erated. The product ratio would then be determined by differences in transition-state energies for the reaction of **6** with 2,2,2-trifluoroethanol. Since the product ratios indicate relatively small energy differences in these transition-state energies, the cause of the differences in product ratio is difficult to ascertain.

We are applying our approach of the magnification of neighboring-group participation to other, more controversial situations involving carbocations that may be stabilized by intramolecular interactions with neighboring groups.

Matrix Isolation Infrared Spectra of Oxy(tetraphenylporphyrinato)iron(II)

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Although ferrous porphyrins are highly important as models of hemoglobin and myoglobin, simple (unprotected) ferrous porphyrins such as Fe(TPP) (TPP: tetraphenylporphyrinato anion) cannot bind molecular oxygen reversibly under normal conditions since they are rapidly and irreversibly oxidized to form μ-oxo dimers. So that this oxidation could be prevented, "protected" porphyrins such as picket-fence and cap porphyrins have been synthesized and their oxygenation reactions studied extensively.[1] We now present the first IR evidence for the formation of "base-free" O_2 adducts of "unprotected" ferrous porphyrins with use of matrix cocondensation techniques. Since Fe(TPP) itself is highly air-sensitive, we have developed the following procedure to prevent its oxidation.

A stable, "base-bound" complex, Fe(TPP)(pip)$_2$ (pip: piperidine),[2] was placed inside the Knudsen cell of our matrix isolation system and heated in a vacuum of 10^{-6} torr at 370 K for 4 h until the vacuum gauge indicated complete dissociation of the base from the complex. The "base-free" Fe(TPP) thus obtained was vaporized from the Knudsen cell at 430 K and cocondensed with pure Ar or O_2 diluted in Ar on a CsI window that was cooled to $\sim$15 K by a CTI Model 21 closed-cycle helium refrigerator. The IR spectra were measured on a Beckman Model 4260 IR spectrophotometer with a 25 cm^{-1}/in. chart expansion and 5 cm^{-1}/min chart speed.

Trace A of Figure 1 shows the IR spectrum of Fe(TPP) in an Ar matrix. As is expected, this spectrum is very similar to those of Co(TPP)[3] and Mn(TPP)[4] because the spectra in the 1600–500 cm^{-1} region are dominated by the TPP vibrations. When Fe(TPP) vapor was cocondensed with $^{16}O_2$/Ar ($^1/_{10}$), two new bands were observed at 1195 and 1106 cm^{-1}, as is seen in trace B. Similar spectra were obtained in pure $^{16}O_2$ amd more diluted $^{16}O_2$/Ar ($^1/_{300} - ^1/_{1000}$) matrices. These results suggest that the O_2 adduct has the 1:1 (O_2/Fe) stoichiometry. The bands at 1195 and 1106 cm^{-1} were shifted to 1127 and 1043 cm^{-1}, respectively, by the $^{16}O_2$–$^{18}O_2$ substitution (trace C). The observed isotopic shifts of these bands (68 and 63 cm^{-1}, respectively) are in perfect agreement with that expected for a perturbed diatomic molecule. Thus, we assign both bands to the $\nu(O_2)$ of "base-free" adduct, Fe(TPP)O_2.
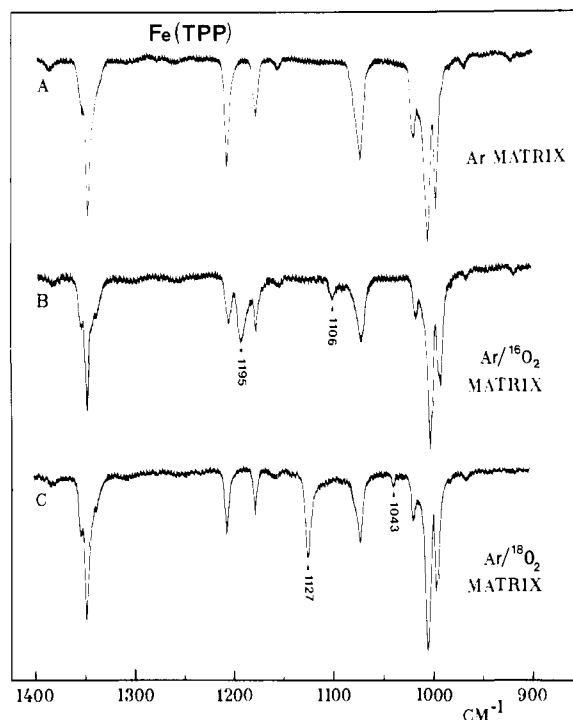

Figure 1. Infrared spectra of (A) Fe(TPP) in Ar matrix, (B) Fe(TPP) cocondensed with $^{16}O_2$/Ar ($^1/_{10}$), and (C) Fe(TPP) cocondensed with $^{18}O_2$/Ar ($^1/_{10}$) at $\sim$15 K. The purity of $^{18}O_2$ gas was 95.2%.

