In support of the contention that a CN groups exerts only a small effect is that in both the ethane–propionitrile and ethylene–acrylonitrile pairs the CN causes about a 5% change in J_{cc}: 34.6[18] and 33 Hz[21] for the former and 67.6 and 70.6 Hz for the latter pair, respectively. In addition the nitrile group on bicyclobutane changes the C_1–C_2 coupling from 21[20] to 22 Hz or also about 5%. In the subsequent discussion the effect of the nitrile group on the coupling constant will therefore be ignored.

By using the C_2–H_{exo} and C_2–H_{endo} coupling constants of 158.3 and 174.0 Hz, respectively,[14] the Muller–Pritchard relationship,[11] and assuming the equivalence of the C_1–C_2 and C_2–C_3 bonds, it can readily be shown that the orbitals on C_2 bonding to C_1 and C_3 contain 16.8% s character each. From the observed coupling constant of 22 Hz and eq 1 the orbitals on carbon 3 (and 1) bonding to C_2 and C_4 contain 23.8% s character.[22] This means, therefore, that the peripheral bonds are $sp^{3.20}$–$sp^{4.95}$ and C_2 and C_4 are cyclopropane like. Now since J_{C_3-H} = 207.8 Hz[14] and the total s character around C_3 = 1.00 this would leave 10.8% s character for the C_3 orbital bonding to C_1, or $sp^{8.26}$. Once again the "direct" measurement (assuming the validity of the hybridization–coupling constant equations) gives 17.1% s character or $sp^{4.85}$. Thus there is a 6% error in the value calculated using unity for total s character as compared with that obtained directly. Errors of this magnitude are often observed in other compounds.[23] Thus estimates of the s character of an orbital from the sum of s characters of the other orbitals around a carbon atom obtained from coupling constants should be done with due caution.[20]

The above discussion assumed the validity of the coupling constant–hybridization relationships and pointed up the error involved in extrapolating from several known to an unknown hybridization. Of utmost importance are the suggestions that these equations are inappropriate to highly strained small ring systems.

For most saturated systems the orbital and dipolar terms are small and for unstrained systems the contact term is large and positive and predominates.[24] However, recently Schulman and Newton[19] have refined their original INDO calculations[6] and shown that for bicyclobutane, 1-cyanobicyclobutane, and benzvalene the 1,3 bond is abnormal in that the contact term is not large and positive but rather small and perhaps negative as are the dipolar and orbital terms. Thus Schulman and Newton calculate a value of +23.4 Hz for the C_1–C_2 coupling constant in bicyclobutane and −7.9 Hz for the C_1–C_3 coupling constant. The corresponding calculated value for the C_1–C_3 coupling constant in 1-cyanobicyclobutane is −8.0 Hz.[25] Other calculations predict a positive value for the C_1–C_3 coupling constant and in particular the maximum overlap method[5,12] predicts 17.8 Hz. The corresponding calculated C_1–C_2 coupling constant[5,12] is 19.4 Hz. It is amusing to point out that the simplest calculations[4] predict a C_1–C_2 coupling constant of 20 and 15 Hz for the sp^2 and sp model, respectively, and a C_1–C_3 coupling constant of 27 and 15 Hz for these respective bicyclobutane models assuming the validity of eq 1.

In conclusion, since the contact term for the C_1–C_2 bonds in bicyclobutane is rather normal according to the INDO calculations, the calculated value for the coupling constant by most methods agrees with that observed. On the other hand these more sophisticated calculations show an abnormality in the C_1–C_3 contact term and suggest a negative coupling constant as opposed to other calculations, such as maximum overlap, which predicts a positive sign. We plan to obtain the sign of the coupling constant experimentally. Of course if J is indeed negative the coupling constant–hybridization relationships cannot therefore apply to these highly strained microcyclic systems.

