3206 *J. Am. Chem. Soc.* **1986**, *108*, 3206–3210

A Persistent T-Shaped 9-S-3 π-Sulfuranyl Radical: Electron Spin Resonance and Electron Spin Echo Studies[1a]

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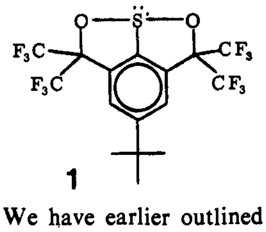
Abstract: Radicals **1** and **2** are shown to be π-type sulfuranyl radicals. The ESR spectrum of **1**, centered at $g = 2.0089$, shows ^1H hyperfine splittings by 2 meta ring protons (0.80 G), identical ^{19}F hyperfine splittings by the 12 fluorines of the 4 trifluoromethyl groups (0.63 G), a ^{13}C splitting (9.9 G), and a ^{33}S splitting (15.7 G). The electron spin echo (ESE) envelope exhibited modulation (ESEEM) arising from ^{19}F interactions (0.63 G) of four CF_3 groups, as well as from ^1H interactions of the meta ring protons (0.80 G) and the *tert*-butyl protons (0.18 G). The ESR of **2** showed ^1H hyperfine splittings by 2 meta ring protons (0.80 G) and a para ring proton (1.90 G), ^{19}F hyperfine splittings by the 12 fluorines of the 4 trifluoromethyl groups (0.63 G), and a ^{13}C splitting (9.9 G). Radicals **1** and **2** are both thermally stable in solution at room temperature with no reduction in concentration over several months.

The interest in the electronic structure of 9-S-3[1] (nine-electron, three-coordinate sulfur) sulfuranyl radicals[1-6] has led us to obtain ESR and electron spin echo envelope modulation (ESEEM) data for radicals **1** and **2**.



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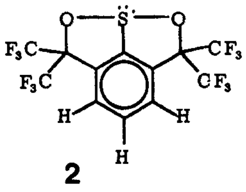

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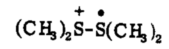
We have earlier outlined three bonding schemes for 9-S-3 sulfuranyl radicals:[1] (a) Recent reviews[2] provide numerous examples of radicals that have been interpreted in terms of one of these possibilities, a nonplanar π^*-type radical with a two-center, three-electron (2c,3e) bond. A well-characterized example of this type of radical is **3**, derived from dimethyl sulfide by one-electron oxidation.[3] (b) A second type of 9-S-3 radical is a planar T-shaped hypervalent[4] sulfur radical with a σ-delocalized three-center, three-electron (3c, 3e) bond. The three electrons occupy molecular orbitals that can be approximately described as combinations of the p orbitals of the three colinear atoms (Figure 1).[4] The odd electron of the SF_3 radical (**4**) was postulated[5] to occupy such an orbital of σ symmetry (ψ_2 of Figure 1). (c) A third type of bonding scheme for the 9-S-3 species is a planar T-shaped π-type radical with the unpaired electron located primarily in the sulfur 3p orbital perpendicular to the three-center, four-electron hypervalent bond. Evidence has been presented[6] which suggests that alkyldialkoxysulfuranyl radicals are best described as T-shaped π radicals (**5**).


$(CH_3)_2\overset{+}{S}\text{-}\overset{\bullet}{S}(CH_3)_2$

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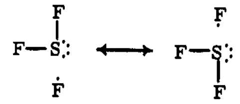

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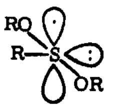

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In many of the T-shaped sulfuranyl radicals, the highest filled orbital and the SOMO may be similar in energy. Calculations on ClF_3[7] indicate that the two highest occupied MOs are, indeed, close in energy. When the $1b_1$ orbital (the orbital composed primarily of the sulfur 3p orbital) is higher in energy than the $3a_1$ orbital (essentially the nonbonding mixture of the colinear p orbitals, ψ_2 of Figure 1, with a small anti-bonding contribution from the sulfur 3s orbital), the ground state of the radical will be of the planar π type. Conversely, when the $3a_1$ orbital is higher in energy than the $1b_1$ orbital, then the planar σ radical will be the ground state. The order of these two energy levels may be inverted by the attachment of appropriate ligands to sulfur.

Using both ESR and ESE techniques, we have measured the principle hyperfine interactions in radicals **1** and **2** and compared the experimental $|a_i|$ values (and the measured g values) with those expected from theory. This has allowed us to determine which type of ground-state electronic structure may be assigned to planar 9-S-3 radicals **1** and **2**.