The appearance of two $\nu(O_2)$ bands for Fe(TPP)O_2 is intriguing. The weaker band at 1106 cm^{-1} is not due to Fe(TPP)(pip)O_2 since exactly the same spectrum was obtained when Fe(TPP)(py)$_2$ was used as the starting complex. The possibility of Fermi resonance with the first overtone of the $\nu(FeO)$[5] or a porphyrin mode[6] is remote since both $^{16}O_2$ and $^{18}O_2$ adducts exhibit the same number of bands without any shifts of the TPP vibrations. The matrix site effect does not seem to be responsible since the intensity ratio of the two bands remains unchanged in a variety of matrix environments. In fact, a thin film of Fe(TPP) reacted with O_2 exhibits spectra similar to those shown in Figure 1. If this film is warmed up, the 1195-cm^{-1} band gains intensity at the expense of the 1106-cm^{-1} band. Although the latter disappears completely at $\sim$100 K, recooling to $\sim$15 K recovers its original intensity. These observations suggest that there are two isomers of Fe(TPP)O_2 and that isomer I (1195 cm^{-1}) is stable up to 240 K (at which it decomposes), whereas isomer II (1106 cm^{-1}) is converted to isomer I by raising the temperature up to $\sim$100 K. These two isomers may differ in the spin state of Fe(II) or the Fe–O–O geometry or both. At present, a more detailed and thorough study is in progress to understand the nature of these isomers.

It should be noted that the order of $\nu(O_2)$ of "base-free" adducts is Co(TPP)O_2 (1278 cm^{-1})[3] > Fe(TPP)O_2 (1195/1106 cm^{-1}) > Mn(TPP)O_2 (983 cm^{-1}).[4] The O_2 in Mn(TPP)O_2 is approximated by the peroxide (O_2^{-2}) ion.[7] The O_2 of "base-free" Co(TPP)O_2 is much more positive than that of "base-bound" Co(TPP)(N-MeIm)O_2 (1142 cm^{-1}),[8] which is regarded as the superoxide (O_2^-) type.[9] Thus, we conclude that the negative charge on the O_2 of "base-free" Fe(TPP)O_2 is between these two extremes and probably close to O_2^-. Although the nature of the Fe–O_2 interaction in "base-bound" adducts is controversial,[10] the present IR

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study seems to favor the superoxide($Fe^{III}O_2^-$)[11,12] over the neutral O_2 ($Fe \rightleftarrows O_2$) model,[13,14] since even the O_2 in "base-free" Fe(T-PP)O_2 is close to O_2^-.

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Conformation of the Progesterone Side Chain: Resolution of the Apparent Conflict between X-ray Data and Force-Field Calculations Using MM2

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Recently, Duax et al.[1] analyzed crystallographic data on 85 20-oxopregnanes and found that in virtually all cases the value for τ (the C(16)–C(17)–C(20)–O(20) torsional angle) lay between 0 and $-46°$ (see Figure 2 in ref 1). They inferred a "conflict between X-ray data and force-field calculations", since such calculations,[2] as well as earlier quantum mechanical calculations,[3] give a minimum energy value for τ of $-60°$. Duax et al.[1] reject the proposal of Schmit and Rousseau[2] that this deviation comes from crystal packing forces. Moreover they conclude that the 6 kcal/mol barrier to complete rotation around τ calculated by Schmit and Rousseau is unrealistically low and that this barrier "might be better represented by rigid-molecule results", suggesting values in excess of 50 kcal/mol, with the $\tau = 120°$ conformation about 25 kcal/mol higher than the $\tau = -30°$ conformation.

In this communication we show that the apparent conflict is due to the use of an inadequate force-field model and that the putative discrepancies are not observed when energy refinement using MM2CDC (hereafter referred to as MM2)[4] is employed. As part of our studies of steroid structures, we carried out force-field calculations on a number of corticosteroids, as well as on models for the steroid D ring. For compounds without a 16β substituent the minimum-energy τ values range from -4 to $-20°$, with generally small deviations from the crystal values (Table I).

