Journal of Fluorine Chemistry, 62 (1993) 31–37

Arenediazonium bis(trifluoromethanesulphonyl)methides. Synthesis and X-ray crystal structure of *p*-$CH_3C_6H_4N_2^+(CF_3SO_2)_2CH^-$

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(Received March 10, 1992; accepted July 26, 1992)

Abstract

The title compounds, *p*-$YC_6H_4N_2^+(CF_3SO_2)_2CH^-$ ($Y = H$, CH_3, F, I, NO_2), have been prepared in good yield from the reaction of arenediazonium chloride with potassium bis(trifluoromethanesulphonyl)methide. The X-ray structural analysis of *p*-$CH_3C_6H_4N_2^+(CF_3SO_2)_2CH^-$ is presented.

Aromatic diazo compound take part in a great variety of chemical reactions and form the largest class of intermediates used in the preparation of dyes stuffs [1]. After a successful preparation of phenyldiazonium tris(trifluoromethanesulphonyl)methide, $PhN_2^+(CF_3SO_2)_3C^-$, and phenyldiazonium bis(trifluoromethanesulphonyl)amide, $PhN_2^+(CF_3SO_2)_2N^-$ [2], we report here the synthesis of the arenediazonium bis(trifluoromethanesulphonyl)methides.

Compounds **1** and **2** were prepared by the reaction of phenyl diazonium chloride with tris(trifluoromethanesulphonyl)methane or bis(trifluoromethanesulphonyl)amide, respectively [2]:

$$C_6H_5N_2^+Cl^- + YH \xrightarrow[0\ ^\circ C,\ -HCl]{H_2O} C_6H_5N_2^+Y^-$$

$Y = (CF_3SO_2)_3C$ (**1**); $(CF_3SO_2)_2N$ (**2**)

Under the same reaction conditions, however, bis(trifluoromethanesulphonyl)methane, $(CF_3SO_2)_2CH_2$, did not react with phenyldiazonium chloride. This may be explained by the difference in acidity between $(CF_3SO_2)_2CH_2$ and $(CF_3SO_2)_3CH$. It has been estimated that the latter is a stronger acid than concentrated nitric acid [3]. If, however, the potassium salt of bis(trifluoromethanesulphonyl)methane, $KCH(SO_2CF_3)_2$, was used, the reaction occurred smoothly and yielded the title compounds. When a solution of $KCH(CF_3SO_2)_2$ was added to a clear solution of $PhN_2^+Cl^-$, a yellow precipitate formed immediately. After filtration and vacuum drying the crude product was obtained in high yield (see Table 1).

0022-1139/93/$6.00

TABLE 1

Range of compounds **5** prepared

Entry No.	Product (**5**)	Yield[a] (%)	Melting point (°C) (decd.)
1	Y=H (**5a**)	95	74
2	Y=CH_3 (**5b**)	92	76
3	Y=F (**5c**)	92	80
4	Y=I (**5d**)	90	96
5	Y=NO_2 (**5e**)	90	84

[a] Isolated yield, based on reactant **3**.

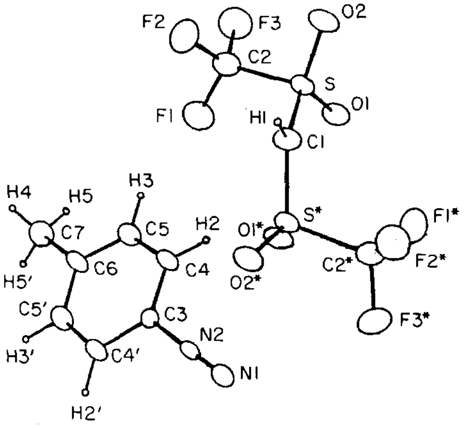


Fig. 1. The X-ray crystal structure of compound **5b**.

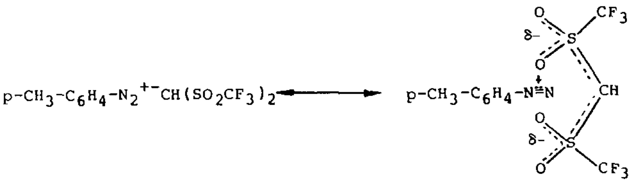
$$\underset{(3)}{(CF_3SO_2)_2CHK} + \underset{(4)}{p\text{-}YC_6H_4N_2{}^+Cl^-} \xrightarrow[\text{°C}\rightarrow\text{r.t.}]{H_2O} \underset{(5)}{p\text{-}YC_6H_4N_2{}^{+\,-}CH(CF_3SO_2)_2}$$

All these diazonium salts are stable and can be stored at room temperature for several weeks without alteration.

