frequencies as those for the photointermediate for bands IV and V. We thus infer that photolysis of COHb leaves Fe^{II} transiently in the heme plane but changes the spin state from $S = 0$ (in the COHb ground state) to $S = 2$ within 30 ps. This must occur in an excited state, since the thermal interconversion rate between $S = 0$ and $S = 2$ states in Fe^{II} complexes lies in the 10^7-10^8-s^{-1} range.[21]

The 576-nm pulses excite the lowest porphyrin singlet π-π^* (Q) state. Although this or the corresponding π-π^* triplet state might be directly responsible for CO photodissociation,[22] the energy also could funnel into a lower-lying ligand field state, as suggested by Shank et al.[8] Eaton et al.[23] place the $^1T_1$ state of COHb just below the Q state; the lowest energy state is estimated to be $^3T_1$ but $^5T_1$ is nearby.[10] The latter is the most plausible parent state for a high-spin photoproduct. "CO photodissociation" may leave the iron porphyrin structure in spin and geometry similar to the "dissociative" excited state.[24] (The large Franck-Condon factor for such a channel would imply a fast dissociation rate.) The broadened deoxyHb-like absorption spectrum detected by Greene et al.[10] within 8 ps of photolysis may be associated with the in-plane, high-spin photointermediate suggested by the Raman spectrum.

The broadened absorption is found to last 680 ps following photolysis,[10] and the Raman frequency lowering relative to deoxyHb persists to 10 ns.[5c] The middle spectrum of Figure 1 shows that the frequencies are the same when the photolysis pulse is widened even to 20 ns. The agreement between this spectrum and that obtained with the YAG laser pulses[5c] is important since the pulse energy of the latter (20 mJ) is much higher than in our experiment (6 nJ) and might have produced multiphoton effects. Further RR experiments in a time scale longer than 20 ns are needed to determine the time required for the iron atom and its proximal imidazole ligand to move away from the heme plane to its characteristic position in deoxyHb.[25]

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Can Cyclopropyne Really Be Made?

Sir:

Monocyclic, otherwise saturated acetylenes, are of considerable current interest in organic chemistry. For example, Anet and Rawdah[1] recently examined the major conformational features of cyclododecyne (twelve carbon atoms, one triple bond) using DNMR. A question of long-standing and fundamental interest concerns the size of the smallest possible, otherwise saturated ring containing a triple bond. The smallest such ring for which a complete structural determination is available is apparently cyclooctyne. However, Chapman[3] has recently synthesized the much smaller cyclopentyne and has speculated that both cyclobutyne and cyclopropyne should exist.

We were uncertain as to whether the triple-bond cyclopropyne species is a relative minimum on the C_3H_2 potential surface. Minimum basis set SCF studies by Pople and coworkers[4] suggest that the singlet lies considerably above the vinylidene $CH_2{=}C{=}C{:}$. Further, preliminary theoretical work here raised the possibility that the singlet isomerization to propadienylidene (eq 1) might proceed with no barrier at

(1)

all. For these reasons it was decided to pursue this possibility in theoretical detail and also examine triplet cyclopropyne. The results should provide definitive answers concerning the ultimate limit of stability of cyclic alkynes.

The first step in the present research was to determine the equilibrium geometries of singlet and triplet ($^3B_2$) cyclopropyne within the constraint of C_{2v} symmetry. For this purpose a standard double zeta (DZ) basis set,[5] labeled C(9s 5p/4s 2p), H(4s/2s), was chosen. From the fact that Hehre et al.[4] used complex molecular orbitals to describe singlet cyclopropyne, this species is expected to have considerable diradical character. Therefore a two-configuration self-consistent-field (TCSCF) procedure[6] was adopted:

$$\psi = c_1 2b_1^2 6a_1^2 + c_2 2b_1^2 3b_2^2 \qquad (2)$$

At the predicted equilibrium geometry for the $^1A_1$ state, the two mixing coefficients are $c_1 = 0.933$ and $c_2 = -0.359$. For the $^3B_2$ state a single configuration description—$2b_1^2 6a_1 3b_2$—is appropriate. Constrained C_{2v} equilibrium structures were determined using recently developed gradient procedures[7] for open-shell and multiconfiguration SCF wave functions. The predicted structures are seen in Figure 1.

The location of C_{2v} minima for singlet and triplet cyclo-

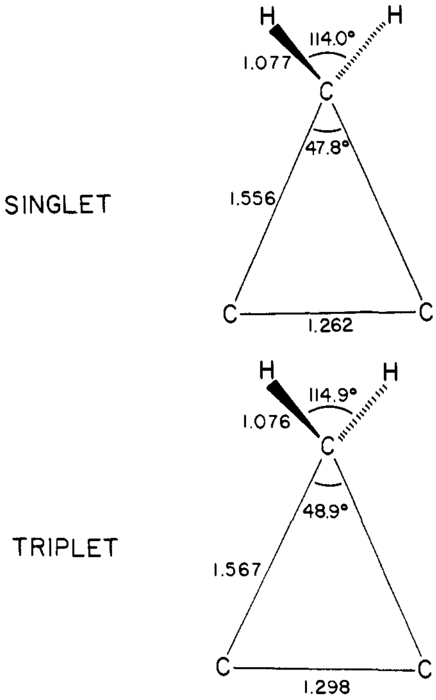

Figure 1. Constrained C_{2v} equilibrium geometries for singlet and triplet cyclopropyne. As discussed in the text, the singlet structure is not a genuine relative minimum on the C_3H_2 potential energy surface.

