2274 *Inorg. Chem.* **1992**, *31*, 2274-2279

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# Synthesis, Characterization, and X-ray Crystal Structure of the Paramagnetic Solid 5-(Trifluoromethyl)-1,2,3,4-trithiazolium Hexafluoroarsenate, Containing the Novel, Planar 7π $CF_3\overline{CNSSS}^{\bullet+}$ Radical Cation

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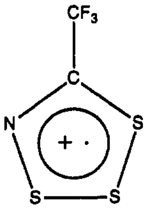
*Received September 5, 1991*

We report the synthesis and characterization of the paramagnetic solid 5-(trifluoromethyl)-1,2,3,4-trithiazolium hexafluoroarsenate, the first salt containing a planar, 7π $\overline{CNSSS}^{\bullet+}$ radical cation. It was prepared in quantitative yield as a purple crystalline solid by the reaction of $CF_3CN$ with a 1:1 mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ in $SO_2$ at room temperature for 2 weeks and characterized by chemical analyses, variable-temperature magnetic susceptibility ($\mu = 1.65\ \mu_B$), IR, Raman, mass, $^{19}F$ NMR, and ESR spectra, and X-ray crystallography. The crystal structure consisted of layers containing both monomeric, planar 7π $CF_3\overline{CNSSS}^{\bullet+}$ cations and $AsF_6^-$ anions: space group $Pn2_1a$, $a = 10.256$ (1) Å, $b = 8.181$ (4) Å, $c = 12.470$ (2) Å, $Z = 4$, $R = 5.52\%$, $R_w = 6.19\%$. The ESR spectrum of $CF_3\overline{CNSSS}^{\bullet+}$ in $SO_2$ consisted of a singlet at $g = 2.016$ and a pair of broad, asymmetric $^{33}S$ satellites ("$a(^{33}S)$" = 8.3 G). The absence of hyperfine coupling to N and F was consistent with the $^{19}F$ NMR spectrum, which exhibited a broad ($\Delta\nu = 440$ Hz), weakly contact shifted, resonance at −45 ppm, and 3-21G* MO calculations, in which the SOMO was shown to reside primarily on the SSS moiety.

The thiazyl radicals[1] $R\overline{CSNSC}R^\bullet$,[2] $R\overline{CNSNS}^\bullet$,[3] and $R\overline{CNSSN}^\bullet$ [1,4] have been the subject of much recent interest in terms of both their unusual molecular properties and their potential application as precursors to "novel materials".[5] We have recently reported the synthesis and characterization of the $CF_3\overline{CSSSC}CF_3^{\bullet+}$ radical cation,[6] which is related to $CF_3\overline{CSNSC}CF_3^\bullet$ by the isovalent substitution of $S^{\bullet+}$ for $N^\bullet$. In an extension of this work, we now report the synthesis and characterization of the $CF_3\overline{CNSSS}^{\bullet+}$ cation (1), which is related



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by a similar isovalent substitution to $CF_3\overline{CNSSN}^\bullet$ and $CF_3\overline{CNSNS}^\bullet$. Although $CF_3\overline{CSSSC}CF_3^{\bullet+}$ and $CF_3\overline{CNSSS}^{\bullet+}$ are radicals, they show no tendency to dimerize in the solid state but instead form paramagnetic solids consisting of layers containing both cations and anions. By suitable manipulation of the molecular and solid-state architecture, these classes of radicals are potentially capable of forming extended arrays of unpaired spins, leading ultimately to novel materials with unusual magnetic and other physical properties.

## Experimental Section

Apparatus, techniques, and chemicals, unless specified, have been previously described.[7] $CF_3CN$ (Matheson) and $AsF_5$ (Ozark-Mahoning) were used as received. $Br_2$ (Anachemia) was dried over $P_4O_{10}$, and $SO_2$ over $CaH_2$; $S_8$ was vacuum-dried prior to use.