Russian chemists have suggested that the decomposition temperatures of the diazonium compounds are determined chiefly by the nature of the diazonium cation [4].

On comparing the stability of $PhN_2{}^+Cl^-$, $PhN_2{}^+CN^-$ and $PhN_2{}^{+\,-}CH(CF_3SO_2)_2$ (their decomposition temperatures are 25 °C, 60 °C, and 75 °C, respectively [5, 6]) it is clear that the stability of these diazonium compounds are also determined by the counteranion.

Recrystallization of the crude products **5** which are powders, gave fine yellowish crystals. The X-ray structural analysis of **5b** (see Fig. 1) shows that the $N_1{-}N_2{-}C_3$ arrangement is linear and that the arenediazonium ion is planar. In the crystal structure, every $N_2{}^+$ group is surrounded by four sulphonyl oxygen atoms, the distances between the nitrogen and oxygen atoms being about 3 Å. The positive charge would thus be shared between



Scheme 1.

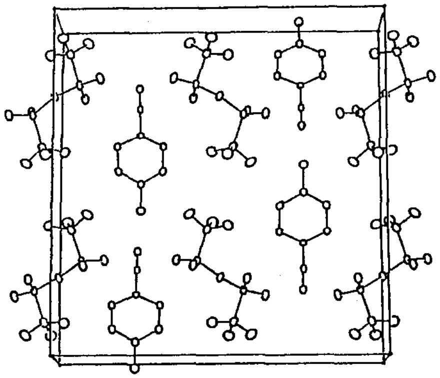


Fig. 2. Stereoview of the unit cell of compound **5b**.

the two nitrogen atoms [7] and this might explain the approximately equal distance from an oxygen atom to the two nitrogen atoms. The double-bond character of the C_I-S and C_I-S^* bonds (1.66 Å) (cf. the C_2-S bond distance of 1.81 Å) indicates that the negative charge of the carbon anion is delocalised as shown in Scheme 1. The stereoview of the unit cell of compound **5b** is shown in Fig. 2.

In conclusion, a series of new arenediazo compound containing bis(trifluoromethanesulphonyl)methide co-ordinated anions has been prepared. The structure of these compounds are fully supported by microanalyses and IR, ^{19}F NMR, ^{1}H NMR and MS spectra. Their chemistries are under investigation.

Experimental

A typical process for preparing arenediazonium bis(trifluoromethanesulphonyl)methide is as follows and exemplifies the preparation of $Ph-N_2^{+}\,{}^{-}CH(CF_3SO_2)_2$ (**5a**). A solution consisting of water (10 ml) and potassium bis(trifluoromethanesulphonyl)methide (1.6 g, 5 mmol), which had been synthesized from the reaction of bis(trifluoromethanesulphonyl)methane with potassium carbonate, was added dropwise into a 50 ml round-bottomed flask charged with an aqueous solution of phenyldiazonium chloride which had been prepared by treatment of aniline (0.5 g, 5.5. mol) with water (10 ml), hydrochloric acid (1 N, 6 ml) and sodium nitrite (0.4 g, 6 mmol) at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 1 h. The yellow precipitate was filtered off and dried under vacuum giving **5a** (1.8 g, 95%). Recrystallization from acetone gave the pure products.