As noted by Duax et al.[1] steroids with a 16β substitution have crystal structures with $\tau = -109°$ as well as $-20°$. Our calculations on 16β substituted and unsubstituted steroids (Figure 1) show a number of local minima in the torsional potential in both series,

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(4) MM2 is available from the Quantum Chemistry Program Exchange (Allinger, N. L.; Yuh, Y. H. *QCPE*, **1980**, *12*, 395. Profeta, S., Jr. *QCPE Bull.* **1981**, *1*, 57). These programs contain the carbonyl force field discussed herein. The calculated τ values reported in Table I represent those obtained by energy minimization of the crystal-structure coordinates. The functions in Figure 1 were derived by fixing τ to a given value and refining the remaining degrees of freedom.

Table I. Comparison of Selected τ Values from X-ray and MM2 Calculations

molecule	X-ray	MM2
progesterone	-6.6	-4.2
16β-methylprogesterone	-108.0	-110.0
21-hydroxyprogesterone	-11.1	-4.6
cortisone	-28.9	-19.7
cortisol	-30.1	-19.4
9α-fluorocortisol	-26.8	-18.0
9α-chlorocortisol	-28.2	-18.4
9α-bromocortisol	-18.4	-17.7
9α-fluorocortisone	$-(28.9)^a$	-20.4
17α-progesterone acetate	-18.9	-8.9
6α-methyl-9α-fluoroprednisolone	$-16, -32$	-18.0
6α-hydroxyprogesterone	-9.0	-4.0

^{a} This structure generated by adding a 9α-fluorine atom to the heavy-atom coordinates of cortisone.
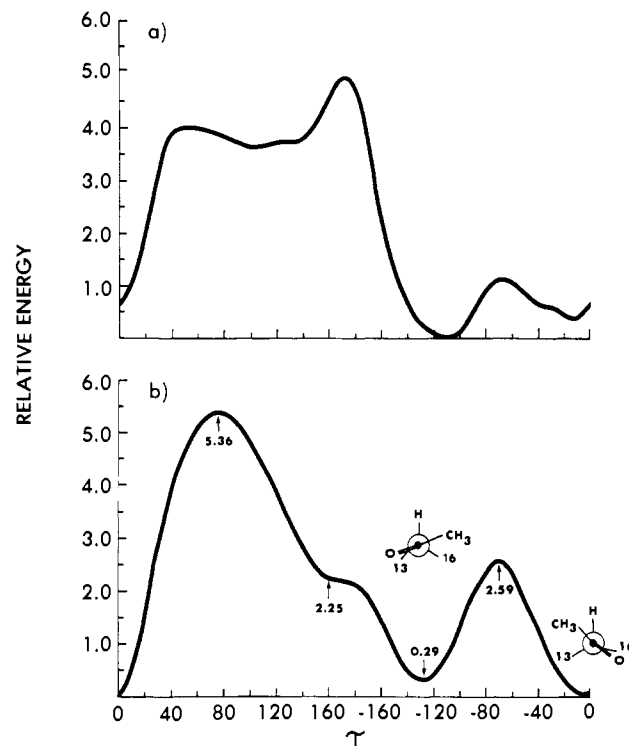

Figure 1. (a) Energy as a function of $f(\tau)$ for 16β-methylprogesterone (II); units of energy in kcal/mol. (b) Energy as a function of $f(\tau)$ for progesterone (I); units of energy in kcal/mol.

the relative energies of which are determined by steric interactions when the C=O bond is close to elipsing the adjacent C–C bond. The local minima in the potential at $\tau = 0$ and $-120°$ come from the tendency for the C=O to eclipse the C(16)–C(17) and C(13)–C(17) bonds, respectively.

The MM2 force field for aliphatic carbonyl compounds[4] was developed by one of us (S.P.) to model the tendency of aliphatic groups to eclipse carbonyl groups. Additionally, the torsional potentials in MM2 have been confirmed for accuracy by ab initio calculations[5,6] at several levels. These ab initio rotational potentials show a clear preference for carbonyl groups to eclipse methyl (or methylene) groups relative to eclipsing hydrogens.[7] Carbonyl

(5) Profeta, S., Jr.; Allinger, N. L., unpublished data. This work details STO-3G and 6-31G calculations of the rotational potential functions of 2-butanone, 2-pentanone, and 3-pentanone. Similar calculations were also performed on the conformers of 2-methylcyclohexanone. In all cases, both calculation and experiment indicate at least a 1 kcal/mol preference for the C=O/C—C eclipsed conformation over the C=O/C—H.

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