$^{19}F$ NMR spectra were acquired at 188.15 MHz on a Varian Associates XL-200 spectrometer and referenced externally to $CFCl_3$ in $SO_2$ with the high-frequency direction positive. Samples were contained in thick-walled 5-mm (sealed) or 10-mm (fitted with J. Young O-Ringette type valves) precision NMR tubes (Wilmad), and a weighed amount of $CFCl_3$ or $SO_2ClF$ was added immediately prior to acquisition as an internal concentration standard. Infrared spectra were obtained as Nujol mulls (for solid samples) or films (liquids) between KBr (4000–350 cm$^{-1}$) or CsI (4000–200 cm$^{-1}$) plates on a Perkin-Elmer 683 instrument. The Raman spectrum of $(1)AsF_6$ was obtained on a Bruker IFS-66 infrared spectrometer outfitted with an FRA-106 Fourier transform Raman accessory, with a sample contained in a sealed, thin-walled 5-mm NMR tube (Wilmad). Samples for mass spectrometry were contained in sealed glass capillaries under dry nitrogen and introduced into the spectrometer by direct inlet. All spectra were obtained at room temperature in the electron impact mode using 27-eV ionizing voltage on a Kratos MS-50TC instrument. ESR spectra were recorded with a custon-built spectrometer, as described in ref 6b. $SO_2$ absorbs microwave radiation, and so samples were contained in 3-mm sealed quartz tubes. Magnetic susceptibility measurements were performed at room temperature by the Guoy method using a Newport Instruments VR3 electromagnet attached to a Mettler AE163 analytical balance. Between 5 and 200 K, the magnetization ($M$) was measured with a SQUID magnetometer and the susceptibilities were obtained directly from $M/H$.

Elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

**Synthesis of $CF_3\overline{CNSSS}AsF_6$.** $SO_2$ (7.048 g), $AsF_5$ (1.725 g, 10.15 mmol), and $Br_2$ (trace) were successively condensed onto $S_8$ (0.582 g, 2.27 mmol) contained in a two-bulb vessel incorporating a medium sintered-glass frit and closed with a J. Young valve. After the blue solution was stirred for 1 week at room temperature, $CF_3CN$ (0.617 g, 6.49 mmol, 7% excess relative to eq 1) was condensed onto the reaction mixture,

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(1) (a) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299. (b) Preston, K. F.; Sutcliffe, L. H. *Magn. Reson. Chem.* **1991**, *28*, 189 and references therein.

(2) (a) Schriver, M. J. Ph.D. Thesis, University of New Brunswick, 1988. (b) Awere, E. G.; Burford, N.; Mailer, C.; Passmore, J.; White, P. S.; Banister, A. J.; Oberhammer, H.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 66. (c) Awere, E. G.; Haddon, R. C.; Parsons, S.; Passmore, J.; Waszczak, J. V.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4821.

(3) (a) Brooks, W. V. F.; Burford, N.; Passmore, J.; Schriver, M. J.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 69. (b) Burford, N.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 140. (c) Banister, A. J.; Rawson, J. M.; Clegg, W.; Birkby, S. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1019.

(4) (a) Hofs, H. U.; Bats, J. W.; Gleiter, R.; Hartmann, G.; Mews, R.; Eckert-Maksic, M.; Oberhammer, H.; Scheldrick, G. M. *Chem. Ber.* **1985**, *118*, 3781. (b) Cordes, A. W.; Goddard, J. D.; Oakley, R. T.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 6147.

(5) (a) Cordes, A. W.; Haddon, R. C.; Oakley, R. T.; Schneemeyer, L. F.; Waszczak, J. V.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, *113*, 582. (b) Andrews, M. P.; Cordes, A. W.; Douglass, R. M.; Fleming, R. M.; Glarum, S. H.; Haddon, R. C.; Marsh, P.; Oakley, R. T.; Palstra, T. T. M.; Schneemeyer, L. F.; Trucks, G. W.; Tycko, R.; Waszczak, J. V.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, *113*, 3559.

(6) (a) Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. *J. Chem. Soc., Chem. Commun.* **1991**, 358. (b) Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. *J. Chem. Soc., Dalton Trans.*, in press.

(7) Murchie, M.; Passmore, J. *Inorg. Synth.* **1986**, *24*, 76.

0020-1669/92/1331-2274$03.00/0

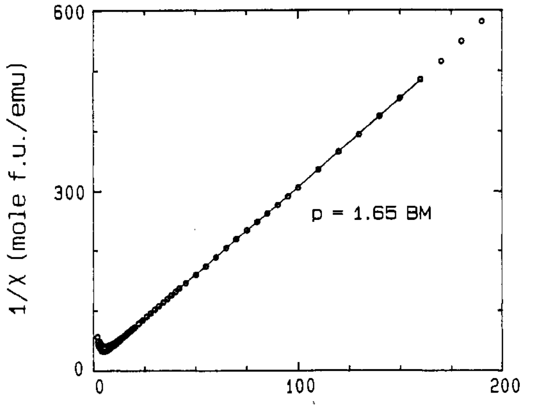

Figure 1. Magnetic susceptibility: plot of $1/\chi$ versus $T$ (K) for the determination of the magnetic moment. Key: f.u. = formula unit.