Benzene diazonium bis(trifluoromethanesulphonyl)methide $C_6H_5N_2{}^{+-}$-$CH(SO_2CF_3)_2$ (**5a**): IR ($\nu_{max.}$) cm^{-1}: 3065(s); 2270(m); 1572(s); 1461(s); 1360(vs); 1220–1120(vs); 1070(vs); 955(vs); 830(m); 750(s); 648(m); 600(vs); 495(s). ^{1}H NMR $(CD_3)_2CO$ (TMS) δ: 3.32 (s, 1H); 8.05 (m, 2 ArH); 8.30 (m, 3ArH) ppm. ^{19}F NMR (TFA) δ: 5.30 (s, 2CF_3) ppm. MS (*m/z*): 385 (M+H, 1.04); 384 (M^+, 0.11); 357 (M^+H-N_2, 28.06); 315 (M^+-CF_3, 2.00); 287 ($M^+-N_2-CF_3SO$, 9.44); 271 ($M^+-N_2-CF_3-O$, 5.01); 239 ($M^+-N_2-CF_3SO$, 9.44); 223 ($M^+-N_2-CF_3SO_2$, 6.94); 153 ($C_6H_5CSO^+$, 27.41); 105 ($C_6H_5N_2{}^+$, 10.97); 77 ($C_6H_5{}^+$, 100); 69 ($CF_3{}^+$, 33.27); 65 ($C_5H_5{}^+$, 64.07). Analysis: Calcd. for $C_9H_6F_6N_2O_4S_2$: C, 28.13; H, 1.56; N, 7.29; F, 29.69%. Found: C, 27.97; H, 1.46; N, 7.08; F, 29.07%.

Compound **5b**: ^{1}H NMR δ: 2.65 (s, CH_3); 3.40 (s, 1H); 7.81–8.80 (AA'BB', 4 $H_{arom.}$) ppm. ^{19}F NMR δ: 5.10 (s, 2×CF_3) ppm. IR ($\nu_{max.}$ cm^{-1}): 3060(m); 3030(m); 2249(m); 1580(s); 1322(vs); 1303(s); 1216–1120(vs); 1090(s); 942(s); 842(m); 811(s); 600(vs). MS (*m/e*): 398 (M^+, 0.54); 371 (M^+H-N_2, 43.44); 355 ($M^+-N_2-CH_3$, 6.01); 253 ($M^+-N_2-CF_3SO$, 14.89); 237 ($M^+-N_2-CF_3SO_2$, 3.89); 151 ($CH_3C_6H_4CSO^+$, 6.86); 119 ($CH_3C_6H_4N_2{}^+$, 6.69); 107 ($CH_3C_6H_4O^+$, 100); 91 ($CH_3C_6H_4{}^+$, 18.40). Analysis: Calcd. for $C_{10}H_8F_6N_2O_4S_2$: C, 30.15; H, 2.01; N, 7.04; F, 28.64%. Found: C, 30.40; H, 2.07; N, 7.16; F, 28.27%.

Compound **5c**: ^{1}H NMR δ: 3.20 (s, 1H); 7.85–9.15 (AA'BB', 4 $H_{arom.}$) ppm. ^{19}F NMR δ: 11.0 (s, 2×CF_3); 15.3 (s, 1F) ppm. IR ($\beta_{max.}$ cm^{-1}): 3080(m); 2450(m); 1580(s); 1481(m); 1325(vs); 1258(m); 1200–1160(vs); 1091(s); 960(s); 840(s); 600(s). MS (*m/e*): 402 (M^+, 1.35); 401 (M^+-1, 8.54); 374 (M^+-N_2, 0.67); 310 ($M^+-N_2-SO_2$, 3.35); 268 ($M^+-H-CF_3SO_2$, 10.60); 110 ($FC_6H_4NH^+$, 52.94); 95 ($FC_6H_4{}^+$, 18.48); 69 ($CF_3{}^+$, 100). Analysis: Calcd. for $C_9H_5F_7N_2O_4S_2$: C, 26.87; H, 1.24; N, 6.97; F, 33.08%. Found: C, 26.67; H, 1.09; N, 6.81; F, 33.71%.

Compound **5d**: ^{1}H NMR δ: 3.40 (s, 1H); 7.83–8.88 (AA'BB', 4 $H_{arom.}$) ppm. ^{19}F NMR δ: 5.30 (s, 2×CF_3) ppm. IR ($\nu_{max.}$ cm^{-1}): 3063(w); 3033(m); 2260(m); 1581(s); 1320(vs); 1305(s); 1240–1140(s); 1088(s); 948(m); 840(m); 600(s). MS (*m/e*): 510 (M^+, 0.22); 482 (M^+-N_2, 1.05); 406 ($M^+-N_2-C_6H_4$, 6.29); 349 ($M^+-N_2-CF_3SO_2$, 10.80); 330 ($M^+-N_2-F-CF_3SO_2$, 100); 279 ($M^+-N_2-C_6H_4I$, 10.00); 203 ($C_6H_4I^+$, 22.29); 127 (I^+, 5.11). Analysis: Calcd. for $C_9H_5F_6IN_2O_4S_2$: C, 21.18; H, 0.98; N, 5.49; F, 22.35%. Found: C, 21.20; H, 1.04; N, 5.64; F, 21.98%.

