that one of the reaction products obtained by heating argentous fluoride and sulfur is the pyrimidal $S{=}SF_2$ form. Seel and Gölitz,[3] using a different synthesis, were also able to establish the existence of the pyrimidal $S{=}SF_2$ form on the basis of its infrared spectrum. Glemser, Heussner, and Haas[4] have also reported a preparation of S_2F_2 but have not drawn any conclusions as to the structure. We are now able to demonstrate that a second isomer of S_2F_2 exists with a nonplanar chain FSSF structure analogous to S_2Cl_2.[5]

The first indication that two isomeric forms of S_2F_2 existed[6] was obtained during the earlier investigation of the $S{=}SF_2$ form.[2] When the crude products of the reaction between AgF and S were volatilized at different rates into the mass spectrometer, a varied cracking pattern was obtained for mass peaks attributable to S_2F_2. In addition, with a sample in the microwave cell at Dry Ice temperature, a set of absorptions was noted whose intensity steadily decreased with a first-order half-life of approximately 15 min. These microwave lines could not be explained by the $S{=}SF_2$ form or known impurities. Both of these properties disappeared when the reaction products were fractionally distilled in order to obtain pure $S{=}SF_2$, presumably due to decomposition of the reactive FSSF species with the distillation apparatus.

In the investigation of the microwave lines from FSSF, it was found possible to enhance their initial intensity by dosing of the bulk reaction product into the absorption cell from slush baths below $-100°$. A complete separation was unnecessary since the characteristic decay rate identified the transitions arising from the FSSF species.

The observed and calculated microwave spectra for this species are listed in Table I. The transitions were assigned on the basis of their Stark effects and agreement obtained with the calculated rigid rotor spectrum. The rotational constants used in the calculations and the derived moments of inertia are listed in Table II

TABLE I

MICROWAVE SPECTRUM OF FSSF[a] (MC./SEC.)

Transition	Observed	Calculated
$0_{00} \rightarrow 1_{11}$	13843.46	13843.47
$1_{01} \rightarrow 2_{12}$	18983.41	(18983.41)[b]
$7_{16} \rightarrow 7_{25}$	23368.35	23366.31
$6_{15} \rightarrow 6_{24}$	23871.05	23869.35
$2_{02} \rightarrow 3_{13}$	24018.83	(24018.83)
$5_{14} \rightarrow 5_{23}$	24355.65	24354.79
$4_{13} \rightarrow 4_{22}$	24798.45	24798.05
$3_{12} \rightarrow 3_{21}$	24178.50	24178.18
$7_{15} \rightarrow 7_{26}$	28806.32	28807.72
$3_{03} \rightarrow 4_{14}$	28954.70	(28954.70)
$8_{18} \rightarrow 8_{27}$	29679.35	29681.16
$1_{10} \rightarrow 2_{21}$	36390.08	36390.47
$1_{11} \rightarrow 2_{20}$	36605.47	36606.50

[a] A conventional Stark modulated spectrometer was employed. Frequencies were reproducible to ±0.1 Mc. [b] Transitions in parentheses used to calculate the rotational constants.

TABLE II

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR $F^{32}S^{32}SF$

A	*B*	*C*
11273.50 Mc./sec.	2782.08 Mc./sec.	2569.97 Mc./sec.
I_a	I_b	I_c
44.8424 Amu. Å.^{2}	181.7097 Amu. Å.^{2}	196.7069 Amu. Å.^{2}

An alternation in intensity due to nuclear spin statistical weights was observed for transitions of different symmetry. Rough intensities for the $3_{12} \rightarrow 3_{21}$, and $5_{14} \rightarrow 5_{23}$ transitions compared to the $4_{13} \rightarrow 4_{22}$ transition indicated a nuclear statistical weight factor of 3 to 1, respectively. This establishes that the molecule has a C_2 symmetry axis which can exchange a pair of equivalent fluorine atoms with nuclear spin of $^1/_2$. Quantitative measurements of the frequency shifts *vs.* voltage squared for the three Stark lobes of the $2_{02} \rightarrow 3_{13}$ transition indicated that only "b" type selection rules were operating, which further confirms the C_2 axis.