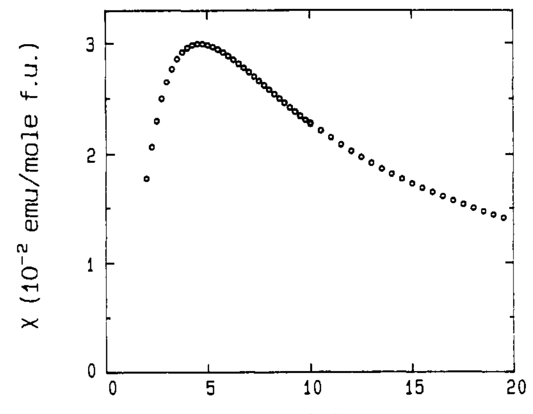

Figure 2. Magnetic susceptibility: plot of $\chi$ versus $T$ between 2 and 20 K.

causing it to become dark green after 1 day and then red-brown after 2 days. The solution was stirred for a further 12 days at room temperature. The volatiles ($SO_2$, $OSF_2$, 0.2 mmol; $AsF_3$, 0.3 mmol; $CF_3CN$, 0.2 mmol; also minor unassigned $^{19}F$ NMR resonances at 53 (br), −85.7, and −86.6 ppm) were condensed into a 10-mm NMR tube, leaving a red-brown solid which was then pumped to constant weight (2.351 g; cf. expected 2.301 g from eq 1).

Infrared spectrum ($\nu_{max}$, cm$^{-1}$): 1552 m ($\nu$(CN)), 1292 s, 1274 s, 1260 vs, 1245 sh, 1200 vs ($\nu_{as}(CF_3)$), 1005 w ($\nu_s(CF_3)$), 980 m, 960 vs, 850 s ($\nu$(SN)), 820 w ($\nu(AsF_6^-)$), 724 sh, 700 vs ($\nu_3(AsF_6^-)$), 675 sh ($\nu_1(AsF_6^-)$), 639 s, 578 w ($\nu_2(AsF_6^-)$), 542 w ($\nu$(SS)), 506 w, 449 vw ($\nu$(SS)), 394 vs ($\nu_4(AsF_6^-)$), 373 sh ($\nu_5(AsF_6^-)$), 332 vvw, 279 m. FT Raman spectrum ($\nu_{max}$, cm$^{-1}$): 1551 w ($\nu$(CN)), 727 m, 680 s ($\nu_1(AsF_6^-)$), 643 m, 575 vw ($\nu_2(AsF_6^-)$), 542 vs ($\nu$(SS)), 449 s ($\nu$(SS)), 410 m, 396 w ($\nu_4(AsF_6^-)$), 371 mw ($\nu_5(AsF_6^-)$), 363 w, 280 s. Mass spectrum ($m/z$, intensity >10%): 191 (14.4, $C_2F_3S_3N^+$, i.e. $M^+$), 151 (100, $AsF_4^+$), 132 (26.2, $AsF_3^+$), 113 (38.8, $AsF_2^+$), 102 (20.3, $S_2F_2^+$), 96 (11.5, $S_3^+$), 83 (11.2, $S_2F^+$), 76 (21.8, $CS_2^+$), 69 (59.2, $CF_3^+$), 64 (53.4, $S_2^+$), 50 (12.1 $CF_2^+$). Six weak peaks were observed above the $M^+$ peak at $m/z$ 191; these were $m/z$ 256 (2.6, $S_8^+$), 254 (1.9, $C_4F_6S_2N_2^+$), 252 (1.0, ?), 229 (3.0, $MF_2^+$), 194 (1.7, $^{34}S^{32}S_5^+$), 193 (2.7, $C_2F_3{}^{34}S^{32}S_2N^+$), and 192 (3.2, $S_6^+$). Copies of the spectra have been deposited as supplementary material, along with an extended listing of mass spectral peaks with assignments. Anal. Found (calc): C, 6.44 (6.32); N, 3.65 (3.68); F, 45.30 (44.98); S, 25.39 (25.30); As, 19.78 (19.71).