Compound **5e**: ^{1}H NMR δ: 3.15 (s, 1H); 8.75–9.35 (AA'BB', 4 $H_{arom.}$) ppm. ^{19}F NMR δ: 6.0 (s, 2×CF_3) ppm. IR ($\nu_{max.}$ cm^{-1}: 3080(m); 2280(m); 1600(m); 1540(s); 1392(m); 1325(vs); 1220–1100(s); 962(s); 858(m); 740(m); 600(s); MS (*m/e*): 429 (M^+, 1.89); 307 ($M^+-O_2NC_6H_4$, 1.34); 295 ($M^+-H-CF_3SO_2$, 3.90); 150 ($O_2NC_6H_4N_2{}^+$, 2.29); 122 ($O_2NC_6H_4{}^+$, 7.14); 117 (CF_3SO^+, 5.11); 69 ($CF_3{}^+$, 100). Analysis: Calcd. for $C_9H_5F_6N_3O_6S_2$: C, 25.17; H, 1.17; N, 9.79; F, 26.57%. Found: C, 25.43; H, 1.39; N, 10.08; F, 25.97%.

Crystal data

$C_{10}H_8O_4N_2F_6S_2$, M = 398.30, orthorhombic; space group *Pcmb*; $a = 5.153(1)$ Å, $b = 17.017(3)$ Å, $c = 18.330(2)$ Å, $V = 1607.2$ Å^3, $Z = 4$, $D_c = 1.646$ g cm^{-3}); $F(000) = 800$, $\mu(\mathrm{MoK}\alpha) = 3.970$ cm^{-1}, crystal dimensions 0.2×0.1×0.1 mm. Intensity data were collected at 20 °C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation. 1693 unique reflections were measured in the range $2° < 2\theta < 50°$ with $0 \leqslant h \leqslant 6$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 21$. LP and absorption corrections were applied to the intensity data. The structure was solved by a direct method using MULTAN 11/82. The positions of the H atoms were defined via difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by a full-matrix least-squares technique. Final *R*,

TABLE 2

Compound **5b**: bond distances in ångstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S	O(1)	1.428(4)[a]	C(3)	C(4)	1.380(6)[a]
S	O(2)	1.423(4)	C(4)	C(5)	1.368(8)
S	C(1)	1.66(4)	C(5)	C(6)	1.378(7)
S	C(2)	1.811(7)	C(6)	C(7)	1.50(1)
F(1)	C(2)	1.334(8)	N(1)	O(1)	2.988(4)
F(2)	C(2)	1.324(8)	N(1)	O(2)	3.043(7)
F(3)	C(2)	1.319(7)	N(2)	O(1)	3.024(4)
N(1)	N(2)	1.091(9)	N(2)	O(2)	2.939(7)
N(2)	C(3)	1.40(2)			

[a] Numbers in parentheses are estimated standard deviations for the last digit.

TABLE 3

Compound **5b**: bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O(1)	S	O(2)	120.0(2)[a]	S	C(2)	F(3)	111.8(5)[a]
O(1)	S	C(1)	113.2(3)	F(1)	C(2)	F(2)	106.9(6)
O(1)	S	C(2)	102.7(3)	F(1)	C(2)	F(3)	105.7(6)
O(2)	S	C(1)	110.5(4)	F(2)	C(2)	F(3)	107.1(6)
O(2)	S	C(2)	101.7(4)	N(2)	C(3)	C(4)	118.0(4)
C(1)	S	C(2)	107.0(2)	C(4)	C(3)	C(4′)	123.9(8)
N(1)	N(2)	C(3)	180(1)	C(3)	C(4)	C(5)	116.3(5)
S	C(1)	S′	123.0(5)	C(4)	C(5)	C(6)	123.4(6)
S	C(2)	F(1)	112.6(5)	C(5)	C(6)	C(5′)	116.9(8)
S	C(2)	F(2)	112.4(5)	C(5)	C(6)	C(7)	121.5(4)

[a] Numbers in parentheses are estimated standard deviations for the last digit.