Acknowledgment. We wish to thank Dr. S. C. Cherkofsky of E. I. du Pont de Nemours for a generous gift of the cyanobicyclobutane M. P. wishes to thank the Chemistry Department of the University of Wisconsin for their hospitality and support during the fall of 1972 while a Visiting Professor and Professor J. M. Schulman for informative discussions and results of unpublished calculations.

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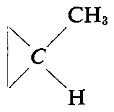
[21] G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).

[22] See ref 18 for a discussion of the C_1–C_2 bonds in bicyclobutane itself.

[23] The sum of the s character of the bonds around the italicized carbon atom is given in parentheses. The value should be compared to unity: PhC≡*C*H (1.07);[15] PhC≡*C*CH$_3$ (1.04);[15] and



(using 161 Hz for the C–H and 13 Hz for the C–C coupling,[17] 0.95).

[24] A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).

[25] It should be pointed out that the observation that the calculated values for $J_{C_1-C_3}$ do not differ supports the idea that the nitrile group exerts only a minimal pertubation on the ring system.

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Solution Behavior of a Synthetic Myoglobin Active Site

Sir:

We recently described[1] the synthesis of a section of the myoglobin active site[2,3] which is capable of binding oxygen as a solid material. The compound and its derivatives are shown in Figure 1.

We now report the rather spectacular solution behavior of this compound. The hemin II was dissolved in 3 ml of methylene chloride at about 10^{-4} *M* concentration. This solution was shaken at 25° with 0.05 ml of a (pH 7) phosphate buffer containing an excess of sodium dithionite. The resulting solution had a broad band centered at 545 nm which is remarkably similar to that of deoxymyoglobin.[3] Cooling this solution to

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[1] C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S.*, in press.

[2] (a) J. H. Wang in "Oxygenases," O. Hayaishi, Ed., Academic Press, New York, N. Y., 1962, p 502; (b) J. H. Wang in "Heamatic Enzymes," Part 1, J. E. Falk, R. Lemberg, and R-K. Morton, Ed., Pergamon Press, New York, N. Y., 1961, p 98.

[3] E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands," North Holland Publishing Co., Amsterdam, 1971, p 76.

Table I. Spectra of Heme Compounds I–IV and Deuteromyoglobin Derivatives

	Reduced			CO			O_2		Met (pH 7)		
	Soret	β	α	Soret	β	α	Soret	α	Soret	β	α
Deuteromyoglobin[a]	421	544		409	528	554	532	565	393	496	620
Compounds I–IV[b] (CH_2Cl_2) (25°)		545		412	528	555					
Compounds I–IV[b] (CH_2Cl_2) (−45°)		517	545	412	527	556	530	562	388	500	628
Compounds I–IV (solid)[c]		522	548	412	528	555	530	564	389	500	628

[a] A. Rossi-Fanelli and E. Antonini, *Arch. Biochem. Biophys.*, **72**, 243 (1957). [b] This work. [c] Reference 1.

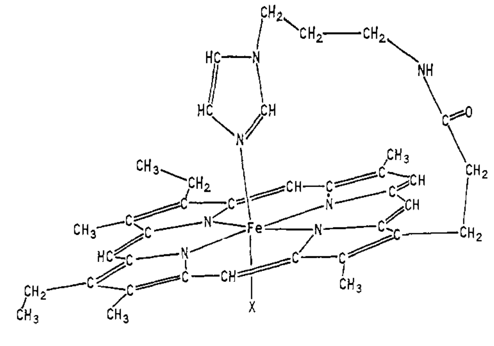

Figure 1. Structure of pyrroheme-*N*-[3-(1-imidazolyl)propyl]-amide and its derivatives: I, X = no substituent or H_2O, Fe^{II}; II, X = Cl, Fe^{III}; III, X = O_2, Fe^{II}; IV, X = CO, Fe^{II}.