Large, purple, blocklike crystals of (**1**)$AsF_6$ were obtained directly from reaction mixtures when the solvent and volatiles were evaporated over 3 days by cooling the second bulb of the reaction vessel in cold running water. The crystals were carefully cut and loaded into dried glass capillaries under nitrogen, the capillaries then being sealed off.

(**1**)$AsF_6$ dissolves readily in $SO_2$ to give dark red-purple solutions. The ESR spectrum of a $10^{-2}$ M solution of (**1**)$AsF_6$ in $SO_2$ (modulation amplitude 0.8 G, power attenuation 10 dB, temperature −70 °C) showed only a singlet, $g = 2.016$. Lowering the modulation amplitude to 0.08 G and increasing the gain 50 times revealed two broad, asymmetric $^{33}S$ satellites ("$a$" = 8.3 G). A copy of the spectrum has been deposited as supplementary material. Spectra obtained after systematic lowering of the radical concentration by 5-min periods of UV irradiation did not show any further hyperfine interactions. The $^{19}F$ NMR spectrum of (**1**)$AsF_6$ (0.061 g, 0.16 mmol) in $SO_2$ (0.867 g) in the presence of $CFCl_3$ (0.071g, 0.52 mmol) as an internal concentration standard exhibited resonances at −30 ppm (vbr, $AsF_6^-$, 0.14 mmol) and −45 ppm ($\Delta\nu$ = 440 Hz, **1**, 0.14 mmol) in addition to the $CFCl_3$ peak.

**Magnetic Moment of (1)$AsF_6$.** In the temperature regime 25–200 K, (**1**)$AsF_6$ behaves as an ordinary Curie–Weiss paramagnet, $\mu = 1.65\ \mu_B$. Antiferromagnetic ordering occurs at 15 K, and the magnetic susceptibility shows a broad maximum at 5 K. Plots of $1/\chi$ versus $T$ (used in the determination of $\mu$) and $\chi$ versus $T$ from 2 to 20 K are shown in Figures 1 and 2, respectively. At room temperatures, the magnetic moment was determined by the Guoy method to be 1.61 $\mu_B$.

**Crystal Structure of (1)$AsF_6$.** The data were collected on a purple, blocklike crystal of size 0.18 × 0.22 × 0.30 mm using a CAD-4 four circle diffractometer with an $\omega$–$2\theta$ scan, $\theta_{max}$ = 25.00°, and the ranges of $hkl$ were −1 to +9, −1 to +12, and −1 to +14, respectively. After reduction to a standard scale[8] and the application of Lp and absorption corrections,[9] the positions of the As and S atoms were derived from an $E$ map (SHELXS)[10] and the positions of the remaining N and F atoms were determined from a subsequent Fourier synthesis. The structure was refined, initially using large-block least squares (SHELX76)[11] and subsequently with full-matrix least squares (CRYSTALS).[12a] The refinement converged at $R$ = 5.52% with anisotropic temperature factors on all atoms. The extinction conditions are in agreement with two space groups, $Pn2_1a$ (No. 33) and $Pnma$ (No. 62). However, since the $E$ map statistics clearly indicate the lack of a symmetry center, the structure was solved in the noncentrosymmetric space group, $Pn2_1a$. In the final stages of the refinement, the enantiomer was checked by refining the structure in both possible "hands", and the parameters reported here give a final $R$ of 5.52% compared to 5.68% for the other hand; the numbers of measured, unique, and observed ($I > 2\sigma(I)$) reflections were 1512, 959, and 953, respectively, and the number of parameters was 212. The hand which gives an $R$ of 5.52% was selected, since the ratio (1.029) between the $R$ factors for the two alternative hands remains significant even at the 0.005 significance level.[12b] The $AsF_6^-$ anion is disordered in two distinct orientations with relative occupancies of 55% (F) and 45% (F′). The two orientations are only very loosely related by the false mirror. The anisotropic thermal parameters for $CF_3$ show clear signs of a group libration. One F atom lies close to the false mirror, and the other two are approximately related by the mirror. However, the observed libration cannot be convincingly resolved into a mirror-related disorder. The $S_3NC$ ring also lies close to the false mirror, but it is inclined at an angle to the mirror with S(1) and S(2) displaced significantly from the plane. A refinement in space group $Pnma$ still requires a disordered $AsF_6^-$ ion, still produces an unsatisfactory $CF_3$ group, and needs, in addition, a disordered $\overline{\text{CNSSS}}$ ring system. The final $R$ from the refinement in $Pnma$ depends on the extent of the disorder that is introduced. Crystallographic data and final fractional coordinates for this refinement are presented in Tables I and II, respectively. A more detailed listing of crystal data and table of anisotropic thermal parameters has been deposited as supplementary material.

