

Figure 1. I_2 (%) vs. surfactant concentration in solutions of DAP in benzene, cyclohexane, and *n*-hexane and AOT in benzene (at room temperature).

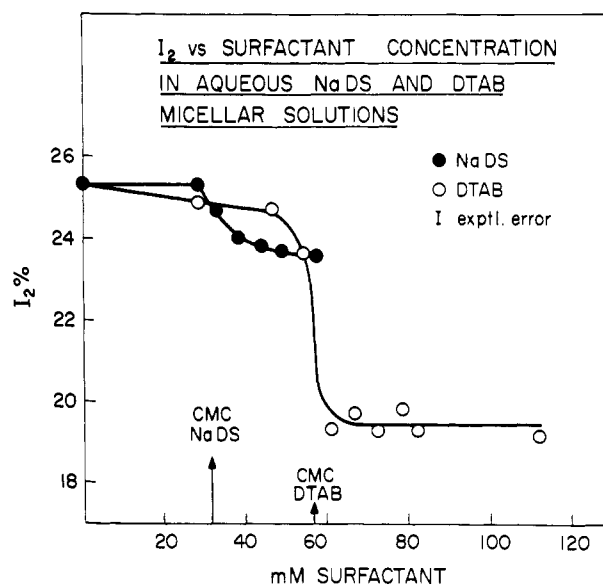


Figure 2. I_2 (%) vs. surfactant concentration in aqueous solutions of NaDS and DTAB in water (at room temperature).

The solutions were prepared following the previously reported procedures.^{2b}

Positronium lifetime distributions were obtained by standard techniques.⁸ The lifetime spectra were separated as previously discussed into two components, a short-lived component, which is the result of *p*-Ps, free positron annihilation, and epithermal Ps interactions, and the long-lived component, with a decay constant λ_2 and an associated intensity, I_2 , which originates from the reactions and subsequent annihilation of thermalized or nearly thermalized *o*-Ps atoms. While, the λ_2 values seem to be only slightly affected by micelle formation in these solutions, a drastic change in the intensities I_2 can be observed at the previously reported cmc as shown in Figures 1 and 2. In contrast to the results obtained by optical and spectroscopic techniques, where the cmc is characterized by a more gradual change,^{2b-e,9} in the present investigation the I_2 values show a very abrupt discontinuity at the cmc and thus allow a more accurate determination.

Table I. Cmc Values Obtained in This Study by Positron Annihilation Techniques and Previously Reported Literature Values^a

Surfactant	Solvent	cmc, mM	
		This study	Lit.
DAP	Benzene	8.75 ± 0.25	3-7
	Cyclohexane	8.26 ± 0.25	8 ^b
	<i>n</i> -Hexane	6.15 ± 0.45	6 ^c
AOT	Benzene	2.20 ± 0.10	2.0-2.7
NaDS	Water	32 ± 1	33
DTAB	Water	57 ± 1	65

^a Reference 2b. ^b Dodecylammonium butanoate. ^c In octane.

Although the parameters which control the positronium formation process, and consequently I_2 , are not unambiguously known,³ the results of this study clearly show that this simple technique can be easily used for the determination of cmc's, not only in aqueous solutions, but that it is also very effective in nonaqueous solutions and therefore provides a generally applicable method for the study of properties of micelles and inverted micelles.

The cmc's obtained in this study are listed in Table I where for comparison previously reported literature value^{2b} can also be found.

References and Notes

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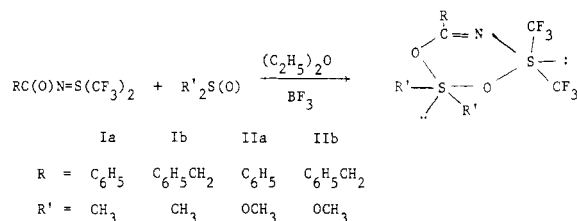
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A Cyclic Disulfurane with S-O, S-C, and/or S-N Bonds. 3. Some New Cyclic S,S-Bis(trifluoromethyl)catecholatosulfur(IV) Compounds¹

Sir:

Tetracoordinate sulfur(IV) compounds have been studied² over the years and several routes have been developed for their synthesis.³⁻¹⁷ In our continuing design of routes to sulfuranes, we now wish to report two new syntheses of sulfuranes. It has been possible to synthesize sulfuranes I and II, the first stable members of a new family with two tetracoordinate sulfur(IV) atoms bonded to carbon, oxygen, and/or nitrogen per molecule,

by the cycloaddition of *S,S*-bis(trifluoromethyl)-*N*-benzoyl- (or 2-phenylacetyl-) sulfimide with sulfoxides. Although there is considerable indirect evidence for sulfuranes as intermediates in hydrolysis^{18,19} and/or nucleophilic displacement²⁰ of sulfimides, none has been isolated. *S,S*-bis(trifluoromethyl)-*N*-benzoyl- (or 2-phenylacetyl-) sulfimide is most conveniently synthesized²¹ through the reaction of lithium bis(trifluoromethyl)sulfimide and benzoyl chloride (or 2-phenylacetyl chloride), and characterized ($R = C_6H_5$, mp 93–94 °C; $R = C_6H_5CH_2$, mp 118.5–119.5 °C).



In a typical reaction, boron trifluoride (0.1 mmol) was condensed into the mixture of *S,S*-bis(trifluoromethyl)-*N*-benzoylsulfimide (2 mmol) and dimethyl sulfoxide (2 mmol) in freshly dried $(C_2H_5)_2O$ (10 mL) and allowed to warm to ambient temperature. After 5-h stirring at that temperature, the solvent was removed under dynamic vacuum. The residual material was recrystallized from tetrahydrofuran to yield the sulfurane Ia ($R = C_6H_5$) in 88% yield, mp 145–147 °C. Spectroscopic data support the existence of this new family. The ^{19}F NMR spectrum contained two quartet resonances at ϕ 55.2 and 57.3 in the ratio 1:1 ($J = 3.2$ Hz). In the 1H NMR spectrum ($CDCl_3$), three signals appeared at τ 1.71 ($R-H$) and two quartets at 6.09 and 6.21 ($S-CH_3$, $J = 0.6$ Hz). Also, the infrared spectrum had absorption bands at 3002 (w), 2997 (w), 1614 (m), 1599 (m), 1484 (m), 1381 (w), 1261 (vs), 1225 (s), 1183 (ms), 1081 (s), 981 (m), 745 (cm^{-1}). When the mass spectral data were measured at 150 °C and 17 eV, the molecular ion was absent; however, other fragment peaks, such as m/e 352 ($M^+ - CH_3$), 348 ($M^+ - F$), 298 ($M^+ - CF_3$), 103 (C_7H_5N), and 69 (CF_3) appeared appropriately. Anal. Calcd for $C_{11}H_{11}NO_2S_2F_6$: C, 35.97; H, 3.02; N, 3.81. Found: C, 35.95; H, 3.06; N, 3.71.

Ib ($R = C_6H_5CH_2$): mp 161–162 °C; 79% yield; 1H NMR ($CDCl_3$) τ 1.76 ($R-H$), 6.01, 6.13 ($S-CH_3$, q, $J = 0.7$ Hz), and 6.49 (CH_2); ^{19}F NMR, two quartets, ϕ 56.8 and 58.9 ($J = 3.1$ Hz); mass spectrum m/e 366 ($M^+ - CH_3$), 362 ($M^+ - F$), 312 ($M^+ - CF_3$); IR 3003 (w), 2998 (w), 1616 (m), 1601 (m), 1490 (m), 1380 (w), 1265 (vs), 1218 (s), 1176 (ms), 1081 (s), 988 (m), 748 (cm^{-1}). Anal. Calcd for $C_{12}H_{13}NO_2S_2F_6$: C, 37.80; H, 3.44; N, 3.67. Found: C, 37.69; H, 3.36; N, 3.56.

IIa ($R = C_6H_5$): mp 171–172 °C; 81% yield; 1H NMR ($CDCl_3$) τ 1.75 ($R-H$), 6.23, 6.41 ($S-OCH_3$, s); ^{19}F NMR, two quartets, ϕ 55.9 and 57.6 ($J = 3.3$ Hz); IR 3002 (w), 2999 (w), 1614 (m), 1600 (m), 1489 (m), 1382 (w), 1271 (vs), 1231 (s), 1185 (s), 1076 (s), 991 (m), 746 (cm^{-1}); mass spectrum m/e 380 ($M^+ - F$), 353 ($M^+ - C_2H_6O$), 330 ($M^+ - CF_3$). Anal. Calcd for $C_{11}H_{11}NO_4S_2F_6$: C, 33.09; H, 2.78; N, 3.51. Found: C, 33.11; H, 2.75; N, 3.48.

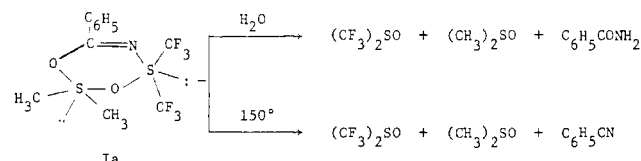
IIb ($R = C_6H_5CH_2$): mp 186–187 °C; 83% yield; 1H NMR ($CDCl_3$) τ 1.78 ($R-H$), 6.29, 6.36 ($S-OCH_3$, s), and 6.51 (CH_2); ^{19}F NMR, two quartets, ϕ 56.1 and 58.2 ($J = 3.1$ Hz); IR 3003 (w), 2996 (w), 1617 (m), 1599 (m), 1491 (m), 1381 (w), 1268 (vs), 1221 (s), 1167 (ms), 1078 (s), 993 (m), 748 (cm^{-1}); mass spectrum m/e 394 ($M^+ - F$), 367 ($M^+ - C_2H_6O$), 344 ($M^+ - CF_3$). Anal. Calcd for $C_{12}H_{13}NO_4S_2F_6$: C, 34.87; H, 3.17; N, 3.39. Found: C, 34.76; H, 3.05; N, 3.41.

Although molecular ions were not obtained in the mass spectra of I and II, molecular weights which were determined cryoscopically support the existence of these compounds as monomeric species, i.e., experimental (calculated): Ia, 368

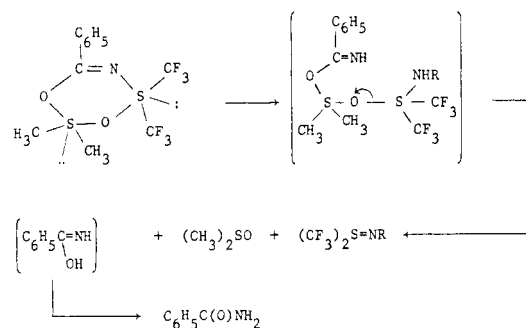
(367); Ib, 380 (381); IIa, 402 (399); and IIb, 413 (413).

It is of particular interest to compare our results of chemical shift of methyl groups (or methoxy groups) on the sulfur atom in the sulfurane with those of Johnson,²² who found a downfield shift of the methyl group on a tetracoordinated sulfur(IV) atom with trigonal bipyramidal geometry. This phenomenon, also observed by us, suggests a similar geometry at sulfur in compounds I and II. Further study on the geometry of these compounds is being undertaken and will be reported later.

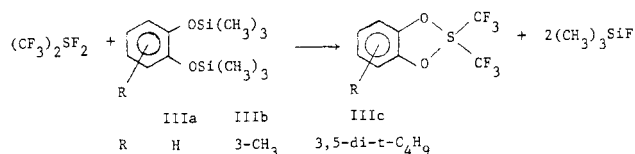
Sulfurane Ia forms bis(trifluoromethyl) sulfoxide, dimethyl sulfoxide, and benzamide slowly in the presence of water. When heated at 150 °C for 3 h in a stainless steel Hoke vessel, bis(trifluoromethyl) sulfoxide, dimethyl sulfoxide, and benzonitrile were generated quantitatively.



An interesting synthetic application of Ia was in the formation of bis(trifluoromethyl)-*N*-alkylsulfimides by the reaction with primary amines.^{23–27} This result suggests that reaction was initiated by attack on the more highly electropositive sulfur(IV) atom to which the two trifluoromethyl groups are bonded.

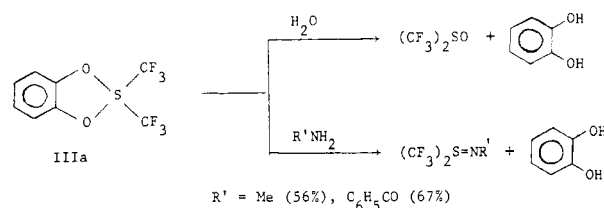


The reaction of bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$, with bis(trimethylsilyl)catechols in tetrahydrofuran was examined also. In this reaction, compound III is produced.



In a typical reaction, bis(trifluoromethyl)sulfur difluoride (2 mmol) was condensed at –196 °C into a glass vessel which contained bis(trimethylsilyl)catechol (2 mmol) and freshly dried THF (5 mL). After 5-h stirring at 0 °C, the solvent was removed. The product was separated by chromatography on silica through use of *n*-hexane–benzene (1:1). For final purification it was recrystallized from cyclohexane to yield IIIa in a yield of 34%, mp 183–185 °C.

The compound, IIIa, was stable enough to be characterized at room temperature; however, it was hydrolyzed rapidly to yield bis(trifluoromethyl) sulfoxide and catechol. Its behavior



was similar to that of sulfuranes I and II. The reaction of IIIa with primary amine also gave the corresponding *S,S*-bis(tri-fluoromethyl)-*N*-alkyl- (aryl-) sulfimides.

Support for structure IIIa came from the spectral data. When the mass spectral data were measured at 100 °C and 17 eV, no molecular ion was found; however, other fragment peaks such as m/e 209 ($M^+ - CF_3$), 170 (C_2SF_6), 151 (C_2SF_5), 132 (C_2SF_4), 108 ($C_6H_4O_2$), 101 (CSF_3), 92 (C_6H_4O), and 69 (CF_3) appeared appropriately. The ^{19}F NMR spectrum showed only one singlet signal at δ 58.6. The 1H NMR spectrum ($CDCl_3$) had a resonance at τ 1.88–1.97 (Ar–H). The infrared spectrum has absorption bands at 3001 (w), 1598 (m), 1490 (m), 1251 (vs), 1186 (ms), 1113 (s), 1065 (ms), 746 (m) cm^{-1} . Anal. Calcd for $C_8H_4O_2SF_6$: C, 34.54; H, 1.45. Found: C, 34.45; H, 1.42.

IIIb ($R = 3-CH_3$): mp 169–170.5 °C; 41% yield; 1H NMR ($CDCl_3$) τ 1.64–1.97 (Ar–H), and 7.97 (CH_3); ^{19}F NMR ϕ 57.6; IR 3002 (w), 2988 (w), 1599 (m), 1496 (m), 1381 (w), 1271 (vs), 1183 (s), 1126 (s), 1083 (s), 747 (m) cm^{-1} ; mass spectrum m/e 223 ($M^+ - CF_3$), 122 ($C_7H_6O_2$). Anal. Calcd for $C_9H_6O_2SF_6$: C, 37.00; H, 2.07. Found: C, 36.75; H, 2.02.

