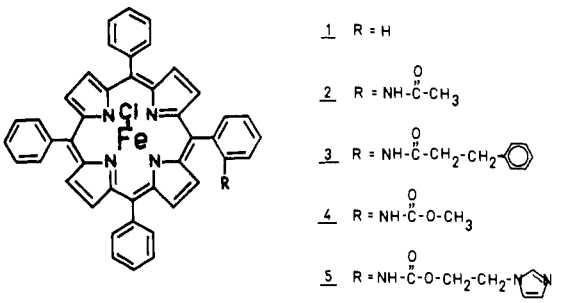

Figure 2. Structures of the iron porphyrins used in this study.

Models of the Cytochromes *b*. 1. Effect of Substituents, Axial Ligand Plane Orientation, and Possible Axial Ligand Bond Strain on the Pyrrole Proton Shifts of a Series of Low-Spin Monosubstituted Tetraphenylporphinatoiron(III)–Bisimidazole Complexes

Sir:

The factors affecting the magnitude of contact shifts of low-spin iron(III) porphyrins in high-symmetry synthetic compounds,[1,2] simple natural hemins,[1,3] and hemoproteins[4-9] have been investigated in detail for some time. In particular, attempts have been made to explain the variation in the position of the methyl resonances of iron(III) protoporphyrin containing hemoproteins.[1,3-9] Since the contact shift pattern of low-spin iron(III) porphyrins indicates spin delocalization mainly to the pyrrole positions,[1,2] involvement of the porphyrin $3e(\pi)$ orbitals[10] in ligand-to-metal π-back-bonding to the remaining hole in the d_{xz}, d_{yz} orbitals of iron has been postulated as the mechanism of unpaired spin delocalization for both synthetic and natural low-spin iron(III) porphyrins.[1-3]

One hypothesis[1,5] which may explain the variation in methyl contact shifts is that planar axial ligand(s) split the degeneracy of the $3e(\pi)$ filled molecular orbitals of the porphyrin ring and the *e*-symmetry d_{xz}, d_{yz} orbitals of the metal; thus unpaired electron delocalization to certain pyrrole positions is favored over others. This situation is explained more clearly by reference to Figure 1, in which the electron densities and nodal properties of the $3e(\pi)$ orbitals[10] of porphine are presented. Although the energies of d_{xz} and d_{yz} are expected to be split by the dynamic Jahn–Teller effect,[5] the electron populations of the two d orbitals appear to be equal at room temperature, in the absence of symmetry-breaking effects. Such is the case for low-spin tetraphenylporphyrin, octaethylporphyrin, and *meso*-tetra-*n*-propylporphyrin complexes of iron(III), all of which have fourfold molecular symmetry because the axial ligands rotate freely about the metal–ligand bonds. All of these compounds show only one pyrrole-H or $-CH_2-$ peak.[1,2] The presence of one planar axial ligand whose freedom to rotate has been restricted is sufficient to break the degeneracy of the $3e(\pi)$ orbitals of Figure 1 (a, b or c, d). Such restriction in the free rotation is not unexpected in hemoglobins, myoglobins, the cytochromes, and other hemoproteins where the axial ligands are provided to the metal by side chains of the protein backbone. Two planar axial ligands (as are present in the cytochromes b_5[9,11] and b_2[9]) will split the degeneracy of the $3e(\pi)$ orbitals unless their axial ligand planes are mutually perpendicular.

Traylor and Berzinis[12] have recently demonstrated the importance of restricted rotation of an axial ligand in changing