Experimental Section

General Remarks. ESR spectra were recorded on a Varian E-109 spectrometer operating at X-band frequency. The g values were measured relative to α,α'-diphenyl-β-picrylhydrazyl (DPPH, $g = 2.0036$) by using a frequency counter and a dual (TE_{104} mode) cavity. ESE experiments were performed at X-band frequencies by using a pulsed spectrometer.[8] Temperature was controlled by an Oxford Instruments liquid helium cryostat. The 2-kW ESE spectrometer was controlled by a Nicolet 1280 computer with a Nicolet 293B pulse programmer. ESEEM data were deconvoluted and analyzed on the Nicolet 1280. All ESEEM data were obtained using a three-pulsed stimulated echo sequence. ESR and ESEEM samples were prepared by distillation (10^{-5} torr) of predried, degassed solvents into thoroughly dried, 4 mm o.d. quartz tubes (that were previously charged with N_2) and then sealed.

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(1) (a) For an explanation of the N-X-L classification scheme, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (b) Current address for J.C.M.: Vanderbilt University, Nashville, TN 37235.

(2) (a) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436. (b) Musker, K. W. *Ibid.* **1980**, *13*, 200. (c) Coleman, B. R.; Glass, R. S.; Selzer, W. N.; Prabhu, U. D. G.; Wilson, G. S. *Adv. Chem. Ser.* **1982**, 417.

(3) (a) Gilbert, B. C.; Hodgeman, K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 1*, 1973, *2*, 1748. (b) A persistent radical postulated to be of this type was reported (Musker, W. K.; Woolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416) to be formed in transannular reaction during the oxidation of 1,5-dithiacyclooctane in H_2SO_4. Recent evidence (Russell, G. A.; Law, W. C.; Zaleta, M. *J. Am. Chem. Soc.* **1985**, *107*, 4175) suggest, however, that a degradation product was in fact the observed species.

(4) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(5) (a) Morton, J. R.; Preston, K. F. *J. Phys. Chem.* **1973**, *77*, 2645. (b) Colussi, A. J.; Morton, J. R.; Preston, K. F.; Fessenden, R. W. *J. Chem. Phys.* **1974**, *61*, 1247. (c) In a more recent study (Morton, J. R.; Preston, K. F.; Strach, S. J. *Ibid.* **1978**, *69*, 1392), an anisotropic ESR spectrum observed in γ-irradiated crystals of $SF_3^+BF_4^-$ was ascribed to a planar SF_3 radical with σ symmetry. The SOMO was assigned as an antibonding combination of in-plane sulfur 3p and fluorine 2p atomic orbitals. It was suggested by Symons (Symons, M. C. R. *Annu. Rep. Prog. Chem., Sect. A* **1978**, *75*, 123) that the ESR spectral data were consistent with the SF_4^+ radical, which could be formed by fluorine atom transfer.

(6) Gara, W. B.; Roberts, B. P.; Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *J. Chem. Res., Miniprint* **1977**, 1748. Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1497.

(7) Brown, R. D.; Peel, J. B. *Aust. J. Chem.* **1968**, *21*, 2605.

(8) Norris, J. C.; Thurnauer, M. C.; Bowman, M. K. In *Advances in Biological and Medical Physics*; Lawrence, J. W., Goffman, J. W.; Hayes, T. L., Eds.; Academic: New York, 1980; Vol. 17, p 365.

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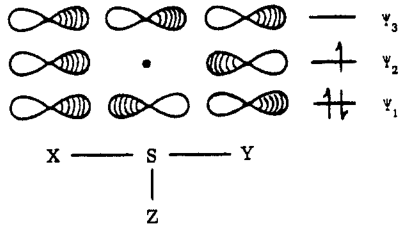


Figure 1. Approximate hypervalent bonding scheme[4] for a planar, T-shaped σ-sulfuranyl radical.

When Br_2 was used as a reactant, it was introduced by distillation on a high-vacuum line.

6,8-Dihydro-4-*tert*-butyl-2,2,6,6-tetrakis(trifluoromethyl)-8-chloro-2*H*-[1,2]oxathiolo[4,3,2-*hi*][2,1]benzoxathiole-8-S^{IV} (Chlorosulfurane 6). Excess chlorine was bubbled into a solution of 249 mg (0.5 mmol) of 2,6-bis-(1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)-4-*tert*-butylthiophenol[9] in 25 mL of CCl_4. The reaction solution was kept under a −78 °C condenser for 2 h at 25 °C. After solvent removal (1 torr), the remaining white solid (242 mg, 91%) was recrystallized from ether/pentane to give transparent, multifaceted crystals of **6**: mp 119–120 °C; ^1H NMR ($CDCl_3$) δ 8.0 (s, 2, ArH), 1.5 (s, 9, $C(CH_3)$); ^{19}F NMR ($CDCl_3$) δ −74.1 (q, 6, J_{FF} = 9 Hz, CF_3), −75.9 (q, 6 J_{FF} = 9 Hz, CF_3). Anal. ($C_{16}H_{11}ClF_{12}O_2S$) C, H.