**Table I.** Crystal Data

| | | | |
|---|---|---|---|
| mol formula | $C_2NF_9S_4As$ | $Z$ | 4 |
| $M$ | 380.1159 | $D_x$, g·cm$^{-3}$ | 2.4129 |
| space group | $Pn2_1a$ (No. 33) | abs coeff, cm$^{-1}$ | 39.1218 |
| $a$, Å | 10.256 (1) | radiation (λ, Å) | Mo Kα (0.709 26) |
| $b$, Å | 8.181 (4) | temp, K | 291 |
| $c$, Å | 12.470 (2) | $R^a$ | 0.0552 |
| $V$, Å$^3$ | 1046.3 (5) | $R_w{}^b$ | 0.0619 |

[a] $R = \sum(|F_o| - |F_c|)/\sum F_o^2$. [b] $R_w = \sum[w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

**Preparation of (1)$AsF_6$ Studied in Situ by $^{19}F$ NMR and ESR Spectroscopy.** $SO_2$ (0.796 g), $AsF_5$ (0.185 g, 1.1 mmol), and $Br_2$ (2.2 mg) were successively condensed onto $S_8$ (0.058 g, 0.2 mmol) in a 5-mm

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(8) Cameron, T. S.; Cordes, R. E. *Acta Crystallogr. Sect. B* **1979**, *B35*, 748.

(9) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *A39*, 158.

(10) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds., Oxford University Press: Oxford, England, 1985; p 175.

(11) G. M. Sheldrick, SHELX: A system of computer programs for X-ray structure determination, as locally implemented at Dalhousie University and Cambridge University, 1976.

(12) (a) Curruthers, J. R.; Watkin, D. J. *CRYSTALS (Issue 8)*; Chemical Crystallography Laboratory: Oxford, England, 1989. (b) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 506 (example 4).

**Table II.** Fractional Atomic Coordinates for $(C_2NF_3S_3)(AsF_6)$ $(\times 10^4)^a$

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{mod}$, Å$^2$ |
|---|---|---|---|---|
| S(1) | -1080 (3) | -2285 (8) | -4121 (2) | 806 (13) |
| S(2) | -3084 (3) | -2352 (8) | -4087 (2) | 626 (11) |
| S(3) | -3376 (2) | -2440 (8) | -5670 (2) | 553 (10) |
| N(1) | -798 (7) | -2424 (14) | -5422 (6) | 708 (16) |
| C(1) | -1765 (9) | -2486 (14) | -6042 (6) | 627 (16) |
| C(2) | -1496 (9) | -2573 (13) | -7261 (7) | 839 (16) |
| F(21) | -911 (10) | -1202 (10) | -7546 (7) | 1135 (8) |
| F(22) | -2630 (7) | -2643 (14) | -7781 (5) | 1542 (22) |
| F(23) | -694 (10) | -3782 (11) | -7539 (9) | 1269 (16) |
| As(1) | -2927 (1) | 2500 (0) | -5945 (1) | 511 (5) |
| F(11) | -1863 (10) | 3887 (13) | -5502 (12) | 1312 (23) |
| F(12) | -4105 (11) | 1205 (12) | -6461 (11) | 1287 (19) |
| F(13) | -3266 (13) | 3789 (13) | -7031 (10) | 1394 (18) |
| F(14) | -2727 (14) | 1273 (12) | -4895 (10) | 2090 (28) |
| F(15) | -4122 (11) | 3584 (12) | -5333 (11) | 1550 (18) |
| F916) | -1839 (12) | 1510 (13) | -6709 (11) | 1737 (17) |
| F(11′) | -3369 (11) | 1064 (12) | -6872 (9) | 767 (16) |
| F(12′) | -2434 (12) | 3824 (13) | -5026 (10) | 917 (16) |
| F(13′) | -1934 (10) | 1045 (10) | -5354 (9) | 523 (28) |
| F(14′) | -3926 (11) | 3866 (13) | -6537 (9) | 975 (17) |
| F(15′) | -1689 (11) | 3029 (14) | -6772 (11) | 1503 (16) |
| F(16′) | -4130 (12) | 1824 (15) | -5156 (10) | 1468 (16) |

$^a U_{mod} = (U_{11}U_{22}U_{33})^{1/3}$. In disordered $AsF_6^-$, the occupancies are 55% (F) and 45% (F″).