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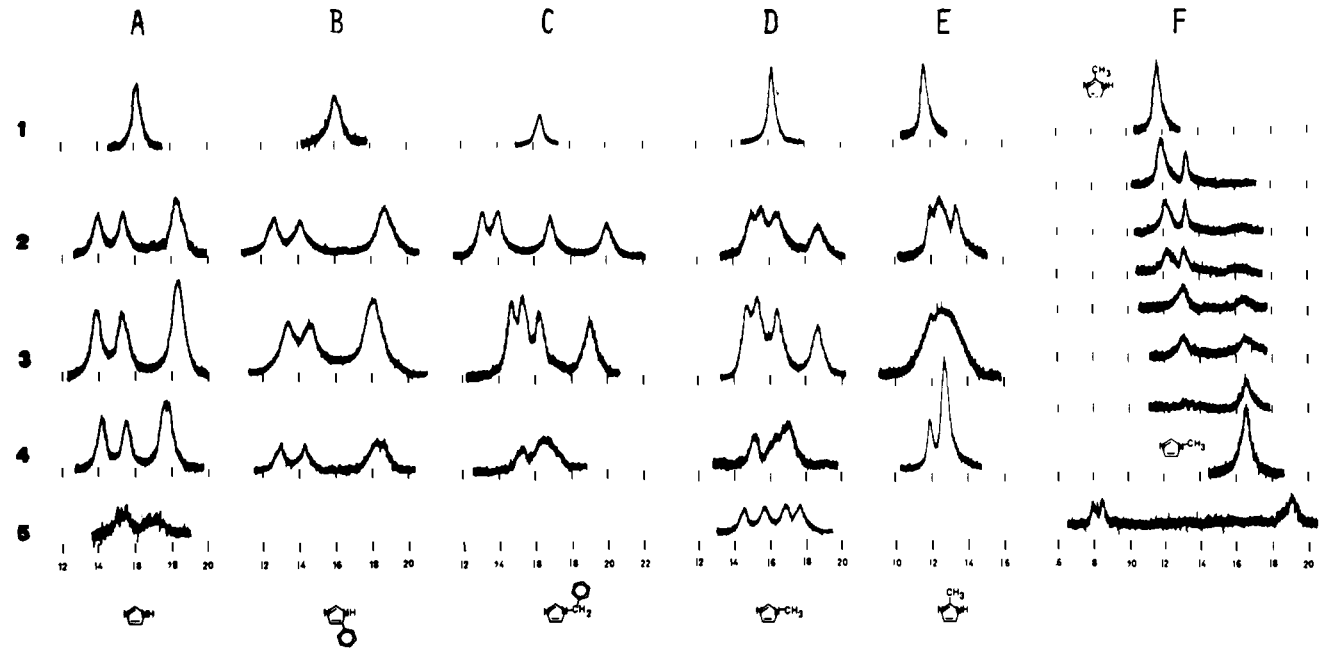

Figure 3. ^{1}H NMR spectra of the pyrrole-H region for compounds **1–5** in the presence of ~0.1 M ligand; A, imidazole; B, 4(5)-phenylimidazole;[16] C, *N*-benzylimidazole; D, *N*-methylimidazole; E, 2-methylimidazole. F shows **1** in the presence of ~0.1 M 2-methylimidazole (top) and then changes in the spectrum of this sample as successive aliquots of 1.0 M *N*-methylimidazole are added: the next-to-the-bottom trace is of **1** in the presence of ~0.1 M *N*-methylimidazole alone; the bottom trace is of **5** in the presence of ~0.02 M 2-methylimidazole. Scale is parts per million upfield from Me_4Si. All samples are ~0.02 M iron(III) porphyrin in $CDCl_3$, recorded at 34 °C on a Varian EM390 NMR spectrometer.

the spread of the methyl resonances of cyanohemins having one covalently attached imidazole ligand using their "chelated hemes" derived from covalent attachment of imidazole amines to iron(III) protoporphyrin IX. In this porphyrin system the situation is complicated by the lack of symmetry of the protoporphyrin ring, and it is difficult to derive the appropriate molecular orbital wave functions and electron densities, analogous to those of Figure 1. An investigation has therefore been undertaken in this laboratory of the NMR spectra of a series of more symmetrical synthetic iron(III) porphyrins in an attempt to understand the relationship between restricted rotation of planar axial ligands and the isotropic shifts of symmetry-related protons.

A series of chloroiron(III) tetraphenylporphyrins which carry one ortho substituent, shown in Figure 2, have been synthesized by methods reported elsewhere,[2,13] and their NMR spectra in the presence of various imidazole derivatives investigated. In Figure 3 are shown representative spectra of the pyrrole proton region of this series of compounds. Several observations may be made concerning these results.

(1) Introduction of one substituent into the fourfold symmetrical TPP ligand, in conjunction with the binding of two planar axial ligands, breaks the degeneracy of the $3e(\pi)$ orbitals such that three or four pyrrole proton resonances are generally observed. This is in contrast to the single resonance for the pyrrole H of bisimidazole complexes of **1**[1,2] (Figure 3). This is true whether or not one of the axial ligands is covalently attached. The effect of this single substituent on the pyrrole peaks of diamagnetic analogues of **2–5** is small but real: the pyrrole resonance is split into two AB patterns where the chemical-shift differences ($\Delta\delta = 0.2$ ppm) and coupling constants ($J \sim 5$–6 Hz) are small.[14]

(2) The nature of the axial ligand has a profound effect upon the spread and pattern of the pyrrole-H resonances. This is presumably a contact shift effect, since the ESR spectra (whose *g*-value anisotropy is proportional to the dipolar contribution to the observed isotropic shift[1]) of all the non-2-methylimidazole-containing complexes are identical. [Complexes containing 2-methylimidazole as axial ligand(s) do not give resolved ESR spectra down to 4.2 K.[15]]

(3) The similarity in the spectra of imidazole and 4(5)-phenylimidazole[16] (Figure 3A and 3B, respectively) complexes of **2, 3,** and **4** suggests that all of these complexes have one ligand whose rotation is similarly hindered, perhaps because of hydrogen bonding of the N–H proton[17] to the polar amide or urethane oxygen. One might speculate that the average projection of the plane of this imidazole on the porphyrin ring closely coincides with the nodal plane of Figure 1c or 1d, passing through the meso position which carries the substitute phenyl group, which in turn perturbs the electron density distribution at the closest and farthest points from its position of attachment, making the contact shift of protons at these positions somewhat different. The effect of this ortho substituent appears to be of similar magnitude for the amide and urethane groups of compounds **2, 3,** and **4.**

(4) N-Substituted imidazoles, which cannot participate in hydrogen bonding, exhibit four pyrrole-H resonances (Figure 3C and 3D). This again suggests restricted rotation of one axial ligand, but in this case to produce an average ligand plane angle more nearly coinciding with the porphyrin nitrogens, and dependent upon the size of the groups attached to the ortho substituent and the nitrogen of the imidazole. Thus, the orbital containing the unpaired electron probably more nearly resembles that shown in Figure 1a or 1b, perturbed by the substituent on one meso position. The fact that **5** also shows four resonances when in the presence of 1 equivalent of *N*-methylimidazole is consistent with this hypothesis, since the two molecular structures of covalently attached planar axial ligand complexes derived from ortho-substituted tetraphenylporphyrins reported thus far have shown the axial ligand plane to lie very close to coincidence with the porphyrin nitrogen axis.[18,19]

(5) The pyrrole resonance of bis-2-methylimidazole complexes of **2, 3,** and **4** (Figure 3E) show less spread than the corresponding bis nonhindered imidazole complexes, perhaps because of a sensitive dependence of the iron and porphyrin orbital splittings on bond length. However, the difference in Fe–N(axial) bond lengths for the bisimidazole (1.974-Å average)[20] and bis-2-methylimidazole (2.015 Å)[21] complexes of **1** is very small.

(6) 2-Methylimidazole produces a significantly smaller pyrrole isotropic shift for **1** than do nonhindered imidazoles (Figure 3F). This fact, together with the lack of a resolved ESR spectrum for bis-2-methylimidazole tetraphenylporphinatoiron(III),[15] and differences in the low-temperature Mössbauer spectra of hindered vs. nonhindered imidazole complexes[22] suggest the possibility of different d-orbital energies for hindered and nonhindered imidazole complexes of **1.**

(7) The NMR resonance of the pyrrole protons of the mixed axial ligand complex of **1** can be obtained by titration of the bis-2-methylimidazole complex with *N*-methylimidazole (Figure 3F). The mixed-ligand complex also has its pyrrole resonance significantly downfield of that of the bis-*N*-methylimidazole complex of **1.**

(8) The pyrrole resonances of the mono-2-methylimidazole complex of **5** show the largest spread found so far, which may suggest a role for bond strain (tension) or lengthening of the Fe–N(2-methylimidazole) bond in increasing the spread, as suggested by Goff in the accompanying communication.[23] However, it is difficult to understand how two sterically hindered ligands can give rise to a decreased spread, while only one in combination with a nonhindered imidazole gives rise to an increased spread of the pyrrole-H resonances.