3,3-Bis(trifluoromethyl)-7-(1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)-3*H*-2,1-benzoxathiole (Sultene 7). After 6 h at 55 °C, a solution of 996 mg (2 mmol) of 3,3-bis(trifluoromethyl)-5-*tert*-butyl-7-(1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)-3*H*-2,1-benzoxathiole[9] in 10 mL of trifluoromethanesulfonic acid was poured into 30 mL of ice water to give a white precipitate. It was extracted into 30 mL of CH_2Cl_2. The pH of the two-phase mixture was first raised to 4 by addition of $NaHCO_3$; the mixture was then acidified by addition of concentrated aqueous HCl. Extraction (3 × 50 mL) into CH_2Cl_2, drying ($MgSO_4$), and solvent removal left a yellow oil. The oil was dissolved in 5 mL of CH_3CH_2OH and boiled for 5 h with 15 mL of 40% aqueous HI. The mixture was extracted (3 × 30 mL) with CH_2Cl_2. The organic layer was washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). The solid remaining after solvent removal was chromatographed on 100 g of silica, eluting with CH_2Cl_2 and then CH_3OH. After CH_3OH removal, recrystallization from CH_2Cl_2/pentane gave white crystals: mp 132.5–133 °C; ^1H NMR ($CDCl_3$) δ 7.6 (br s, 1, ArH), 7.5 (br s, 2, ArH), 6.6 (br s, 1, OH); ^{19}F NMR δ −76.3 (br s, 12, CF_3); mass spectrum (70 eV), *m/z* (rel intensity) 440 (23, $M^{+\cdot}$), 371 (100, $M^{+\cdot} - CF_3$), 301 (63, $M^{+\cdot} - 2CF_3$, H), 233 (22, $M^{+\cdot} - 3CF_3$).

ESR Spectroscopy of 1. The ESR samples were prepared by (a) vacuum-line distillation of 0.4 mL of CH_2Cl_2 into an ESR tube containing 5.13 mg (0.01 mmol) of chlorosulfurane **6** and 6.3 mg (0.01 mmol) of tetraethylammonium sulfuranide **8** or (b) vacuum-line distillation of 0.35 mL of perfluorobenzene, *cis*- and *trans*-perfluorodecalin, CCl_2FCClF_2, chlorobenzene, or toluene-d_8 into an ESR tube containing 2.6 mg (2.6 × 10^{-3} mmol) of the bisulfuranyl **9**.[10]

ESR Spectroscopy of 2. Sultene **7** was titrated with tetraethylammonium hydroxide in 50:50 v/v aqueous ethanol. Solvent removal gave the white solid sulfuranide salt. Both CCl_2FCClF_2 (0.4 mL) and Br_2 (2 μL, 0.004 mmol) were distilled into an ESR tube containing the above white solid (5.7 mg, 0.01 mmol) and 2.6 mg of silver trifluoromethane sulfonate (0.01 mmol). The spectrum of **2** was obtained at 25 °C.

Results

The well-resolved but slightly broadened (ΔH_{pp} = 0.4 G) ESR spectrum shown in Figure 2 was obtained on a solution of chlorosulfurane **6** and sulfuranide salt **8** in CH_2Cl_2 at 25 °C. The same spectrum was obtained by dissolving bisulfuranyl **9**[10] (from the action of Br_2 on the silver sulfuranide as shown in Scheme I) in CH_2Cl_2, CH_2ClCH_2Cl, toluene-d_8, chlorobenzene, CCl_2FCClF_2, perfluorobenzene, or a mixture of *cis*- and *trans*-perfluorodecalin at 25 °C. The signal appeared to be remarkably persistent,[12] losing no intensity over a 6-month period at 25 °C in CH_2Cl_2, perfluorobenzene, or perfluorodecalins in a sealed tube.

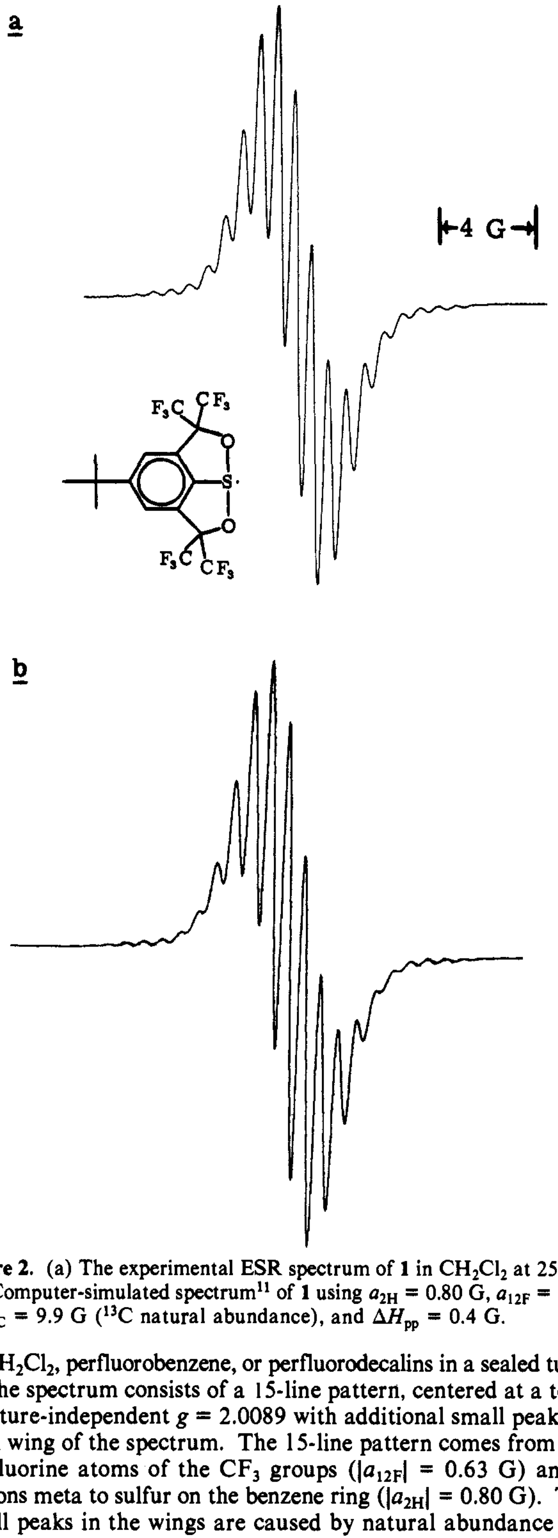
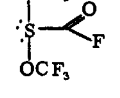