NMR tube, equipped with a Rotoflo valve. After 45 min, $CF_3CN$ (0.061 g, 0.64 mmol) and $SO_2ClF$ (0.059 g, 0.5 mmol, as an internal concentration standard) were condensed onto the dark blue solution, causing it to become dark green in 30 min and deep red within 14 h. In addition to the resonance at 106 ppm due to $SO_2ClF$, the $^{19}F$ NMR spectrum after 14 h showed resonances at 84 ppm ($OSF_2$, <0.03 mmol), -20 ppm (br, $AsF_3/AsF_5/AsF_6^-$), -40 ppm (**1**, 0.6 mmol), and -50 ppm ($CF_3CN$, trace). The spectrum had not changed significantly after 13 days, except that more $OSF_2$ was present (0.06 mmol).

$SO_2$ (0.258 g), $AsF_5$ (35 mg), and $Br_2$ (0.5 mg) were condensed onto $S_8$ (ca. 0.1 mg) in a dry 3-mm ESR tube fitted with a J. Young valve, giving a pale blue solution, which became orange-brown after 20 min. $CF_3CN$ (24 mg) was then condensed onto the frozen solution, and the tube was sealed off. The solution was allowed to stand at room temperature for 14 h, with no change in appearance. The ESR spectrum showed a singlet at $g = 2.016$ and was unchanged after 2 days at room temperature.

**Molecular Orbital Calculations.** UHF and ROHF 3-21G* calculations were performed using the GAUSSIAN-86 suite of programs.[13] $H\overline{CNSSS}^{\bullet+}$ was used as a model for **1**; the geometry of the $\overline{CNSSS}$ ring was taken from the crystal structure of (**1**)$AsF_6$, and the CH distance was set at 1.09 Å. The value of $\langle S^2 \rangle$ in the UHF calculations was 0.80 before and 0.75 after spin annihilation.[14]

## Discussion

**Preparation of (1)$AsF_6$.** (**1**)$AsF_6$ is the first example of a 1,2,3,4-trithiazolium salt. It is related by the isovalent substitution of $S^{\bullet+}$ for $N^{\bullet}$ in the $7\pi$ systems $CF_3\overline{CNSNS}^{\bullet}$ and $CF_3\overline{CNSSN}^{\bullet}$ [1,2a,3-5] and by the substitution of N< for $CF_3C$< in $CF_3\overline{CSSSCCF_3}^{\bullet+}$. We have shown[6] that the last of these may be prepared by the reaction of $CF_3C{\equiv}CCF_3$ with a 1:1 mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$, and (**1**)$AsF_6$ was synthesized in an analogous way using $CF_3CN$ (eq 1).

$$S_8(AsF_6)_2 + S_4(AsF_6)_2 + 4CF_3CN \rightarrow 4(\mathbf{1})AsF_6 \quad (1)$$

Equation 1 proceeds at room temperature in the presence of an 8% excess of $S_4(AsF_6)_2$ and a 7% excess of $CF_3CN$ and gives analytically pure (**1**)$AsF_6$ in quantitative yield after 2 weeks with no detectable ($^{19}F$ NMR, ESR) intermediates. Reactions utilizing larger excesses of $CF_3CN$ or smaller excesses of $S_4(AsF_6)_2$ and/or shorter reaction times gave products that were shown by their mass spectra to consist mostly of (**1**)$AsF_6$, but peaks at $m/z$ 256 and 254 suggested contamination with $S_8^{2+}$ and $CF_3\overline{CSC(CF_3)NSN}^{\bullet+}$.[15] These peaks were also present in the mass spectrum of the product of the optimized reaction, but their intensities were only 2.6% and 1.9%, respectively. No evidence for $CF_3\overline{CSC(CF_3)NSN}^{\bullet+}$ or $S_5^{\bullet+}$ (arising from the presence of $S_8^{2+}$ [16]) was observed in the ESR spectra of isolated (**1**)$AsF_6$ redissolved in $SO_2$ or of reaction mixtures leading to (**1**)$AsF_6$, and it is likely that these cations were only ever present in minor amounts.