In summary, the single pyrrole-H resonance of bisimidazole tetraphenylporphinatoiron(III) is split into three or four peaks when one substituent is placed on an *o*-phenyl position. We speculate that this splitting and its magnitude are due to a sensitive balance of three factors: restricted rotation of one axial ligand by the *o*-phenyl substituent, the symmetry-breaking effect of that substituent, and, possibly, the axial ligand bond length and/or iron orbital energies. Further NMR, ESR, and structural studies now underway on these complexes and related bis covalently attached axially liganded iron(III) porphyrins may shed further light on the interrelationship of these effects.

Acknowledgments. The financial support of NSF (CHE-75-20123 and 79-18217) and NIH RCDA (5 K04 GM 00227) are gratefully acknowledged. The author thanks Dr. Robert Lundin and Ms. Mabry Benson for use of the NMR facilities of the U.S. Department of Agriculture, Berkeley, Calif., for part of this work.

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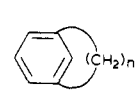
F. Ann Walker[24]
Department of Chemistry, San Francisco State University
San Francisco, California 94132
Received December 17, 1979

Tricyclo[6.1.1.0^{3,9}]deca-2,8(10)-diene, the Dewar Isomer of [4]Metacyclophane

Sir:

Recently, we reported the formation of [5]metacyclophane (**1b**), so far the smallest member of the metacyclophane series.[1] While our attempts to synthesize the next lower homologue [4]metacyclophane (**1a**) have so far not met with success, they led to the unexpected discovery of the highly strained Dewar isomer of **1a**, tricyclo[6.1.1.0^{3,9}]deca-2,8(10)-diene (**2**), which has the additional interesting feature of being a double Bredt olefin. Previously, [5]- and [6]metacyclophane had been ob-



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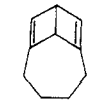

2

tained as byproducts in the synthesis of the corresponding 3,3′-bridged bicyclopropenyls. To make these interesting compounds more easily available, we devised a more rational approach. The new route resembles the general approach to [6]- and higher metacyclophanes of Hirano et al.,[2] however, with important modifications which make it more suitable for the preparation of the sensitive smaller members of the group such as **1a** and **1b**.

Addition of chlorocarbene to 5,6,7,8-tetrahydroindan-2-ol[3] yielded an ~2:1 mixture of isomeric endo alcohols **3** (94% yield) (Scheme I). The assignment of the stereochemistry of **3**-anti is based on the directing effect of the hydroxyl group in carbene additions, for which there is some precedent in literature[4] and which also manifests itself in the stereochemistry of **3**-syn; the latter follows from the X-ray crystal structure determination of **4**,[5] and **3**-anti and **3**-syn were correlated by reduction with sodium in liquid ammonia to the same *endo*-tricyclo[4.3.1.0^{1,6}]decan-8-ol.[3] When the mixture of **3** was treated with 2 equiv of tosyl chloride in pyridine,[6] **3**-syn, the minor component, was tosylated to yield **4** (70%), while the major isomer, **3**-anti, was hardly affected. Treatment of **4** with 1 equiv of *t*-BuOK in Me_2SO afforded **6**-syn which, upon treatment at room temperature with an excess of *t*-BuOK in Me_2SO, slowly polymerized. However, **3**-anti could be converted into its mesylate **5** (90%), which on treatment with 1 equiv of *t*-BuOK in Me_2SO afforded **6**-anti (70%). The reaction of **5** or of **6**-anti with 3 to 5 equiv of *t*-BuOK in Me_2SO (16 to 40 h at room temperature) yielded three isomeric dienes, **2**, **7**, and **8**. The structures of **2**, **7**, and **8** were assigned on the basis of their spectral[7] and chemical properties. Catalytic reduction (H_2, 10% Pd/C) of **2**, **7**, or **8** produced bicyclo[4.3.1]decane (**9**);[8] treatment of **2** or **7** with diimide afforded tricyclo[6.1.1.0^{3,9}]decane (**10**).[9]

The formation of **2**, though not fully understood at present, may be rationalized as follows. Upon treatment with *t*-BuOK, both **6**-syn and **6**-anti split off an allylic proton to give the

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