Figure 2. (a) The experimental ESR spectrum of **1** in CH_2Cl_2 at 25 °C. (b) Computer-simulated spectrum[11] of **1** using a_{2H} = 0.80 G, a_{12F} = 0.63 G, a_C = 9.9 G (^{13}C natural abundance), and ΔH_{pp} = 0.4 G.

The spectrum consists of a 15-line pattern, centered at a temperature-independent *g* = 2.0089 with additional small peaks in each wing of the spectrum. The 15-line pattern comes from the 12 fluorine atoms of the CF_3 groups ($|a_{12F}|$ = 0.63 G) and 2 protons meta to sulfur on the benzene ring ($|a_{2H}|$ = 0.80 G). The small peaks in the wings are caused by natural abundance ^{13}C splitting of a single carbon (9.9 G). The carbon ipso to sulfur is the likely origin of the satellite patterns observed in the wings. The sp^2 carbon directly attached to sulfur in **10** has a similar value of $|a_{^{13}C}|$ (7.65).[5a]



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The assignments are supported by the computer simulated[11] spectrum shown in Figure 2, based on the assigned hyperfine splitting values for 12 fluorines, 2 hydrogens, and ^{13}C of natural abundance. Figure 3 shows the ^{33}S satellites ($|a_{^{33}S}|$ = 15.7 G) in

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(9) Perkins, C. W.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209.

(10) Perkins, C. W.; Martin, J. C. *J. Am. Chem. Soc.*, following paper in this issue.

(11) The ESR spectra were simulated by using PROGRAM QPOW (Maurice, A. M. Ph.D. Thesis, University of Illinois, Urbana, 1980) developed by Belford et al. with modifications for isotropic spectra by Cornelius and Belford.

(12) We use the term "persistent" as defined by: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

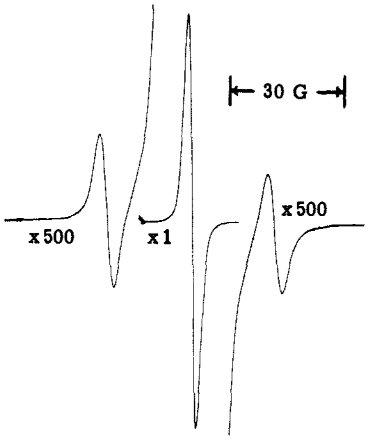
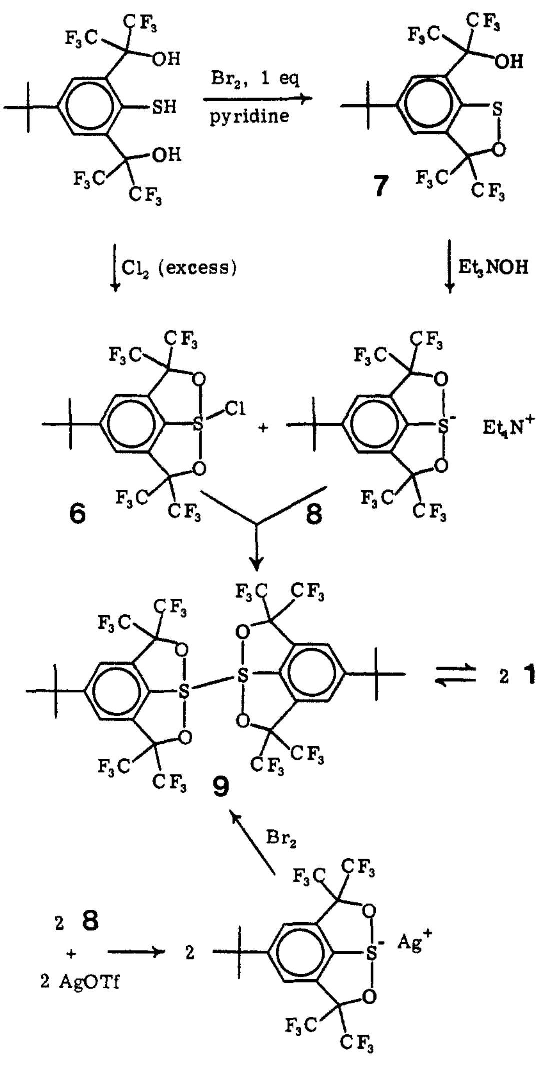


Figure 3. ESR spectrum of **1** showing ^{33}S satellites. This spectrum, taken at 25 °C, is of a 3×10^{-2} M solution of **9** in perfluorobenzene. Note the loss of fine structure in the spectrum at this concentration. Only two outer peaks of the four ^{33}S satellites are visible because the broadness of the ^{32}S peak obscures the inner two.

Scheme I



a concentrated sample of bisulfuranyl **9**[10] in perfluorobenzene at 25 °C.

Figure 4 gives a stick diagram representation of the ENDOR frequencies found by deconvoluting the ESEEM data from three-pulse stimulated echos derived from a sample of **1** in a mixture of *cis*-and *trans*-perfluorodecalin. Because both ^{1}H and ^{19}F nuclei in this sample obey the inequality $\nu_n > |a_i|/2$, where ν_n denotes the resonance frequency for unperturbed nuclei of type n and $|a_i|$ is the absolute value of the ith hyperfine coupling constant, the ENDOR lines revealed by a Fourier transformation of the ESEEM data occur in pairs, split by $|a_i|$ and centered about ν_n. This provides for the unambiguous assignment of lines, as well as for separation of ^{1}H and ^{19}F ENDOR lines which otherwise would overlap and not be resolved. Through-bond ^{19}F and ^{1}H hyperfine couplings are observed in addition to the matrix lines arising from fluorine and hydrogen nuclei ($\nu_{^{19}F}$ and $\nu_{^1H}$) interacting with the radical via electron–nuclear dipole–dipole terms. Proton coupling constants of 0.5 MHz (0.18 G) and 2.25 MHz (0.80 G) are measured. The ^{19}F coupling of 1.75 MHz (0.63 G) can be distinguished from the proton interactions because it is centered about the free fluorine frequence ($\nu_{^{19}F}$ = 13.3 MHz).

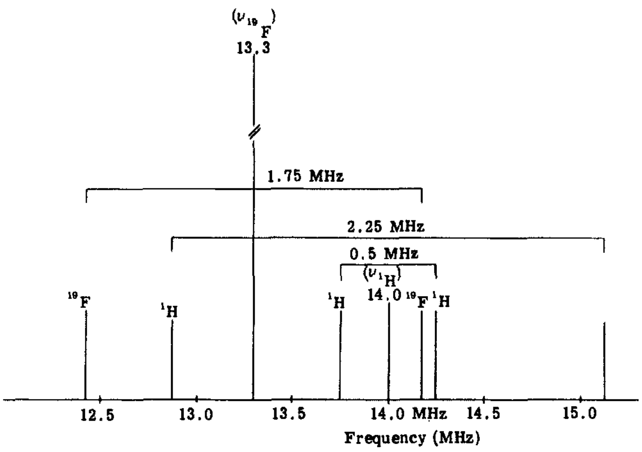


Figure 4. Stick diagram showing ENDOR transition calculated from ESEEM data from radical **1** in *cis*/*trans*-perfluorodecalin at 32 K.