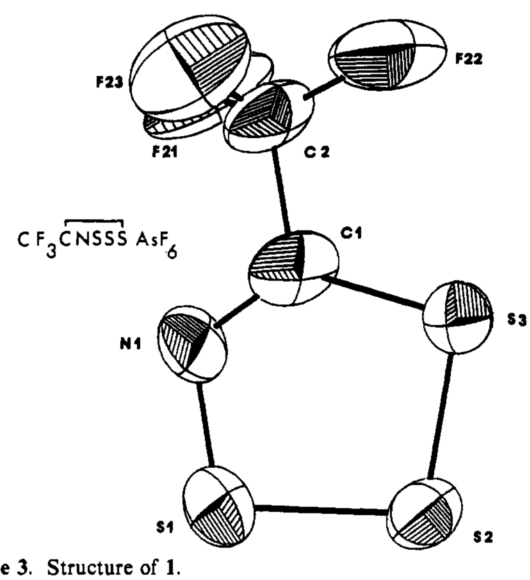

Figure 3. Structure of **1**.

Equation 1 proceeds more quickly, and with higher yield, than the analogous reaction involving $CF_3C{\equiv}CCF_3$, used to obtain $CF_3\overline{CSSSC}CF_3AsF_6$. The difference in yield is associated with the absence of side reactions, which lead to high molecular weight, neutral polysulfides in the $CF_3CCCF_3$ system.[6] In addition, much less $OSF_2$ is formed in the $CF_3CN$ reaction. Equation 1 may proceed by donation of electrons from the HOMO ($CF_3CN$) to the LUMO ($S_4^{2+}$), followed by reaction pathways that are analogous to those we have described[6b] for the related $CF_3CCCF_3$ reaction. According to simple frontier molecular orbital (FMO) theory, the rate of the initial reverse electron demand step depends inversely on the energy difference between HOMO ($CF_3CCCF_3$ or $CF_3CN$)[17a] and LUMO ($S_4^{2+}$) and should be higher for $CF_3CCCF_3$ (IP = 12.83 eV[18a]) than for $CF_3CN$ (IP = 14.3 eV[18b]). In fact, $CF_3CN$ reacts more quickly than $CF_3CCCF_3$, and this may be due to the steric hindrance of the extra $CF_3$ group in the alkyne and/or the polarity of the nitrile, which are not considered in the simple FMO model.[19]

**Characterization of (1)$AsF_6$ in the Solid State.** The elemental analyses and vibrational[20a] and mass spectra of (**1**)$AsF_6$ are

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(13) Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, P.; Stewart, J. P. P.; Defrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fludel, E.; Pople, J. A. *GAUSSIAN86*; Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA, 1986.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio molecular orbital theory*; Wiley: New York, 1986.

(15) $CF_3\overline{CSC(CF_3)NSN}^{\bullet+}$ is related to the 1,4-dithiin radical cations $R\overline{CSC(R)C(R)SCR}^{\bullet+}$ which have been observed in similar $RC{\equiv}CR$-containing systems. See for example: Bock, H.; Rittmeyer, R.; Stein, U. *Chem. Ber.* **1986**, *119*, 3766.

(16) Low, H. S.; Beaudet, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 3849.

(17) (a) Both $CF_3CN$ and $CF_3CCCF_3$ are not normally thought of as electron donors. However, both undergo quantitative reverse-demand cycloaddition reactions with $SNS^+$ (which is less electrophilic than $S_4^{2+}$). (b) Parsons, S.; Passmore, J.; Schriver, M. J.; Sun, X. *Inorg. Chem.* **1991**, *30*, 3342.

(18) (a) Cullen, W. R.; Frost, D. C.; Leader, W. R. *J. Fluorine Chem.* **1971/2**, *1*, 227. Baybutt, P.; Guest, M. F.; Hillier, I. H. *Mol. Phys.* **1973**, *25*, 1025. (b) Bien, G.; Heilbronner, E.; Horning, V.; Kloster-Jensen, E.; Mailer, J. P.; Thoomen, F. *Chem. