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Trifluoromethylsulfonylmethanides Functionalized by a CN Group

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ABSTRACT: *Novel stable carbanions of the general formula* $^{-}C(SO_2CF_3)_n(CN)_{3-n}$ *(n = 1,2) were synthesized. The solid-state structure of cesium cyanobis(trifluoromethylsulfonyl)methanide was determined by single-crystal X-ray diffraction. Phenyldiazonium cyanobis(triluoromethylsulfonyl)-methanide underwent decomposition to yield the oxo-sulfonium ylide—trifluoromethyl(phenoxy)oxo-sulfonium cyano(trifluoromethylsulfonyl)methanide.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 565–570, 1998

INTRODUCTION

For some time, our group [1,2] as well as others [3,4] has been engaged in efforts to synthesize new types of superstrong CH-acids—methane derivatives with three acceptor substituents. Applying principles of physical organic chemistry, we have exploited the powerful electron-withdrawing effect of the SO_2F and SO_2CF_3 groups for the synthesis and investigation of the stable carbanions $^{-}(SO_2R)_3$ [R = F, CF_3] and their conjugate-free acids.

In continuation of our work, it would be desirable to functionalize the central carbon atom in the above-mentioned methanes in order to generate new types of acids $HC(SO_2R)_2(X)$ and $HC(SO_2R)(X)_2$ in addition to $HC(SO_2R)_3$. In the case of X = CN, the expected compounds would be of particular interest. As it was shown by ab initio theoretical calculations, compound $HC(SO_2CF_3)(CN)_2$ may be predicted to be a super strong acid ($\Delta G = 281$ kcal/mol) [5].

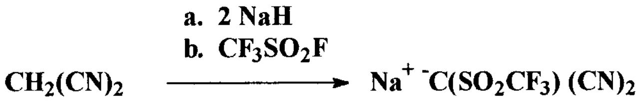
In this article, we report the synthesis of two novel salts of carbanions of general formula $^{-}C(SO_2CF_3)_n(CN)_{3-n}$ (*n* = 1,2) as well as their X-ray crystallographic analyses and some chemical properties.

RESULTS AND DISCUSSION

Synthesis of Sodium Dicyanotrifluoromethylsulfonylmethanide Na^{+} $^{-}C(SO_2CF_3)(CN)_2$ (1)

Sodium salt **1** was synthesized by the procedure depicted in Scheme 1.

Treatment of the presumed dianion of malononitrile [6] with trifluoromethylsulfonylfluoride afforded, in 88% yield, the desirable methanide **1** as a stable crystalline substance. The IR spectrum of compound **1** showed strong bands at 2230 and 2210 cm^{-1}, characteristic for CN stretching frequency,



$$CH_2(CN)_2 \xrightarrow[\text{b. } CF_3SO_2F]{\text{a. } 2\,NaH} Na^{+}\,{}^{-}C(SO_2CF_3)(CN)_2$$

1

SCHEME 1

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along with absorptions typical for the SO_2CF_3 group (see Experimental). The structure of methanide **1** was confirmed also by ^{19}F NMR spectroscopic data and elemental analyses.

Synthesis of Cesium Cyanobis(trifluoromethylsulfonyl)methanide $Cs^{+-}C(SO_2CF_3)_2(CN)$ (**2**)

Among the approaches for the synthesis of methanide **2**, the introduction of the CN fragment in the molecule of the well-known bis(trifluoromethylsulfonyl)methane [7] was viewed as most simple. We tried to prepare the title compound as shown in Scheme 2.

Unfortunately, attempts to prepare salt **2** by treatment of the dianion of bis(trifluoromethylsulfonyl)methane with halogencyanides failed to give the desired product **2**. We were also unable to synthesize methanide **2** using a procedure similar to that used for preparing tricyanomethane [8]. Thus, the reaction of dihalogen derivatives of bis(trifluoromethylsulfonyl)methane with potassium cyanide led to liberation of the cyanogen bromide or chloride and formation of salt **3** [7] in almost quantitative yield. The structure of the latter was confirmed by its ^{19}F NMR spectrum containing only a signal at δ −78.26, typical for the anion **3**.

An alternative route to methanide **2** illustrated in Scheme 3 was successful. Salt **2** was prepared by one-pot reaction using stepwise trifluoromethylsulfonation of acetonitrile. Deprotonation of CH_3CN with a threefold excess of butyllithium followed by treatment with 2 equivalents of trifluoromethylsulfonylfluoride afforded the respective methanide **2**. It is noteworthy that carbanion **2** was isolated as the cesium salt, this being insoluble in cold water. As we expected, a side product was isolated—the stable methane **4** [9], which is obviously an intermediate in this reaction. Unfortunately, we failed to circumvent the formation of **4** by variation of the ratio of reagents.

The structure of salt **2** was established on the basis of spectral evidence and elemental analysis data. We have also determined the crystal structure of the cesium salt by X-ray diffraction. These results are shown in Tables 1–5 and Figure 1.

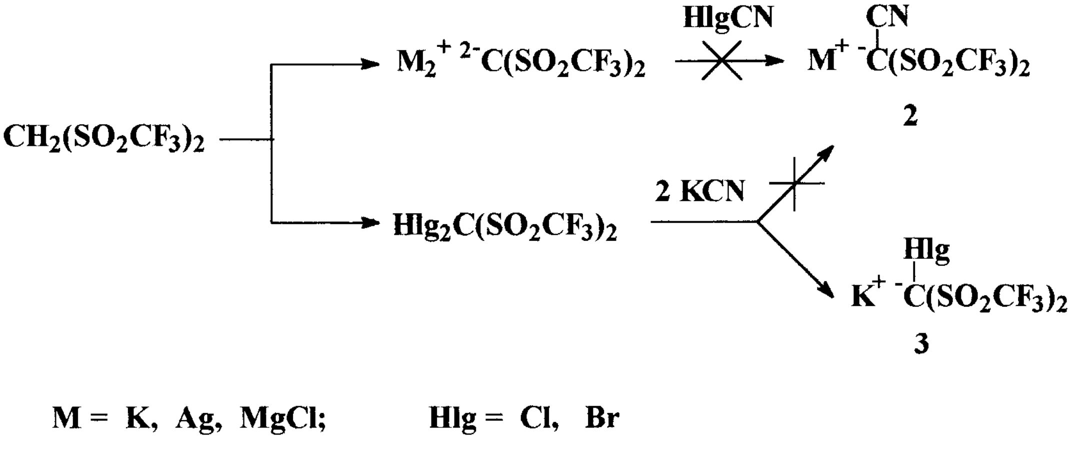
It is worthy of note that the skeleton of the anion **2** consisting of the central carbon C1, the carbon of the CN group C2, and the two sulfur atoms of the SO_2CF_3 groups (S1 and S2) is planar, as previously found for $^-C(SO_2F)_3$ [3] and $^-C(SO_2CF_3)_3$ [4] salts. The nitrogen atom is located in the plane C1C2S1S2, one CF_3 group being located above and another below this plane.

Synthesis and Decomposition of Phenyldiazonium Cyanobis(trifluoromethylsulfonyl)methanide $PhN_2^+\ ^-C(SO_2CF_3)_2(CN)$ (**6**)

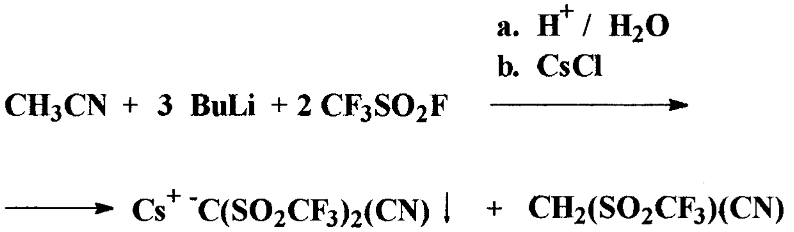
Stable phenyldiazonium salt **6** containing the anion of **2** was obtained according to our published procedure [10,11] (Scheme 4). A mixture of cold aqueous solutions of phenyldiazonium chloride and the CH acid **5** resulted in precipitation of diazonium salt **6**. The aqueous solution of the free acid **5** was easily prepared by passing a hot aqueous solution of the cesium salt **2** through a column packed with an ion-exchange resin Dowex-50 in the H-form.

The structure of methanide **6** was confirmed by a characteristic IR absorption at 2300 cm^{-1} for the $-N_2^+$ group along with absorptions typical for the $^-C(SO_2CF_3)_2(CN)$ anion (see Experimental).

Earlier we have studied pyrolysis of phenyldiazonium methanides $PhN_2^+\ ^-C(SO_2R)_3$ [R = F, CF_3]



SCHEME 2



$$\mathrm{CH_3CN + 3\ BuLi + 2\ CF_3SO_2F \xrightarrow{\text{a. } H^+ / H_2O \quad \text{b. } CsCl} Cs^+\ {}^-C(SO_2CF_3)_2(CN)\downarrow + CH_2(SO_2CF_3)(CN)}$$

2 **4**

SCHEME 3

TABLE 1 Crystallographic Data for Compound **2**

Empirical formula	$C_4CsF_6NO_4S_2$
Formula weight, amu	437.1
Crystal system	tetragonal
Space group	I-4
a, Å	17.139(2)
c, Å	7.927(2)
V, Å^3	2328.5(7)
Z	8
T, K	173
D_{calcg}, Mg/m^3	2.494
μ, mm^{-1}	3.624
Crystal size, mm	0.8 × 0.2 × 0.2
Radiation [λ (Kα)], Å	graphite monochromated 0.71073
Scan range, deg	$5 < 2\theta < 55$
Scan width, deg in ω	1.0
Scan speed, deg/min in ω	4.0 to 60.0
Scan type	ω-2ω
Background counts	static ¼ time each side
Index ranges, *hkl*	−1 to 22, −1 to 22, −1 to 10
Reflections collected	1995
Independent reflections	1844 (R_{int} = 0.0211)
Observed Reflections [$F > 4\sigma(F)$]	1452
Weighting scheme, $w^{-1} = \sigma^2(F) + gF^2$	$g = 0.0000$
Final *R* indices (obs. data)	$R = 0.0393$, $wR = 0.0340$
R indices (all data)	$R = 0.0566$, $wR = 0.0367$
Goodness of fit	1.06
Largest difference peak, e·Å^{-3}	1.15
Largest difference hole, e·Å^{-3}	−0.92

TABLE 2 Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1})

	x	*y*	*z*	*U*(*eq*)^a
Cs(1)	8203(1)	7,429(1)	7,761(1)	23(1)
C(1)	7426(5)	9,862(5)	7,686(13)	21(3)
C(2)	7385(6)	9,308(6)	6,431(13)	23(3)
N(1)	7323(7)	8,847(6)	5,368(12)	40(4)
S(1)	7827(1)	10,747(1)	7,225(3)	23(1)
O(1)	7608(5)	11,347(4)	8,387(9)	32(2)
O(2)	7737(5)	10,874(5)	5,451(9)	38(3)
C(3)	8890(6)	10,616(7)	7,484(17)	41(4)
F(1)	9123(4)	10,010(5)	6,653(12)	69(3)
F(2)	9056(5)	10,556(5)	9,114(10)	63(3)
F(3)	9251(4)	11,241(4)	6,906(11)	59(3)
S(2)	7223(2)	9,587(2)	9,718(3)	23(1)
O(3)	7551(5)	10,108(4)	10,933(9)	33(2)
O(4)	7319(5)	8,758(4)	9,851(10)	28(2)
C(4)	6157(7)	9,709(8)	9,917(15)	37(4)
F(4)	5946(5)	9,399(5)	11,413(9)	60(3)
F(5)	5789(4)	9,337(5)	8,720(9)	53(3)
F(6)	5964(5)	10,444(5)	9,944(11)	56(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[10–12] and have shown that, in neutral medium or without solvents, the phenyl cation formed attacked the anion at the oxygen atom of the sulfonyl group, resulting in the formation of the appropriate oxosulfonium ylide. Zhu and DesMarteau [13] reported, that, in a polar solvent such as CH_3CN, the product due to attack of the phenyl cation at the central carbon atom of the anion $^-C(SO_2CF_3)_3$ was obtained as the major one. In the case of the anion $^-C(SO_2CF_3)_2(CN)$, it might be possible for the phenyl cation to combine with the anion via (1) the sulfonyl oxygen, (2) the methanide carbon, or (3) the cyanide nitrogen. Actually, we observed that the decomposition of the diazonium salt **6** is very complicated. It should be noted that this process is highly dependent on the reaction conditions. Thus, pyrolysis of the salt **6** without solvent has resulted in unidentified tar. However, heating of phenyldiazonium methanide **6** in CH_3CN has produced acid **5** in a yield of 80%, identified by its ^{19}F NMR spectrum and as the cesium salt **2** (obtained by treatment of the aqueous solution with Cs_2CO_3). Finally, decomposition of **6** in boiling benzene or carbon tetrachloride led to a complex mixture (as determined by ^{19}F NMR spectroscopy). Column chromatography on silica gel with carbon tetrachloride as eluent allowed us to separate the major substance—the product of phenyl cation at-

TABLE 3 Anisotropic Displacement Coefficients ($pm^2 \times 10^{-1}$)

	U_{11}	U_{22}	U_{33}	U_{12}	$U1_3$	U_{23}
Cs(1)	22(1)	25(1)	23(1)	0(1)	0(1)	1(1)
C(1)	28(5)	13(4)	20(4)	−7(4)	3(5)	0(4)
C(2)	24(6)	20(5)	24(5)	−7(5)	−6(5)	3(5)
N(1)	47(7)	36(6)	36(6)	−3(6)	5(5)	−14(5)
S(1)	28(1)	17(1)	25(1)	0(1)	−2(1)	0(1)
O(1)	46(5)	19(4)	32(4)	6(4)	5(4)	−1(3)
O(2)	54(6)	32(5)	29(4)	−3(4)	0(4)	8(4)
C(3)	25(5)	39(6)	59(10)	0(5)	−2(6)	3(7)
F(1)	34(4)	52(5)	120(8)	8(4)	9(5)	−29(6)
F(2)	36(4)	91(7)	61(5)	−16(5)	−24(4)	31(5)
F(3)	45(4)	56(5)	75(6)	−25(4)	0(4)	12(5)
S(2)	30(2)	18(1)	22(1)	2(1)	0(1)	3(1)
O(3)	48(5)	27(4)	24(4)	0(4)	−11(4)	1(3)
O(4)	38(5)	12(4)	34(4)	1(4)	0(4)	4(3)
C(4)	38(7)	38(7)	36(6)	−7(6)	6(6)	−1(6)
F(4)	59(5)	67(5)	54(5)	9(5)	21(4)	22(4)
F(5)	30(4)	69(5)	61(5)	−14(4)	2(4)	−6(5)
F(6)	54(5)	48(5)	65(5)	34(4)	12(4)	7(4)

The anisotropic displacement factor exponent takes the following form: $-2\pi^2 (h^2 a^{*2} U_{11} + \ldots + 2hka^* b^* U_{12})$.

TABLE 4 Bond Lengths (pm)

Cs(1)–C(2)	366.6(10)	Cs(1)–N(1)	343.2(11)
Cs(1)–O(4)	319.8(8)	Cs(1)–Cs(1A)	464.4(1)
Cs(1)–Cs(1B)	464.4(1)	Cs(1)–N(1A)	314.2(10)
Cs(1)–O(1A)	330.9(7)	Cs(1)–O(1B)	316.5(7)
Cs(1)–O(2A)	304.4(8)	Cs(1)–O(3A)	308.2(7)
Cs(1)–O(4A)	320.3(8)	Cs(1)–F(4A)	361.8(8)
C(1)–C(2)	137.8(14)	C(1)–S(1)	170.5(9)
C(1)–S(2)	171.4(10)	C(2)–N(1)	116.0(14)
N(1)–Cs(1B)	314.2(10)	S(1)–O(1)	142.9(7)
S(1)–O(2)	143.2(8)	S(1)–C(3)	184.8(11)
O(1)–Cs(1C)	316.5(7)	O(1)–Cs(1E)	330.9(7)
O(2)–Cs(1D)	304.4(8)	C(3)–F(1)	129.2(15)
C(3)–F(2)	132.7(15)	C(3)–F(3)	132.0(14)
S(2)–O(3)	142.9(8)	S(2)–O(4)	143.4(8)
S(2)–C(4)	184.7(13)	O(3)–Cs(1C)	308.2(7)
O(4)–Cs(1A)	320.4(8)	C(4)–F(4)	134.9(14)
C(4)–F(5)	130.6(14)	C(4)–F(6)	130.2(15)
F(4)–Cs(1A)	361.8(8)		

tack at the oxygen atom of trifluoromethylsulfonyl group in the methanide anion—oxosulfonium ylide **7** in 30% yield (see Scheme 5).

The structure of the ylide **7** was established on the basis of spectral evidence and elemental analysis data. In the ^{19}F NMR spectrum, there are signals for two different types of CF_3 groups [δ −78.90 (SO_2CF_3) and δ −72.36 (the CF_3 group at the ylide sulfur atom) in ratio of 1:1]. The IR spectrum showed characteristic absorption bands for the CN, SO_2, and CF_3 groups (see Experimental).

TABLE 5 Bond Angles (°)

C(2)–Cs(1)–N(1)	18.4(2)	C(2)–Cs(1)–O(4)	48.9(2)
N(1)–Cs(1)–O(4)	64.8(2)	C(2)–Cs(1)–Cs(1A)	90.1(2)
N(1)–Cs(1)–Cs(1A)	102.0(2)	O(4)–Cs(1)–Cs(1A)	43.5(1)
C(2)–Cs(1)–Cs(1B)	60.7(2)	N(1)–Cs(1)–Cs(1B)	42.6(2)
O(4)–Cs(1)–Cs(1B)	99.2(1)	Cs(1A)–Cs(1)–Cs(1B)	117.2(1)
C(2)–Cs(1)–N(1A)	133.7(3)	N(1)–Cs(1)–N(1A)	137.0(1)
O(4)–Cs(1)–N(1A)	91.1(2)	Cs(1A)–Cs(1)–N(1A)	47.6(2)
Cs(1B)–Cs(1)–N(1A)	116.7(2)	C(2)–Cs(1)–O(1A)	64.6(2)
N(1)–Cs(1)–O(1A)	55.9(2)	O(4)–Cs(1)–O(1A)	72.6(2)
Cs(1A)–Cs(1)–O(1A)	74.8(1)	Cs(1B)–Cs(1)–O(1A)	42.9(1)
N(1A)–Cs(1)–O(1A)	83.8(2)	C(2)–Cs(1)–O(1B)	106.6(2)
N(1)–Cs(1)–O(1B)	124.9(2)	O(4)–Cs(1)–O(1B)	63.0(2)
Cs(1A)–Cs(1)–O(1B)	45.4(1)	Cs(1B)–Cs(1)–O(1B)	160.9(1)
N(1A)–Cs(1)–O(1B)	60.2(2)	O(1A)–Cs(1)–O(1B)	120.1(2)
C(2)–Cs(1)–O(2A)	78.8(2)	N(1)–Cs(1)–O(2A)	69.1(2)
O(4)–Cs(1)–O(2A)	123.8(2)	Cs(1A)–Cs(1)–O(2A)	167.0(2)
Cs(1B)–Cs(1)–O(2A)	63.1(1)	N(1A)–Cs(1)–O(2A)	145.1(3)
O(1A)–Cs(1)–O(2A)	105.9(2)	O(1B)–Cs(1)–O(2A)	131.5(2)
C(2)–Cs(1)–O(3A)	113.3(2)	N(1)–Cs(1)–O(3A)	123.4(2)
O(4)–Cs(1)–O(3A)	102.8(2)	Cs(1A)–Cs(1)–O(3A)	101.4(1)
Cs(1B)–Cs(1)–O(3A)	140.4(1)	N(1A)–Cs(1)–O(3A)	95.5(2)
O(1A)–Cs(1)–O(3A)	175.4(2)	O(1B)–Cs(1)–O(3A)	55.9(2)
O(2A)–Cs(1)–O(3A)	77.3(2)	C(2)–Cs(1)–O(4A)	104.2(2)
N(1)–Cs(1)–O(4A)	86.0(2)	O(4)–Cs(1)–O(4A)	133.9(1)
Cs(1A)–Cs(1)–O(4A)	120.2(1)	Cs(1B)–Cs(1)–O(4A)	43.4(1)
N(1A)–Cs(1)–O(4A)	87.2(2)	O(1A)–Cs(1)–O(4A)	61.4(2)
O(1B)–Cs(1)–O(4A)	145.5(2)	O(2A)–Cs(1)–O(4A)	69.7(2)
O(3A)–Cs(1)–O(4A)	123.2(2)	C(2)–Cs(1)–F(4A)	146.1(2)
N(1)–Cs(1)–F(4A)	128.9(2)	O(4)–Cs(1)–F(4A)	163.9(2)
Cs(1A)–Cs(1)–F(4A)	120.4(1)	Cs(1B)–Cs(1)–F(4A)	90.1(1)
N(1A)–Cs(1)–F(4A)	72.9(2)	O(1A)–Cs(1)–F(4A)	106.8(2)
O(1B)–Cs(1)–F(4A)	105.7(2)	O(2A)–Cs(1)–F(4A)	72.1(2)
O(3A)–Cs(1)–F(4A)	77.2(2)	O(4A)–Cs(1)–F(4A)	49.4(2)
C(2)–C(1)–S(1)	118.7(8)	C(2)–C(1)–S(2)	118.6(7)
S(1)–C(1)–S(2)	121.9(6)	Cs(1)–C(2)–C(1)	112.3(6)
Cs(1)–C(2)–N(1)	69.3(7)	C(1)–C(2)–N(1)	177.5(11)
Cs(1)–N(1)–C(2)	92.3(7)	Cs(1)–N(1)–Cs(1B)	89.8(3)
C(2)–N(1)–Cs(1B)	168.1(9)	C(1)–S(1)–O(1)	113.3(5)
C(1)–S(1)–O(2)	107.5(5)	O(1)–S(1)–O(2)	119.8(5)
C(1)–S(1)–C(3)	105.4(5)	O(1)–S(1)–C(3)	106.0(5)
O(2)–S(1)–C(3)	103.5(6)	S(1)–O(1)–Cs(1C)	145.4(4)
S(1)–O(1)–Cs(1E)	121.2(4)	Cs(1C)–O(1)–Cs(1E)	91.6(2)
S(1)–O(2)–Cs(1D)	156.8(5)	S(1)–C(3)–F(1)	110.3(8)
S(1)–C(3)–F(2)	109.1(8)	F(1)–C(3)–F(2)	111.6(10)
S(1)–C(3)–F(3)	108.9(8)	F(1)–C(3)–F(3)	109.3(10)
F(2)–C(3)–F(3)	107.5(10)	C(1)–S(2)–O(3)	112.4(4)
C(1)–S(2)–O(4)	108.6(4)	O(3)–S(2)–O(4)	121.6(5)
C(1)–S(2)–C(4)	104.5(5)	O(3)–S(2)–C(4)	105.2(5)
O(4)–S(2)–C(4)	102.7(5)	S(2)–O(3)–Cs(1C)	141.9(4)
Cs(1)–O(4)–S(2)	136.2(4)	Cs(1)–O(4)–Cs(1A)	93.0(2)
S(2)–O(4)–Cs(1A)	130.6(4)	S(2)–C(4)–F(4)	107.2(8)
S(2)–C(4)–F(5)	111.1(8)	F(4)–C(4)–F(5)	108.5(10)
S(2)–C(4)–F(6)	111.2(9)	F(4)–C(4)–F(6)	107.4(10)
F(5)–C(4)–F(6)	111.2(10)	C(4)–F(4)–Cs(1A)	119.5(7)

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Varian VXR-300 spectrometer with $CFCl_3$ as the internal reference. IR spectra were recorded as KBr pellets on a Specord M-80 spectrophotometer.

Sodium Dicyanotrifluoromethylsulfonylmethanide (**1**). A solution of malononitrile (1.42 g, 21.5 mmol) in THF (10 mL) was added dropwise at 20°C

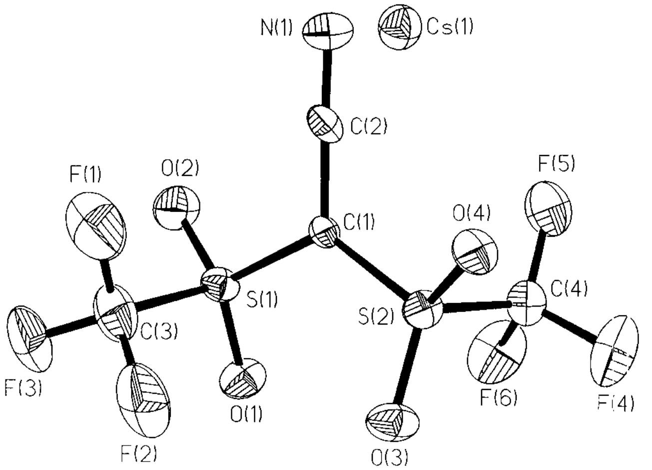


FIGURE 1 Molecular structure of compound **2**.

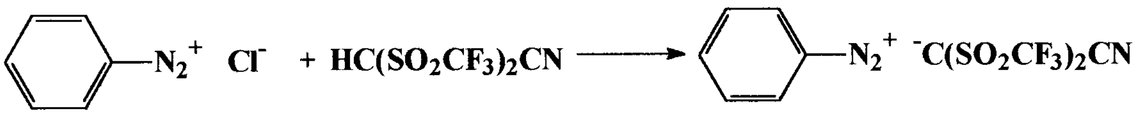
to a suspension of NaH (1.03 g, 43 mmol) in THF (25 mL). The mixture was stirred at this temperature until the evolution of hydrogen ceased. Trifluoromethylsulfonylfluoride (3.8 g, 25 mmol) was bubbled into the resulting mixture over a 0.5 hour period. The temperature was raised to 45°C. Stirring was maintained for 2 hours at 20°C. The solvent was pumped off, and the residue was triturated with ether. The crude product was purified by recrystallization from dioxane, dried azeotropically with toluene, and then in vacuo (48 h, 90°C). **1** was obtained as a white powder, yield 88%. Anal. found: C, 21.76; F, 25.20; N, 12.58; S, 14.09. $C_4F_3N_2NaO_2S$ requires C, 21.82; F, 25.91; N, 12.73; S, 14.55. ^{19}F NMR (CD_3CN): δ −79.9. IR (KBr): ν 2230, 2210, 1365, 1220, 1205, 1185, 1170, 1120, 1080, 780, 665, 620, 610, 590 cm^{-1}.

Cesium Cyanobis(trifluoromethylsulfonyl)methanide (**2**). Acetonitrile (0.85 g, 20 mmol) in THF (15 mL) was added at −78°C to a solution of BuLi (77 mL, 60 mmol, 1.47 M in hexane) in THF (100 mL). The solution was stirred at this temperature for 1 hour. Trifluoromethylsulfonylfluoride (6.1 g, 40 mmol) was bubbled into the resulting mixture over a 1 hour period at −40°C. The temperature was raised to 20°C, and the mixture was stirred at this temperature for 2 hours. The solvents were pumped off, and 3 M aqueous HCl (50 mL) was added to the remaining oil. The resulting mixture was treated with an excess of CsCl; the precipitate that resulted was collected by filtration, washed with ether, and recrystallized from water. **2** was obtained as a pale yellow crystalline solid, yield 20%. Anal. found: C, 10.93; N, 3.28. $C_4CsF_6NO_4S_2$ requires C, 10.98; N, 3.20. ^{19}F NMR (CD_3CN): δ −79.5. IR (KBr): ν 2225, 1375, 1360, 1200–1250, 1130, 1020, 680, 630, 575, 530, 520, 470 cm^{-1}. The filtrate, after removal of **2**, was extracted with ether, the combined extracts dried over $MgSO_4$, solvents evaporated, and the residue distilled. **4** was obtained as a colorless liquid, yield 40%, bp 79–81/10 mm Hg [9].

X-ray Structure of **2**. A single crystal of **2** was prepared by slow evaporation of an aqueous solution. The final cell dimensions of a = 17.139(2) Å and c = 7.972(2) Å at 173 K were found by a least-squares refinement of the setting angles of 72 reflections that had been automatically centered on a Siemens P4 diffractometer. Intensity data were collected at 173 K by the w-2q scan technique. Crystal stability was monitored by recording three standard reflections after every measurement of 197 reflections, and no decay was observed. A total of 1995 intensities were collected, 1844 of which are independent. After processing of Lorentz and polarization corrections, 1452 were treated as observed [$F > 4s(F)$]. An empirical absorption correction was applied [14]. Experimental details and crystal data are shown in Table 1. The structure was solved by direct methods and refined by full matrix least-squares calculations [15], the function $Sw(F - F)$ being minimized. The final refinement on F, including anisotropic thermal parameters of all atoms (164 parameters), resulted in a value R of 0.00393. Final positional and equivalent isotropic displacement parameters are given in Table 2. Anisotropic displacement parameters are reported in Table 3, while bond lengths and angles are given in Tables 4 and 5, respectively.

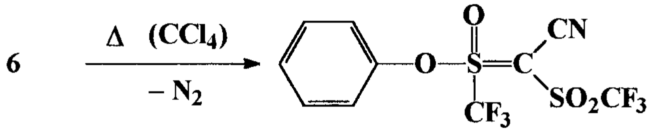
Phenyldiazonium Cyanobis(trifluoromethylsulfonyl)methanide (**6**). A solution of **2** (0.87 g, 2 mmol) in hot water (20 mL) was passed through a column (d 20 mm, L 150 mm) containing Dowex-50 in H-form. The resulting solution was concentrated to 5 mL and added at 0°C to an aqueous solution of phenyldiazonium chloride prepared by treatment of aniline (0.19 g, 2 mmol), with hydrochloric acid (concd, 3 mL), water (5 mL), and sodium nitrite (0.14 g, 2 mmol). After 5 minutes, a white precipitate that had formed was collected by filtration, washed with water, and dried over P_2O_5 in vacuo. **6** was obtained as a white powder, yield 85%. Anal. found: N, 10.11. $C_{10}H_5F_6N_3O_4S_2$ requires N, 10.27. ^{19}F NMR (CD_3CN): δ −79.40. IR (KBr): ν 3110, 2300, 2210, 1580, 1470, 1375, 1355, 1220, 1180, 1140, 1080, 1025, 760, 690, 670, 625, 590, 540, 520, 475 cm^{-1}.

Thermal Decomposition of **6**: *Synthesis of Trifluoromethyl(phenoxy)oxosulfonium Cyano(trifluoromethylsulfonyl)methanide* (**7**). A suspension of **6** (0.40 g, 1 mmol) in anhydrous CCl_4 (10 mL) was



5 6

SCHEME 4



7

SCHEME 5

heated at 80°C until the evolution of nitrogen ceased (15 min). The resulting solution was purified by column chromatography on silica gel, and the solvent was removed under vacuum. The residue was dissolved in hexane, and the solution was kept at -30°C for crystallization. 7 was obtained as white crystals, yield 30%, mp 34–35°C. Anal. found: C, 30.89; H, 1.33; F, 28.98; N, 3.62; S, 16.52, $C_{10}H_5F_6NO_4S_2$ requires C, 31.50; H, 1.31; F, 29.92; N, 3.68; S, 16.80. ^{19}F NMR (benzene): δ -72.36 [s, 3F, $C{=}S(CF_3)$], δ -78.90 [s, 3F, SO_2CF_3]. IR (KBr): ν 3100, 2230, 1500, 1410, 1340, 1270, 1220, 1160, 1140, 1110, 1030, 920, 900, 790, 780, 770, 690 cm^{-1}.

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