oxidation of **6** to **8** proceeds via the valence isomer of **6**, dibenzoyldiphenylisobenzofuran. Reduction of **8** with Ph_3P in benzene or KI in AcOH afforded **7** in good yield. This reduction is analogous to that of IV to II with the same reagents.[2a] Heating of **8** in benzene under reflux for 2 h afforded **7**[9] (7%) (mp 234.5–235.5 °C; ν_{max} 1670 cm^{-1}; λ_{max} 266 nm (ϵ 44 300); ^1H NMR δ 1.12 (s, 18 H), 7.1–7.7 ppm (br s, 20 H)), **11** (48%) (mp 212–213 °C; ν_{max} 3350, 1670 cm^{-1}; ^1H NMR δ 1.30 (s, 9 H), 6.9–8.0 ppm (m, 20 H)), and **13** (3%) (mp 120 °C; ν_{max} 1740, 1670 cm^{-1}; ^1H NMR δ 1.15 and 1.25 (each s, 9 H), 7.0–8.3 ppm (m, 20 H)). This thermal reaction is contrasted with that of IV which affords III mainly in addition to II and some other products.[2a] A reasonable interpretation for this contrast is as follows. Intermediate **12**[2b] of the thermal conversion of **8** into **13** is unfavorable, because of steric crowding between *t*-Bu and Ph groups. Therefore, the pathway which proceeds via the sterically less hindered intermediate, **10**, and leads to **11** by the elimination of isobutylene from **10**, is favorable.

Very interestingly, however, oxidation of **1** in solid state gave **14** mainly. Keeping crystals of **1** in room for 5 days afforded **7** (13%) and **14** (50%): mp 250–251 °C; ν_{max} 1660, 1640 cm^{-1}; λ_{max} 253 nm (ϵ 26 700), 304 (27 400), 320 (sh) (25 900), 335 (sh) (18 500); ^1H NMR δ 0.81 and 0.82 (each s, 9 H), 7.1–8.1 ppm (m, 20 H); ^{13}C NMR δ 30.3 and 32.1 (C_{10}), 34.5 and 35.7 (C_9), 131.9 and 134.4 (C_2, C_5), 141.5 (C_4, C_6), 154.2 (C_1, J_{16} = 35.2 Hz), 192.4 ppm (C_3, J_{34} = 50.8 Hz). Because this oxidation was also performed in the dark, **14** would be produced by the attack of $^3O_2$ on the 3,4 positions of **1**, and **7** would be produced by the attack of two $^3O_2$s on the 4,5 and 9,10 positions. *o*-Quinomethide is unstable and only a few derivatives have been isolated.[10] Stability of **14** is probably due to the reason that the aromatization of its six-membered ring should produce an unfavorable benzocyclobutadiene system. However, acid-catalyzed reaction of **14** with nucleophile easily afforded **15**, stability of which would presumably be due to the same reason as above. Treatment of **14** with H_2SO_4 in aqueous acetone and MeOH at room temperature for 1 h afforded **15a** (80%) (mp 251–253 °C; λ_{max} 305 (sh) nm (ϵ 30 000), 315 (31 900), 330 (sh) (20 500)) and **15b** (83%) (mp 255–256 °C), respectively. Heating of **15a** and **15b** with H_2SO_4 in acetone under reflux for 2 h afforded **15c** (mp 267–268 °C) in 66 and 61% yields, respectively. UV spectra of **15b** and **15c** were comparable with that of **15a**.

It is not clear why oxygen attacks on the different positions of **1** depending on whether the oxidation is carried out in the presence or absence of solvent. Nonetheless, the present work would finally show that the oxidation of benzocyclobutadiene in solvent proceeds successively via cyclobutadiene oxide and isobenzofuran peroxide.

Acknowledgment. We are grateful to Dr. G. Rio for informing us of his unpublished spectral data of 1,3-diphenylisobenzofuran peroxide (IV) and to Drs. T. Oshima and M. Hatakenaka for the measurements of ^{13}C NMR spectra.

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(5) ^{13}C NMR signals of the six-membered ring carbons (C_1–C_6) of **6**, **8**, and **14** were assigned by measuring the spectra of each the two samples enriched by ^{13}C isotope (~40% each carbon) on 2,5 and 1,3,4,6 positions.