TABLE 4

Compound **5b**: positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2)[a]
S	0.7351(4)	0.57176(9)	0.2937(1)	3.70(3)
F(1)	0.550(1)	0.4752(3)	0.3927(3)	8.3(1)
F(2)	0.918(1)	0.5247(3)	0.4196(3)	8.4(2)
F(3)	0.575(1)	0.5936(3)	0.4270(3)	8.3(2)
O(1)	0.4739(9)	0.5823(3)	0.2696(3)	4.8(1)
O(2)	0.901(1)	0.6381(3)	0.3023(3)	5.4(1)
N(1)	0.361(2)	0.750	0.3061(5)	4.6(2)
N(2)	0.293(2)	0.750	0.2497(5)	3.9(2)
C(1)	0.889(2)	0.500	0.250	3.7(2)
C(2)	0.694(2)	0.5400(5)	0.3873(4)	5.4(2)
C(3)	0.203(2)	0.750	0.1774(5)	4.1(3)
C(4)	0.156(2)	0.6785(4)	0.1445(4)	5.2(2)
C(5)	0.067(2)	0.6810(4)	0.0743(4)	6.7(3)
C(6)	0.016(3)	0.750	0.0377(6)	5.3(3)
C(7)	−0.100(4)	0.750	−0.0376(7)	8.5(5)
H(1)	0.082	0.500	0.250	4.0*
H(4)	0.250	0.365	0.332	4.0*
H(5)	0.041	0.365	0.449	4.0*
H(71)	0.957	0.750	0.416	4.0*
H(72)	0.125	0.699	0.449	4.0*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

TABLE 5

Compound **5b**: general displacement parameter expressions[a] (U values)

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
S	0.0417(8)	0.0324(6)	0.0667(9)	−0.001(1)	−0.000(1)	−0.0065(9)
F(1)	0.143(5)	0.084(3)	0.088(3)	−0.039(4)	0.020(4)	0.004(3)
F(2)	0.122(5)	0.103(4)	0.093(3)	0.016(4)	−0.034(4)	0.002(3)
F(3)	0.134(5)	0.095(3)	0.087(3)	0.015(4)	0.029(4)	−0.027(3)
O(1)	0.045(3)	0.044(2)	0.091(4)	0.013(3)	−0.010(3)	−0.012(3)
O(2)	0.060(3)	0.044(3)	0.099(4)	−0.011(3)	0.007(4)	−0.015(3)
N(1)	0.076(6)	0.037(4)	0.062(6)	0	−0.006(6)	0
N(2)	0.071(6)	0.023(3)	0.053(5)	0	0.004(6)	0
C(1)	0.027(5)	0.042(5)	0.070(6)	0	0	−0.014(5)
C(2)	0.074(6)	0.056(4)	0.076(5)	0.004(5)	0.004(5)	−0.016(4)
C(3)	0.091(9)	0.036(4)	0.029(5)	0	0.001(6)	0
C(4)	0.114(7)	0.034(3)	0.050(4)	0.011(5)	−0.013(5)	−0.001(3)
C(5)	0.16(1)	0.039(4)	0.056(5)	−0.008(6)	−0.006(7)	−0.008(4)
C(6)	0.11(1)	0.036(5)	0.058(7)	0	−0.012(8)	0
C(7)	0.21(2)	0.056(6)	0.054(7)	0	−0.03(1)	0

[a] The forms of the anisotropic displacement parameter is: $\exp[-2PI2\{h2a2U(1,1)+k2b2U(2,2)+12c2U(3,3)+2hkabU(1,2)+2hlacU(1,3)+2klbcU(2,3)\}]$ where a, b and c are reciprocal lattice constants.

Rw and *S* values were 0.041, 0.049, 1.92, respectively, for 625 observed reflections ($F^2 > 3\sigma(F^2)$). All computations were performed on a MICROVAX II computer with SDP, MULTAN 11/82 and ORTEP programs. Scattering factors were taken from *International Tables for X-ray Crystallography*, (1974). Full details of the crystallographic data thus obtained are given in Tables 2–5.

Acknowledgement

The author thanks the Shanghai Natural Science & Technology Foundation for financial support of this work.

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