It proved possible to correlate the intensity of the microwave lines with mass spectral peaks. Whenever the microwave lines reported here were absent from a sample, the mass spectrum could be explained in terms of the $S{=}SF_2$ isomer and/or known impurities. However, when these transitions were intense, then the $51(SF^+)$, $64(S_2^+)$, and $83(S_2F^+)$ *m/e* peaks increased while the $70(SF_2^+)$ *m/e* peak decreased relative to the $102(S_2F_2^+)$ *m/e* peak when compared to the cracking pattern of pure $S{=}SF_2$. No unexplained peaks were detected to *m/e* units greater than 102.

The mass spectral data demonstrate that sulfur and fluorine are elements in the molecules giving rise to the microwave spectrum and indicate that it almost certainly has the molecular formula S_2F_2. The nuclear spin statistics and absence of an unpaired electron also permit only two fluorine atoms in the molecule. The moments of inertia alone can eliminate SF_2 and pyrimidal or chain S_3F_2 as possibilities. The only possible species remaining which gives reasonable structural parameters is a nonplanar, chain-type FSSF molecule. The moments of inertia are insufficient to calculate a unique structure for this species without assuming one parameter. Hence, they fit a range of structures with *d*(SS) between 1.85 and 2.05 Å., *d*(SF) between 1.55 and 1.65 Å., and ∠SSF and dihedral angles in the vicinity of 109 and 90°, respectively. This type of structure is similar to that reported for S_2Cl_2 and S_2Br_2.[5] For example, S_2Cl_2 has $d(SS) = 1.97 \pm 0.03$ Å., $\angle SSCl = 107 \pm 2.5°$, and a dihedral angle of $82.5 \pm 12°$.[5] The range of sulfur–fluorine bond lengths is also reasonable compared to other molecules.[7,8]

Therefore, on the basis of the correlation of the microwave spectrum with mass spectral peaks, the alternating intensities due to fluorine nuclear spin statistical weights, and the reasonable structure which will fit the moments of inertia, we conclude that the reported microwave spectrum is due to the nonplanar chain FSSF form of sulfur monofluoride and consequently that S_2F_2 exists in two isomeric forms.

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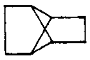
Use of a π-Complex of an Olefin as a Photochemical Catalyst

Sir:

We wish to report an unusual catalytic effect due to a π-complex on the photochemistry of 1,5-cyclooctadiene in solution. The π-complex was that of cuprous chloride with 1,5-cyclooctadiene, the structure of which, in the solid state, has been reported recently.[1]

It was found that at 2537 Å.[2] in ether solution (undegassed) (i) 1,5-cyclooctadiene (c 1%) by itself underwent hardly any photoreaction, although it has a weak absorption (ϵ ~10) at this wave length[3]; (ii) 1,5-cyclooctadiene together with benzene (c 1%) as a sensitizer gave mainly a yellow polymer[4]; and (iii) the cuprous chloride–cyclooctadiene complex, which is sparingly soluble (solubility: 0.06 g./l. at 25°), gave rise to four products, all of which are believed to originate from the solvent *via* radical processes.

However, if about 1% of 1,5-cyclooctadiene was added to the solution of the complex as in (iii), it was observed that the quantum yield of the formation of the adducts was greatly diminished, while the chief product was tricyclo[3.3.0.0^{2,6}]octane (I). The latter was found to be identical in its infrared spectrum, refractive index, and retention time on a gas chromatographic column with the material which had previously been synthesized in less than 1% yield by the mercury-photosensitized isomerization of 1,5-cyclooctadiene in the vapor phase.[5] The yield of I in the present instance was 30%, which makes this a very convenient route to the synthesis of I in quantity.[6]


I

Although at first sight it appears that the π-complex sensitizes the photoisomerization of 1,5-cyclooctadiene by a transfer of electronic excitation energy, the reaction cannot be simply that. Ultraviolet absorption spectra of solutions of 1,5-cyclooctadiene (1%) and the π-complex (saturated) showed that the two solutions absorbed light at 2537 Å. to an equal extent. Further, the spectrum of the complex in solution was quite similar to that of cuprous chloride itself in ether solution (saturated). It would appear that in a saturated solution of the π-complex in ether, to which an excess of 1,5-cyclooctadiene had been added, the radiation is as likely to be absorbed by the π-complex as by free 1,5-cyclooctadiene.

Addition of 1,5-hexadiene instead of 1,5-cyclooctadiene to a solution of the π-complex in ether, followed by photolysis, did not lead to any isomerization of 1,5-hexadiene. The catalytic effect of the π-complex seems to be quite specific, which suggests that it may involve the formation in solution of a second complex between the original π-complex and the excess of cyclooctadiene. The details of the reaction mechanism are presently under investigation. Since numerous π-complexes of olefins with a great variety of inorganic compounds have been described,[7] the present method may lead to other interesting reactions of great utility in organic synthesis. For example, photolysis of 1,3-butadiene as a solution (1%) in ether in the presence of cuprous chloride is found to give a 30% yield of cyclobutene. Although photolysis of 1,3-butadiene by itself in solution does lead to cyclobutene, the addition of cuprous chloride makes it possible to carry out the reaction with 2537-Å. radiation and seems to involve fewer side reactions. However, it is not obvious if a complex between 1,3-butadiene and cuprous chloride is involved in this reaction. A complex that is structurally similar to the 1,5-cyclooctadiene complex is not possible with 1,3-butadiene.

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[1] J. H. Van den Hende and W. C. Baird, Jr., *J. Am. Chem. Soc.*, **85**, 1009 (1963).

[2] The light source that was used has been described before [R. Srinivasan, *ibid.*, **83**, 4923 (1961)]. This source is now available from the Southern N. E. Ultraviolet Co., Middletown, Conn.

[3] Cyclohexene also has a weak absorption which extends to 2800 Å. Landolt-Bornstein, "Zahlenwerte und Funktionen," Vol. 1, Springer-Verlag, Berlin, 1951, part III, p. 262.

[4] Photosensitization of 1,5-cyclooctadiene by benzophenone leads mainly to polymer formation. (D. I. Schuster, private communication).

[5] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

[6] The preparation of I may be carried out by photolyzing for 40 hr. a saturated solution (2000 ml.) of the complex in ether to which 1,5-cyclooctadiene (12 ml.) had been added. It was desirable to filter and resaturate the solution after the first 20 hr. of irradiation. From the photolysate, the ether was removed by distillation following which fractionation gave I (5–6 ml.) and unreacted 1,5-cyclooctadiene (2 ml.). I was obtained pure by preparative gas chromatography.

[7] R. G. Guy and B. L. Shaw, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 4, edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1962, Chapter II.

Concerning the Existence of High-Spin Planar Cobaltous Complexes: Bis(1,2-dicyanomaleonitriledithiolato)cobalt(II) Dianion

Sir:

Several years ago it was shown from simple ligand field theory for d^7 systems that the spin multiplicity of the ground state of coordinated Co(II) could be either doublet or quartet in planar symmetry, depending upon the strength of the in-plane ligand field.[1] Consideration of the electronic properties of a series of high-spin cobaltous complexes of the type Co-O$_4$ led to exclusion of a tetrahedral structure. A planar configuration was suggested for these complexes, although stabilization of the quartet spin state due to axial perturbation of the in-plane field could not be excluded.[2] Hence, the existence of high-spin planar Co(II) complexes has been open to genuine question. There seems little doubt that four-coordinate low-spin complexes are planar.[4]

The most encouraging evidence to date for the existence of high-spin planar Co(II) complexes has been presented by Gray, *et al.*,[5] who first prepared bis(1,2-dicyanomaleonitriledithiolato)cobalt(II) dianion, $[CoS_4C_4(CN)_4]^{-2}$ (**1**) and reported μ_{eff} = 3.92 B.M. Our previous work[6,7] demonstrates that this complex is one of a number of apparently planar species of the general type $[MS_4C_4R_4]^z$ (z = 0, −1, and −2) which are related by electron-transfer reactions and as such it is formally isoelectronic with $[MS_4C_4R_4]^{-1}$, M = Ni, Pd, and Pt; R = CN; M = Ni and Pt; R = CF$_3$; M = Ni; R = C_6H_5.[6,7] In contrast to the reported behavior of **1**, all of these complexes are low spin in the solid and in solution; in acetone all moments fall in the range 1.78–1.88 B.M. The comparison of **1** with the mononegative anions is especially pertinent. From a thorough magnetic susceptibility and electron spin resonance study of **1**, we have concluded that this complex is, in fact, low-spin ($S = 1/2$).

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[1] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

[2] Evidence is accumulating that at least in one such complex, *viz.*, bis(acetylacetonato)cobalt(II), molecular association in solution[3] and an attendant increase in the effective coordination number above four may be partially responsible for the large magnetic moments (~4.8 B.M.) observed in solution.[1]

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