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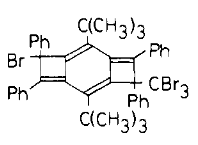

i

(9) Previously reported physical and spectral data for **7**[3] should be corrected to read as those described in this paper.

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Structure of 1,4,8,11-Tetrathiacyclotetradecanecopper(I) Perchlorate: Comparative Geometries of Analogous Copper(I) and Copper(II) Complexes

Sir:

The geometry of copper complexes has been implicated as an important factor in copper redox chemistry.[1] Arguments involving the role of coordination geometry in copper protein chemistry have been especially prominent[1,2] even though only one copper protein structure has been reported to date.[3] A wide variety of structure types has been found for low molecular weight Cu(II)[4] and Cu(I)[5] complexes with Cu(II) favoring

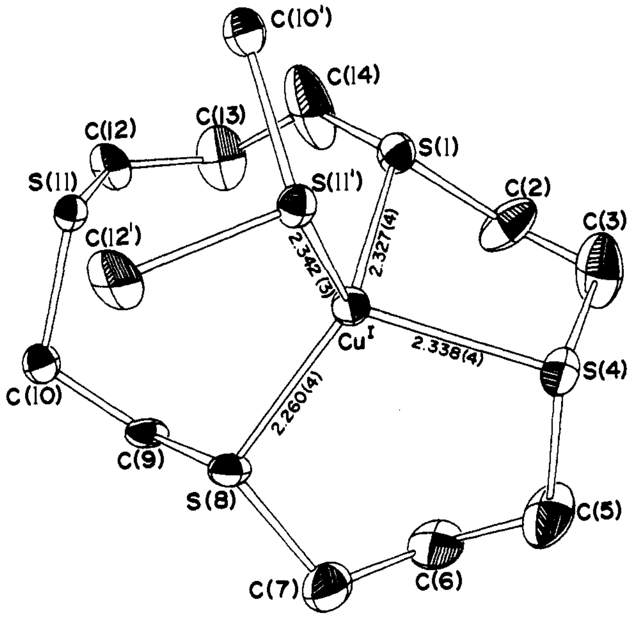


Figure 1. The $Cu^I(14\text{-ane-}S_4)(ClO_4)$ subunit with atomic labeling. Atoms C(10′), S(11′), and C(12′) belong to the adjacent ligand molecule and atom S(11) is bonded to an adjacent Cu(I) ion.

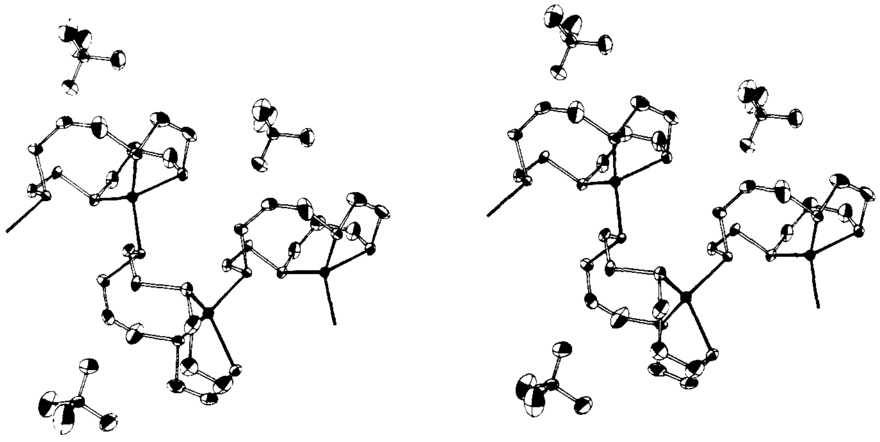
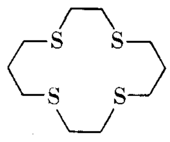


Figure 2. Stereoscopic view of the Cu^{I}(14-ane-S$_4$)(ClO$_4$) polymer showing the novel 3:1-coordination pattern. (The Cu-S bonds are darkened for easier identification.) The adjacent subunits are related by a 2_1 screw axis in the b direction.

tetragonal coordination and Cu(I) favoring tetrahedral (as well as trigonal and digonal) coordination. Since the Cu(I) structures, in particular, appear to be strongly influenced by the nature of the coordinated groups, the lack of corresponding structural data for Cu(II) and Cu(I) compounds with exactly the same set of donor atoms has prevented a direct evaluation of the geometric effect associated solely with the change in the oxidation state of copper.

We wish to report at this time the crystal structure of a Cu(I) compound for which the crystal structure of the analogous Cu(II) compound is also available. The compound involved, 1,4,8,11-tetrathiacyclotetradecanecopper(I) perchlorate, Cu^{I}(14-ane-S$_4$)(ClO$_4$), also represents the first macrocyclic Cu(I) complex which has been successfully crystallized and structurally characterized.



14-ane-S$_4$

In the previously reported structure of Cu^{II}(14-ane-S$_4$)(ClO$_4$)$_2$,[6] the copper(II) ion was found to be coplanar with the four sulfur donor atoms, with loosely interacting perchlorate ions along the perpendicular axis. The solid-state structure[6] and the solution thermodynamic stability of this complex (relative to complexes involving related ligands of other ring sizes)[7] suggest that this ligand provides an optimal fit for planar coordination around Cu(II). Since the 14-ane-S$_4$ ligand is incapable of attaining a tetrahedral array of sulfur atoms with normal Cu-S bond distances, it seemed feasible that a planar Cu(I) geometry might obtain in the reduced complex. Instead, we find in Cu^{I}(14-ane-S$_4$)(ClO$_4$) that the four sulfur donor atoms coordinated to Cu(I) form an irregular tetrahedron.[8] However, as a result of the inability of a single 14-ane-S$_4$ ligand to distort sufficiently to accommodate a tetrahedral geometry, the tetrahedral environment is accomplished by coordination of Cu(I) to three sulfur donor atoms from one ligand molecule and a fourth coordinated sulfur from an adjacent ligand molecule (Figure 1). As shown in Figure 2, the result is a stepwise chain polymer involving a novel 3:1 ligand coordination pattern. (In solution, it is likely that the fourth coordination site is occupied by a solvent molecule.) The extent of geometric change is emphasized by the S(1)-Cu-S(8) bond angle which is 129.7° in the Cu(I) complex as compared to 180° in the corresponding Cu(II) complex. The S-Cu-S angles involving adjacent sulfur donor atoms from the same ligand are 88.8 and 106.3° (compared to 90° in the Cu(II) species), whereas the three S-Cu-S angles involving the single sulfur from the adjacent ligand are nearly those of a regular tetrahedron, averaging 110.0° (range 106.7-113.0°).

The average Cu-S bond length of 2.32 Å (range 2.260 (3)-2.342 (3) Å) in the Cu(I) complex is almost identical with that of 2.303 (1) Å found in the corresponding Cu(II) complex. Thus, the change in coordination geometry on going from Cu(II) to Cu(I) is independent of bond length influences and must result solely from a very strong preference of Cu(I) for tetrahedral geometry.

Although the precision of the carbon parameters is limited by the relatively low data/parameter ratio, the apparent bond distances, bond angles, and torsion angles in the ligand framework indicate extensive conformational strain in the portion of the ligand containing the bridging sulfur donor atom. Thus the adoption of tetrahedral coordination in the Cu(I) complex provides direct evidence for an exceptionally large thermodynamic preference for this geometry. Detailed discussion of the strain parameters must await our efforts, in progress, to produce large single crystals and to carry out a complete strain energy analysis on the crystallographic structure as well as on the strain-minimized conformation.

However, the existence of a tetrahedral Cu(I) geometry in this compound, in spite of the incumbent ligand strain brought about by this geometry, indicates that Cu(I) will not exist in a planar environment except under the most severe constraints. This strongly argues against the existence of a geometry approaching planarity in Cu(I) proteins and indicates that the reduction of copper-zinc superoxide dismutase, for example (which is planar in the oxidized form),[3] must be accompanied by significant rearrangements at the active site. Nonetheless, these proteins are characterized by high turnover rates (approaching diffusion limiting rates) suggesting that such geometric rearrangements are not significant barriers to redox catalysis.

The contrasting geometries of the Cu(I) and Cu(II) complexes provide a further example of the considerable flexibility of the 14-ane-S$_4$ ligand. Structural determinations have now been reported in which this ligand is involved in 4-coordinate mononuclear Cu(II) and Ni(II) complexes,[6,9] a 3:1-coordinate polynuclear Cu(I) complex (this work), a 2:2-coordinate binuclear Hg(II) complex,[10] and a 1:1-coordinate binuclear Nb(V) complex.[11] Moreover, the previously reported structures for 14-ane-S$_4$ in both complexed and free forms have shown the ligand to occur as either an exodentate[10-12] or endodentate conformer.[6,9]

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Thermal Isomerization and Fragmentation of 1,1-Difluoro-2,3-dimethylcyclopropane

Sir:

In recent years there has been considerable interest both experimentally and theoretically on the effect of hetero substituents on the structure and reactivity of cyclopropane compounds. Hoffmann and Günter have predicted dramatic changes in the properties of cyclopropane derivatives when electron donors or electron acceptors appear as substituents.[1,2] Richey[3] and Kirmse[4] have provided a number of examples of cases in which alkoxy substituents have been shown to accelerate sigmatropic rearrangements and geometrical isomerizations of cyclopropanes.

Fluorine is of considerable interest as a substituent on cyclopropane owing to its unique but often inscrutable potent π-donor and inductive acceptor properties. Hoffmann and Günter predicted that it would behave as a π donor in cyclopropanes with the net result of lengthening and weakening the C_2-C_3 bond.

Microwave spectra of cyanocyclopropane[5] and nitrocyclopropane[6] tend to corroborate Hoffmann's and Gunter's predictions as to the effect of π acceptors, but the microwave spectrum and a theoretical structural analysis of 1,1-difluorocyclopropane[7,8] tend to implicate fluorine as an *acceptor.* Nevertheless the lengthening and hence weakening of the C_2-C_3 bond is confirmed by these studies.

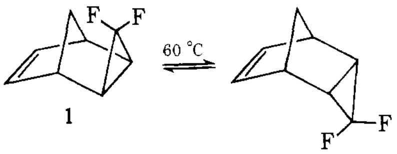
Table I. Equilibrium Constants for the Cis-Trans Isomerization

Temp, °C	297.3	306.3	314.5	325.3	336.4	344.9
K	1.917	1.911	1.890	1.871	1.847	1.828

Table II. Rate Constants for the Cis-Trans Isomerization

Temp, °C	297.3	306.3	317.0	326.3	336.3	344.9
$10^5 k_1$ (s^{-1})	3.96	8.21	16.2	33.6	68.2	116.9

While quantitative confirmation of the enhancement of C_2-C_3 homolytic bond cleavage in *gem*-difluorocyclopropanes has not heretofore been reported, there have been qualitative corroborative reports,[9-11] perhaps the best example being the rapid thermal interconversion of exo and endo isomers **1** and **2** at 60 °C.[11]



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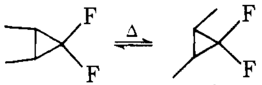
As a first step in our efforts to quantify the effects of fluorine substitution on thermal homolytic processes of cyclopropanes and of hydrocarbons in general,[12] we wish to report our study of the geometrical isomerization and fragmentation of *cis*-1,1-difluoro-2,3-dimethylcyclopropane (**3**).



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cis- and *trans*-1,1-difluoro-2,3-dimethylcyclopropane were synthesized using Burton's method[13] and were purified >99.5% pure by GLC. Pyrolysis at pressures varying from 4-25 mm were carried out in a well-conditioned 200-mL Pyrex vessel[14] which was heated in a fused-salt, high temperature thermostat. The reaction was found to follow good reversible first-order kinetics throughout. Equilibrium constants were obtained at six temperatures (see Table I) and a plot of ln K vs. the reciprocal of the absolute temperature yielded a ΔH for the cis-trans isomerization of -0.72 ± 0.05 kcal/mol. Rate constants were also obtained at six temperatures (see Table II), and an Arrhenius plot of this data gave a good straight line with the frequency factor and energy of activation being calculated by the method of least squares.

$$k_1 = 14.7 \pm 0.2 \exp(-49700 \pm 600/RT)\ s^{-1}$$

While the reaction was free of hydrogen-shift side reactions, such as those which complicated the pyrolysis of the analogous hydrocarbon,[15] there was observed a significantly higher energy competitive reaction which took place cleanly at a rate of ~1/25 that of the isomerization process. This process was the extrusion of CF_2 to form 2-butenes. Such an extrusion process has previously been observed for perfluoro-, tetrafluoro-, and chlorofluorocyclopropanes[16,17] and for perfluoro epoxides,[18] but to our knowledge has not heretofore been reported for simple *gem*-difluorocyclopropanes. This reaction was examined carefully at 297.3 °C and it was found to take place with high stereospecificity (>96%). Moreover it was found that **3**