tions and Professor W. N. Speckamp (University of Amsterdam) for generously supplying us with a sample of 1-azaadamantane. R.C.R. acknowledges the Phillips Petroleum Company for a fellowship (1973-1974).

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(11) A program, soon to be available through the Quantum Chemistry Program Exchange, for complete geometry optimization has been written by Professor K. F. Purcell of this department. By allowing treatment of both open and closed shell molecules according to either the CNDO or INDO prescriptions, the program is a generalization of those discussed in ref 12. The final geometries of **1**, **2**, and **3** are the energy minimum structures for C_s, C_{3v}, and C_{3v} symmetries, respectively.
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Wayne C. Danen,* Robert C. Rickard
Department of Chemistry, Kansas State University
Manhattan Kansas 66506
Received January 20, 1975

Structural Interpretation of Heme Protein Resonance Raman Frequencies. Preliminary Normal Coordinate Analysis Results[1]

Sir:

Much current interest attaches to the stereochemistry of the heme group and its consequences for biochemical function in heme proteins. In hemoglobin, the transition from a five-coordinate, out-of-plane, high-spin heme to a six-coordinate, planar, low-spin heme has been proposed as the stereochemical trigger for the cooperative binding of oxygen.[2] This transition produces appreciable frequency shifts in certain porphyrin ring vibrational modes, which can be sensitively monitored by the technique of resonance Raman spectroscopy. From an examination of various heme proteins, it has been possible to identify characteristic vibrational shifts associated with the electronic and stereochemical concomitants of changes in oxidation and spin state.[3]

We present here results of a normal coordinate analysis on octamethylporphyrin (OMP) designed to elucidate the parameters responsible for the observed vibrational shifts. Application of the porphyrin Urey-Bradley force field suggested by Nakamoto and coworkers[4] gave ~100 cm^{-1} errors for the high-frequency A_{2g} and B_{1g} modes. Addition of two stretch-stretch interaction constants ($F_{C_\alpha C_m, C_\alpha C_m}$ = 0.4 mdyn/Å and $F_{C_\alpha N, C_\alpha N}$ = 0.6 mdyn/Å)[5a] and an adjustment of the CN stretching constant (K_{CN} = 4.5 mdyn/Å) yielded eigenfrequencies in good agreement with the observed resonance Raman frequencies of ferrocytochrome c, as shown in Table I. The molecular parameters of bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II)[6] were used with slight alteration to ensure D_{4h} symmetry, and the methyl groups were treated as point masses.[5b] OMP adequately models those physiological porphyrins which have eight peripheral substituents attached to the pyrrole rings through saturated carbon atoms, as in c-type cytochromes. Peripheral vinyl groups, found in protoheme proteins, are known to couple the porphyrin ring and produce extra bands, but the basic vibrational patterns remain unaltered.[3b] Bands which are assigned to A_{1g} and A_{2g} are consistent with their reported depolarization ratios.[3] All the observed depolarized bands (ρ = ¾) were reasonably assigned to B_{1g} symmetry modes. The B_{2g} modes, as had been earlier predicted,[3a] are not observed.

Low-spin hemes are planar but, in high-spin hemes, the iron atom lies out of the plane, and the pyrrole rings tilt in the same direction, producing a doming of the porphyrin.[7] This transition is reflected in relatively large frequency decrements, up to 35 cm^{-1}, in three Raman bands:[8] ~1640 (dp = depolarized), ~1580 (ap = anomalously polarized), and ~1500 (p = polarized) cm^{-1}. The potential-energy distribution (Table I) shows that the first two are mainly methine bridge C-C stretching, and the third is mainly pyrrole C-N stretching. The next calculation was of domed OMP, using the same force constants as for the planar case, in order to investigate the purely kinematic effects of doming. The shifts produced by a 19° dome angle (the angle of the pyrrole rings with respect to the mean heme plane) are compared in Table I with experimental frequency differences[3b] between ferrocytochrome c[10] and deoxyhemoglobin. The main kinematic effects of doming do show up in the spin-state marker bands and are in the right direction, but

Table I. Summary Results of Preliminary Normal Coordinate Calculations for Octamethylporphyrin

Frequency, cm^{-1}		Frequency shift, cm^{-1}			Potential-energy distribution
Exptl[a]	Calcd[b]	19° dome[c]	+ Force field[d]	Exptl[e]	(contributions above 10%)
1626[f]	1626 (B_{1g})	5	24	14	51% $C_\alpha C_m$,[g] 20% $C_\beta C_\beta$, 16% $C_\alpha C_\beta$
1592	1598 (A_{1g})	0	7	4	54% $C_\beta C_\beta$, 16% $C_\alpha C_m$
1585[f]	1587 (A_{2g})	8	33	33	73% $C_\alpha C_m$, 16% δCH, 14% $C_{\alpha\beta}$
1547	1534 (B_{1g})	6	20[14]	1	57% $C_\beta C_\beta$, 16% $C_\alpha C_m$
1497[f]	1493 (A_{1g})	6	18	23	46% $C_\alpha N$, 17% $C_\alpha C_\beta$, 13% $C_\beta C_\beta$
h	1476 (B_{2g})	0	4	*h*	45% $C_\alpha C_m$, 37% $C_\alpha N$
1405	1424 (B_{1g})	5	8	3	60% $C_\alpha N$, 16% $C_\alpha C_m$
1400	1399 (A_{2g})	8	1	*i*	40% $C_\alpha N$, 28% δCH, 13% $C_\alpha C_\beta$
h	1387 (B_{2g})	0	2	*h*	75% $C_\alpha C_\beta$
1362	1376 (A_{1g})	−6	3	4	38% $C_\alpha C_\beta$, 31% $C_\alpha C_m$, 17% $C_\beta C_\beta$
1310	1284 (A_{2g})	−4	−8	0	45% $C_\alpha C_\beta$, 37% δCH
1228	1257 (B_{1g})	−6	−7	0	29% $C_\alpha C_\beta$, 58% δCH

[a] Ferrocytochrome c data.[3b] [b] Planar octamethylporphyrin (see text). [c] Planar minus domed (19° angle), same force field. [d] Planar minus domed (19° angle), altered force field (see text). [e] Ferrocytochrome c minus deoxyhemoglobin. [f] Spin-state marker bands. [g] Coordinate labels as in ref 4. [h] These modes have not been detected. [i] Not detected in deoxyhemoglobin.

the calculated shifts are only about 25% of the observed shifts. Elimination of the discrepancies requires an unrealistically high dome angle, ~35°. Dome angles less than 19° produce corresponding smaller shifts. Perutz' estimate (0.75 Å)[2] of the iron-to-mean heme plane displacement in deoxyhemoglobin requires a dome angle of 19° if the Fe–N bond length is 2.086 Å as suggested[11] for high-spin Fe(II). In the single available high-spin Fe(II) porphyrin X-ray crystal structure,[11] both the displacement and the dome angle are somewhat lower, 0.55 Å and 7°, respectively. The significance of this difference is currently under debate.[11,12] In any event, it is most unlikely that the actual dome angle in deoxyhemoglobin is much larger than 19°.

We found that the observed shifts can be satisfactorily reproduced if, in the 19° domed structure, small alterations were made in the force field, consistent with Hückel molecular orbital calculations (to be published elsewhere) of the changes in π-bond order on doming, resulting from decreased π overlap at the methine bridges. These changes, amounting to 2–5%, were translated into force constant changes ($\Delta K_{C_\alpha C_\beta} = 0.1$, $\Delta K_{C_\alpha N} = 0.1$, $\Delta K_{C_\alpha C_m} = -0.2$, and $\Delta K_{C_\beta C_\beta} = -0.1$ mdyn/Å), using Gordy's relation.[13] In addition the $C_mC_\alpha N$ bending force constant was reduced by 0.2 mdyn/Å. No attempt was made to refine these force constant changes, and the similarity of the patterns of observed and calculated frequency shifts lends strong support to the view that spin-state effects on the resonance Raman spectra are largely the result of disruption of the porphyrin π conjugation brought about by doming.

It is of interest that the ~1375 cm^{-1} oxidation-state marker band[3b,15] is shifted to higher frequency by the kinematic effects of doming but to lower frequency by the change in force field. Thus its essential invariance (i.e., 1362 cm^{-1} in cytochrome c and 1358 cm^{-1} in deoxyhemoglobin) to changes in spin state appears to result from effective cancellation of kinematic and force-field effects. This mode, which produces the strongest Raman feature in resonance with the Soret band,[3b,16] had previously been assigned[3b,17] to C–N stretching. In fact it involves bonds in the outermost part of the porphyrin ring.

While further calculations are needed to explore alternative plausible force-field variations, it is encouraging that the preliminary calculations have yielded straightforward results: (1) a simple force field fits the porphyrin-ring frequencies with good accuracy; (2) the kinematic consequences of doming, while not negligible, are relatively small; (3) the frequency shifts associated with conversion of low-spin to high-spin heme proteins can be reproduced with force-field changes that are plausibly related to changes in electronic structure.

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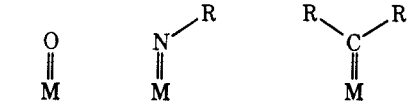
P. Stein, J. M. Burke, T. G. Spiro*
Chemistry Department, Princeton University
Princeton, New Jersey 08540
Received October 30, 1974

A New Reaction. Stereospecific Vicinal Oxyamination of Olefins by Alkyl Imido Osmium Compounds

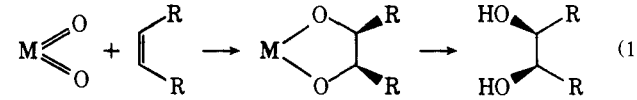
Sir:

During our studies on the oxygen atom transfer chemistry of transition metal oxocompounds (**1**) with olefins, it occurred to us that similar reactions might take place with the nitrogen (**2**) and carbon (**3**) analogs of the oxo species. The

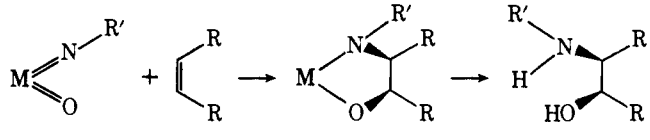


1 **2** **3**

transition metal oxo compounds which react with olefins are typically d^0 substances having from two to four oxo groups. Cis dihydroxylation of olefins to form vicinal diols is a unique reaction of these oxidants (eq 1). We report here the first example of an aza analog of this transformation (eq 2).



(1)



(2)

The only known d^0 alkyl imido transition metal species are compounds of vanadium[1] and osmium.[2] In the case of vanadium the compounds have the general structure **5**, and in the case of osmium only the single substance **6a** has been described.[2] In addition to the known *tert*-butyl imido compound **6a**, we have prepared the new adamantyl derivative **6b**. Both were synthesized in about 90% yield by treating the amine with OsO_4 in olefin-free pentane.[3] We were pleased to find that both imido reagents **6a** and **6b** react