IIIc ($R = 3,5-di-t-C_4H_9$): mp 191.5–192.5 °C; 26% yield; 1H NMR ($CDCl_3$) τ 1.59–1.81 (Ar–H) and 8.69–9.02 (*t*-Bu); ^{19}F NMR ϕ 58.1; IR 3001 (w), 2987 (w), 1601 (m), 1486 (m), 1391 (m), 1387 (m), 1276 (vs), 1218 (s), 1186 (s), 1118 (s), 1079 (ms), 748 (m) cm^{-1} ; mass spectrum m/e 321 ($M^+ - CF_3$), 220 ($C_{14}H_{20}O_2$). Anal. Calcd for $C_{16}H_{20}O_2SF_6$: C, 49.23; H, 5.16. Found: C, 48.96; H, 5.15.

Both electronegativity and apicophilicity effects must be considered in determining the conformation of the compound III. Although a few sulfuranes are known in which rings occupy the diequatorial positions on sulfur,^{28–31} compound III may instead have a zwitterionic structure which could account for its solubility in several solvents and its ^{19}F NMR spectrum and would be in agreement with electronegativity rules. Further structural studies will be reported.

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Spectroscopic and Magnetic Properties of an Exchange Coupled Copper(II)–Manganese(II) Dimer

Sir:

When crystals of dichloro(aquo(pyridine *N*-oxide)copper(II)) are doped with manganese(II), measurable quantities of an exchange coupled copper(II)–manganese(II) dimer are produced. Although hundreds of investigations of the magnetic and spectroscopic properties of dimeric complexes have appeared in the literature, relatively few studies have involved dimeric systems containing two different metal ions. This communication presents the results of an EPR study of the copper(II)–manganese(II) dimer.

The host material, $Cu(pyO)Cl_2 \cdot H_2O$, is one of a series of dimeric complexes which can be formed by reacting copper(II) halides ($CuCl_2$ and $CuBr_2$) with aromatic amine *N*-oxides.^{1,2} In these dimeric complexes, a pair of copper(II) ions is bridged by oxygen atoms from two *N*-oxide ligands. The halide ions are bound terminally so that each copper(II) ion is surrounded by an approximately square-planar arrangement of two oxygen atoms and two halide ions. Each copper(II) ion adds an axial ligand (water in the case of $Cu(pyO)Cl_2 \cdot H_2O$) in a manner which retains a centrosymmetric structure for the dimer. Although the actual crystal structure of $Cu(pyO)Cl_2 \cdot H_2O$ has not been determined, the close resemblance of the spectroscopic and magnetic properties of this complex to those of several similar complexes which have been structurally characterized leaves little doubt as to its basic structure. Kokoska and co-workers found that $Cu(pyO)Cl_2 \cdot H_2O$ exhibits the temperature-dependent EPR spectrum characteristic of an antiferromagnetically coupled pair of copper(II) ions.³ They estimated the singlet–triplet separation to be approximately 885 cm^{-1} which is typical of the *N*-oxide bridged dimer of copper(II) chloride. Our preliminary x-ray studies show $Cu(pyO)Cl_2 \cdot H_2O$ to be triclinic with one dimeric molecule per unit cell.

When crystals of this type of complex are doped with another divalent metal ion it appears that one of the two copper(II) ions in a small fraction of the dimeric molecules is replaced by the new metal ion. This results in small but measurable concentrations of mixed metal dimers. Kokoska and coworkers observed this phenomenon and were able to characterize copper(II)–zinc(II) and copper(II)–nickel(II) pairs.⁴ Clearly, copper(II)–manganese(II) dimers also can be formed in this fashion. From the standpoint of magnetic interactions the copper(II)–manganese(II) dimer is a particularly interesting system since the two ions contribute different numbers of unpaired electrons and both metals have nuclear spins. If the magnitude of the exchange interaction is large compared to the other magnetic interactions, the copper(II) ions ($S = 1/2$) will couple with the manganese(II) ion ($S = 5/2$) to produce a two-state system. One state is characterized by a total spin