Table I. Displacement of the Methylene Group from Its Constrained C_{2v} Equilibrium Position in Singlet Cyclopropyne[a]

	DZ TCSCF	DZ + *P* TCSCF	DZ CI
absolute C_{2v} energy, hartrees	−114.46490	−114.54008	−114.70296
relative C_{2v} energy, kcal	0	0	0
$d = 0.05$	−0.03		
$d = 0.10$	−0.12		
$d = 0.20$	−0.57	−1.63	
$d = 0.40$	−4.96	−6.96	−0.26
$d = 0.80$	−17.84	−18.33	−9.69

[a] See text for a description of the displacement *d*.

Table II. Predicted Harmonic Vibrational Frequencies for $^3B_1$ Cyclopropyne

symmetry	frequency, cm^{-1}	description
b_1	3400	asymmetric hydrogen stretch
a_1	3300	symmetric hydrogen stretch
a_1	1840	symmetric $C\equiv C$ stretch
a_1	1650	symmetric hydrogen bend
a_2	1170	asymmetric hydrogen bend
b_2	1170	hydrogen wag
a_1	1040	symmetric ring stretch
a_2	900	torsion
b_2	700	asymmetric ring stretch (opening)

Table III. Relative Energies[a] of Singlet and Triplet C_3H_2 Isomers

	DZ SCF	DZ + *P* SCF	DZ CI	DZ + *P* CI
triplet cyclopropyne	68.0	56.3	65.1	55.0
singlet cyclopropyne[b]	59.8	44.3	58.7	45.4
triplet $H_2C{=}C{=}\dot{C}\cdot$[c]	22.6	21.3	34.5	32.5
singlet $H_2C{=}C{=}C{:}$[c]	0	0	0	0

[a] In kilocalories/mole. [b] Constrained C_{2v} equilibrium geometry; not a true relative minimum. [c] Singlet and triplet propadienylidene structures were separately optimized at the DZ TCSCF and SCF levels of theory, respectively.

propyne by no means guarantees that these minima are genuine, i.e., stable with respect to the four remaining nuclear degrees of freedom. In fact, our very first chosen distortion of singlet cyclopropyne proved to be an energetically downhill pathway. This choice was simply to displace the entire methylene group in a manner parallel to the $C\equiv C$ triple bond, that is, if the z axis coordinates of the unique C and two H atoms are increased (relative to their C_{2v} equilibrium positions) by a constant displacement d. Since the singlet potential surface is quite flat with respect to this displacement, several more complete levels of theory were examined. First polarization basis functions [orbital exponents $\alpha(d_c) = 0.80$, $\alpha(p_H) = 1.0$] were added at the TCSCF level. Returning to the double zeta basis set, configuration interaction (CI) was performed including all single and double excitations relative to the two reference configurations[8] in eq 2. With the three lowest occupied TCSCF orbitals held doubly occupied in all configurations and the three highest virtual orbitals deleted, this amounts to 11 178 configurations when only the three-carbon plane of symmetry is retained.

Table I summarizes the present results for the above-described displacement d. Given that no attempt has been made to vary geometrical parameters other than d, it is apparent that singlet cyclopropyne is not a genuine relative minimum, but freely distorts via eq 1 toward propadienylidene, $H_2C{=}C{=}C{:}$.

Since $^3B_2$ cyclopropyne was energetically stable with respect to distortions of the general type outlined in Table I, a more complete vibrational examination was deemed necessary. Using analytical first derivatives, the quadratic cartesian force constants were obtained numerically[9] and subjected to a standard harmonic vibrational analysis. These results are summarized in Table II, which demonstrates that triplet cyclopropyne is a true relative minimum. However, experience suggests that the predicted DZ SCF vibrational frequencies are too high, typically by ~10%. Thus it would appear that, at least in principle, triplet cyclopropyne is "makable".

Finally, the relative energies of singlet and triplet cyclopropyne and propadienylidene are summarized in Table III. The DZ + *P* CI wave functions included 23 738, 14 804, 23 360, and 14 365 spin and symmetry (C_{2v}) adapted configurations, respectively. When polarization functions and correlation effects are simultaneously considered, the energy of cyclopropyne is lowered from 68 to 55 kcal relative to singlet $H_2C{=}C{=}C{:}$. Thus while triplet cyclopropyne lies considerably lower than previously suggested,[4] it remains, as expected, an energy-rich species. The simplest (and perhaps best) explanation of why the triplet three-membered ring is a relative minimum while the singlet is not is the fact that the former diradical species contains a double, rather than triple, bond. Although the C_{2v} constrained singlet cyclopropane has some diradical character, the unique C—C bond is of order ~2.85, i.e., much closer to a triple than a double bond.

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