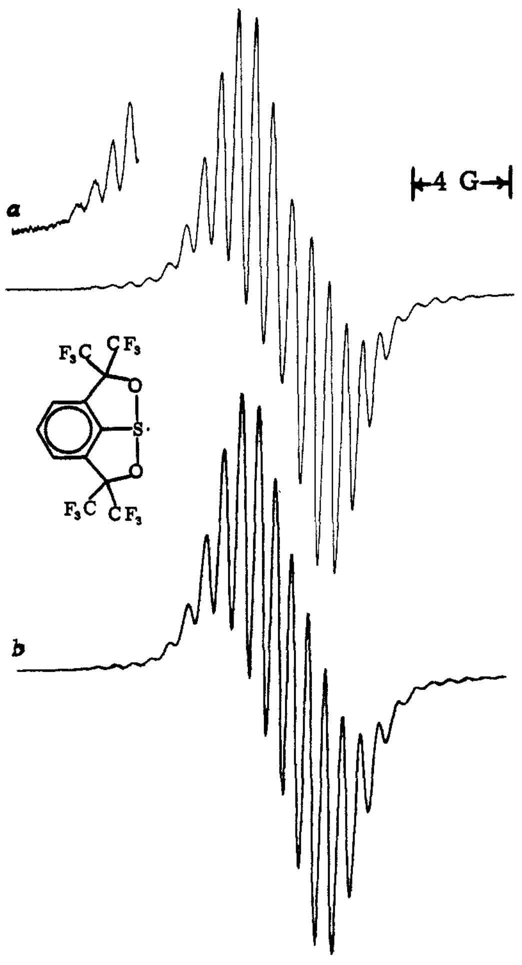
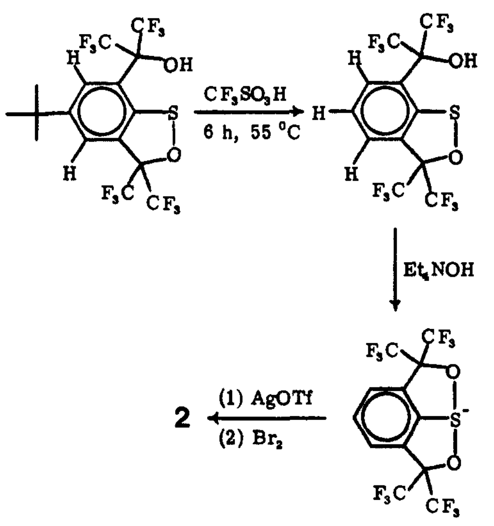


Figure 5. (a) ESR spectrum of **2** obtained in CFCl$_2$CF$_2$Cl at 25 °C. (b) Computer-simulated spectrum[11] with $|a_{12F}|$ = 0.63 G, $|a_{2H}|$ = 0.80 G, $|a_{1H}|$ = 1.9 G, and $|a_C|$ = 9.9 G (^{13}C natural abundance).

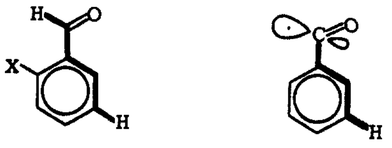
Scheme II



The well-resolved but slightly broadened spectrum (ΔH_{pp} = 0.03 G) shown in Figure 5 results from the reaction of Br_2, silver triflate, and tetraethylammonium sulfuranide **7** (see Scheme II) in $CFCl_2CF_2Cl$ at 25 °C. This spectrum consists of two 15-line patterns separated by 1.9 G with the three small peaks in each of the wings of the spectrum virtually identical with those seen in the spectrum of **1**. The pattern was closely simulated by using the hyperfine constants determined by the ESEEM study of **1** for 12 equivalent fluorines (0.63 G), 2 equivalent meta protons (0.80 G), and carbon-13 splitting (9.9 G) for a carbon (presumably ipso to sulfur) in natural abundance, very similar to the values used for the spectrum of **1**, with the added hyperfine splitting by the para proton (1.9 G).

Discussion

The meta proton (0.80 G) and fluorine (0.63 G) hyperfine splittings of **1** and **2** are consistent with either a T-shaped σ- or π-sulfuranyl radical. The expected value for meta splittings may be explained by analogy to the long-range through-bond interaction (via the zig-zag chain of bonds shown in **11**) that explains the nuclear spin–spin coupling between the aldehyde proton and the meta protons of benzaldehydes[13a] or by analogy to the hyperfine coupling to the meta protons of the benzoyl radical.[13b] A similar coupling mechanism would be expected for **1** or **2** if the SOMO were the approximately nonbonding orbital shown in Figure 1 (ψ_2). The same long-range interaction is thought[1] to be the cause of the observed hyperfine splitting to a single aromatic ring proton, H(6) only, of the σ-sulfuranyl radical **12**: H(6) ($|a_H|$ = 1.5 G) was the only ring proton to show resolved hyperfine splitting. The meta proton splittings of **1** and **2** (0.8 G) are quite close to half (0.75 G) the magnitude of the hyperfine splitting to H(6) of **12**. The SOMO of **12** has most of its electron density located on one side of the colinear C–S–O hypervalent bond, while the symmetry of the illustrated SOMO of **1** or **2** has an approximately equal amount of electron density on both sides of sulfur. One might therefore expect the hyperfine splitting of the meta protons of **1** or **2** to be approximately half that of the splitting of H(6) in **12**. The fluorine splittings (0.63 G) of **1** or **2** might also result from spin-delocalization expected for a T-shaped 9-S-3 σ ground state, which would place a large amount of electron density on the oxygen atoms.



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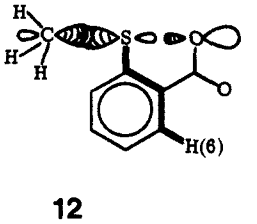

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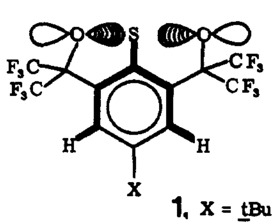
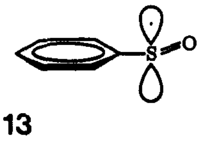


1, X = tBu
2, X = H

The para proton splitting of **2** (1.9 G) and the *tert*-butyl proton splitting (0.18 G) of **1** are indicative of substantial spin density at the para carbon. Greater spin delocalization to the para position than to the meta position is consistent with a π-type radical, but there is no reason to expect it for a σ-type radical. The ESR spectral parameters of the benzenesulfinyl radical[14] **13** have been interpreted in terms of a sulfur-centered π-type radical with delocalization of the unpaired spin density into the phenyl ring. The hyperfine splittings (para $|a_H|$ = 2.4 G and meta $|a_H|$ = 0.7 G) and g (2.0090) are quite similar to those in **2**. The value of $|a_{H_{para}}|/|a_{H_{meta}}|$ measured for **2** (2.5) represents the strongest evidence that it is indeed a π-type 9-S-3 radical.



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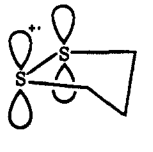
The size of $|a_{^{33}S}|$ of **1** (15.7 G) also appears to be in better agreement with a SOMO of π symmetry than with a σ-symmetry SOMO. Comparison of this splitting to the magnitude of $|a_{^{33}S}|$ expected, if there were 100% occupancy of the sulfur 3s orbital (1264 G),[15] implies 1.24% net contribution of the sulfur 3s orbital to the SOMO of **1**.

Variable-temperature ESR data, interpreted by using INDO calculations, indicate that the SOMO of the 1,2-dithiolanium cation radical **14** is composed essentially of two sulfur 3p atomic orbitals, as might be expected.[16] The $|a_{^{33}S}|$ value (13.3 G) of **14** is in the same range as the $|a_{^{33}S}|$ of **1** (15.7 G). Even the substantially larger $|a_{^{33}S}|$ of **15** (47.0 G) was thought to be small enough to indicate a SOMO comprised mainly of the sulfur 3p orbital.[17] This splitting, however, may also be large enough to be consistent with a SOMO of σ symmetry for a T-shaped radical. Since the $3a_1$ orbital of ClF_3 (the highest occupied σ-symmetric orbital) was calculated to have 8.7% occupancy of the 3s orbital,[7] Morton and Preson considered the $|a_{^{33}S}|$ value (59.9 G) for $S(OCF_3)_3$ (indicating 4.7% occupancy of the sulfur 3s orbital) to be in agreement with the expected value for a T-shaped σ radical centered on sulfur.[5a]



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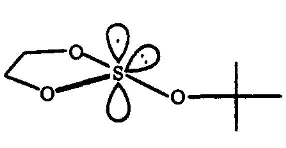

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There are many other species thought likely to be π-sulfuranyl radicals. Radical **16**[6] was postulated to be a T-shaped π radical based on equal hyperfine splitting ($|a_H|$ = 0.8 G) to three unassigned, but presumably ortho and para, ring protons. The different magnitudes of $|a_H|$ in the various alkyldialkoxy radicals **17**[6] are consistent with a dependence of $|a_H|$ on the dihedral angle θ

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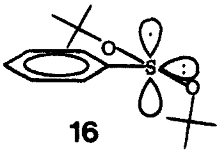
[13] (a) Karabatsos, G. J.; Vane, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 3886. (b) Krusic, P. J.; Rettig, T. A. *Ibid.* **1970**, *92*, 722.

[14] Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C.; Laue, H. A. H. *J. Am. Chem. Soc., Perkin Trans. 2* **1977**, 497.

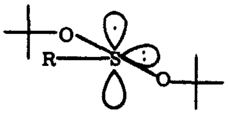
[15] Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

[16] Bock, H.; Stein, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 834.

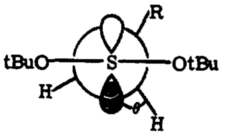
[17] (a) Chapman, J. S.; Copper, J. W.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1976**, 835. (b) Cooper, J. W.; Roberts, B. P. *Ibid.* **1977**, 228.



16



17



R = Me, Et, Pr, iPr, sBu, CF_3

17a

between the carbon–hydrogen bonds (of the directly attached alkyl group) and the singly occupied sulfur 3p orbital of the T-shaped 9-S-3 π radicals (**17a**).

In the phenyldibutoxysulfuranyl radical **16** or any of the alkyldialkoxysulfuranyl radicals **17**, a rapidly equilibrating pair, **18** or pyramidal σ^*-type structures, with three-electron, two-center bonds, cannot be ruled out on the basis of ESR data. The equilibrating pair of σ^* pyramidal 9-S-3 radicals might result in the requisite amount of delocalization of unpaired spin density into the phenyl ring of **16** to account for the observed $|a_H|$ (0.8 G) of the three ring protons.

18a **18b**

Other classes of 9-S-3 sulfuranyl radicals that may be π type include trialkoxy,[17] trifluoro,[5] fluorodialkoxy,[5a] bis(pentafluorosulfuranyloxy)fluoro,[5a] and analogues of some of the above classes with fluorine (directly attached to 9-S-3 sulfur) replaced by carbonyl derivatives (e.g., **10**).[5a] The ESR data for any of these compounds can be explained by either of the two alternative structures with σ symmetry: The T-shaped σ-type (with a 3c, 3e bond) or an equilibrating pair of nonplanar σ^*-type radicals, each of which contains a 2c,3e bond.

The fact that **1** and **2** are persistent, T-shaped π-type 9-S-3 radicals suggests that many of the radicals mentioned above many have similar electronic structures.

In a pyramidal σ^*-sulfuranyl radical (Figure 6a), two of the three electrons in the 2c, 3e bond occupy the S–L_1 bonding orbital and the unpaired electron occupies the antibonding σ^* orbital. The T-shaped radicals (Figure 6b and 6c) would instead utilize one bonding (ψ_1 of Figure 1) and two essentially nonbonding orbitals (ψ_2 of Figure 1 and the sulfur 3p orbital of π symmetry).

The ligands of 9-S-3 radicals determine the relative order of energies of the three possible types of sulfuranyl radicals pictured in Figure 6. We have discussed at length[18] the structural features of ligands that have been shown, by work carried out in our laboratory, to stabilize the 3c, 4e bonds of compounds of closed-shell hypervalent nonmetals. These same features (such as electronegative apical ligands and electropositive equatorial ligands) are also expected to stabilize a colinear 3c, 3e bond, but

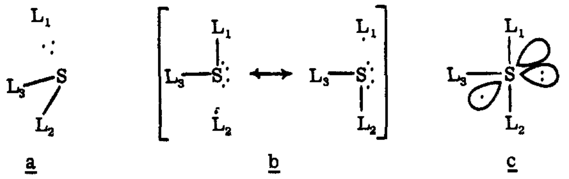
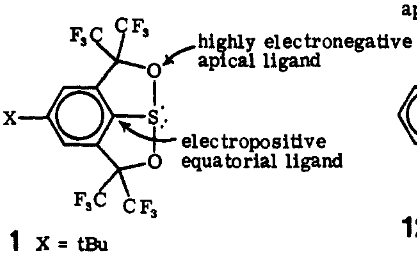


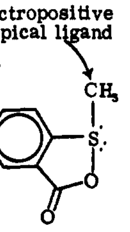
Figure 6. (a) Pyramidal σ^* radical with a 2c, 3e bond. (b) T-shaped σ radical with a 3c, 3e bond. (c) T-shaped π radical with a 3c, 4e bond.

to a lesser degree. The ligands that lower the energy of the bonding (ψ_1) and nonbonding (ψ_2) orbitals (shown in Figure 1) will lower the energy of the T-shaped geometries (σ or π) relative to the pyramidal isomers. When these ligands lower the essentially nonbonding orbital (ψ_2) sufficiently to make it lower in energy than the π orbital (composed primarily of the sulfur 3p orbital), then the T-shaped π radical will be the ground state. Radicals **1** and **2** are examples of this effect. The ligands of **1** and **2** are designed to lower the energy of the electrons in the 3c, 4e bond, hence strenghtening it. The π-symmetric orbital of **1** (or **2**) could be unusually low in energy for a 9-S-3 radical, due to the contribution from the π orbitals of the aromatic ring. The σ-symmetric orbital (ψ_2 of Figure 1) is nevertheless sufficiently low in energy, as a result of the stabilizing effect of the strongly electronegative apical ligands, to be lower in energy than the π orbital. The SOMO is therefore an orbital of π symmetry (Figure 6c).

If the orbital of π symmetry is lower in energy than the nonbonding (ψ_2) σ orbital, then a T-shaped σ radical (Figure 6b) will be the ground state. Radical **12** is an example. The electropositive nature of the apical methyl ligands raises the energy of the σ orbital resembling ψ_2 to make it higher in energy than the π orbital. The ground state of radical **12** is therefore a σ radical with a 3d, 3e bond.



1 X = tBu
2 X = H



12

The proper choice of ligands developed in our laboratories has made possible the preparation and isolation of many unprecedented hypervalent organo-nonmetallic species.[18a] The choice of the tridentate ligand of **1** to provide stabilization for a hypervalent open-shell structure has similarly resulted in a very persistent 9-S-3 radical.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE 79-07-7905692). The NMR spectra were provided by the University of Illinois NSF Regional Instrumentation Facility (Grant CHE-16100) and mass spectra by facilities supported by grants from the National Institutes of Health (Grants CA 11388 and GM 16864). We thank Philip D. Morse II of U. of I. ESR Facility, Dr. Michael Bowman of Argonne National Laboratory, Prof. R. L. Belford, and J. B. Cornelius for assistance in obtaining and interpreting ESR data.

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(18) (a) Martin, J. C. *Science (Washington, D. C.)* **1983**, *221*, 509. (b) Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 1024.