−45° in a liquid propane bath precipitated the water and caused the broad peak at 545 nm to split into two sharp peaks at 517 and 545 nm (Figure 2A). When oxygen was admitted to this solution at −45°, an immediate color change occurred and spectrum 2B was obtained. Replacing the oxygen atmosphere over the solution with carbon monoxide resulted in spectrum 2C, and a brief photolysis with a General Electric photoflood under vacuum produced spectrum 2D, identical with 2A.[4] When the carbon monoxide complex having spectrum 2C was warmed to room temperature, no change occurred. Addition of excess pyridine to the oxygen complex at −45° resulted in a typical pyridine–hemochrome spectrum.

Warming the oxygen complex III to room temperature resulted in the oxidation of the heme to give II.

The maxima for the α and β peaks in Figure 2 are listed in Table I along with those of deuteromyoglobin.[4]

These experiments clearly show, contrary to a number of previous conclusions, that this simple heme compound reversibly binds oxygen in solution and that the iron is not oxidized. We attribute the successful oxygen complexation to two factors. First, the neighboring group effect of the covalently attached imidazole increases oxygen binding. Secondly, the reaction

$$\text{heme-}O_2\text{ (III)} + \text{heme (I)} \longrightarrow 2\text{hemin (II)} \qquad (1)$$

apparently has an activation energy which causes this reaction to be very slow at low temperature. This activation energy, combined with the reduction of the concentration of free heme in solution, causes a severe reduction in the rate of heme oxidation.

The striking similarity of the spectra of compounds I, III, and IV to the deoxy, oxy, and carboxy forms of deuteromyoglobin seen in Table I strongly support the proposed one-to-one stoichiometry of complex III and the theory[1] that simple biological reactions such as oxygen binding do not require the protein.

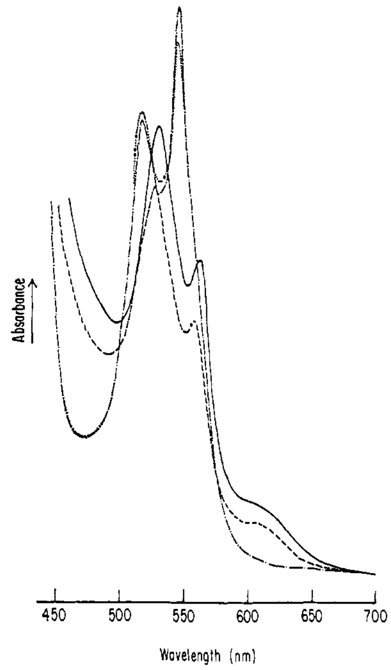

Figure 2. Visible spectra of a methylene chloride solution of pyrroheme-*N*-[3-(1-imidazolyl)propyl]amide (II) and its derivatives at −45° as described in the text and in Figure 1: (A) —·—·—, I, from dithionite reduction; (B) —, III, obtained by adding oxygen to I; (C) - - -, IV, from replacing O_2 gas with CO gas; (D) . . . ., I, obtained from photolysis of IV.

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Mechanism of 1,5-Hydrogen Migration in Diene Iron Carbonyl Complexes

Sir:

We wish to report a mechanistic investigation of a novel rearrangement of diene iron tricarbonyl complexes. When any of a variety of substituted cyclohexadiene–iron tricarbonyl complexes are heated in refluxing xylene for several hours, isomerization resulting from 1,5-hydrogen migration is observed. For example, the phenyl substituted compound **1**[1] is

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[4] In a separate experiment, the oxygen complex was filtered at −45° to remove the ice and excess dithionite before the remaining experiments were done. The results were the same as those with the unfiltered sample.

(1) This compound[2] was prepared as a mixture with **2**[2] by photolysis of phenylcyclohexadiene[3] with $Fe(CO)_5$. The isomers were separable by column chromatography on alumina.

(2) This compound had acceptable elemental analysis.

(3) C. F. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Amer. Chem. Soc.*, 77, 1802 (1955).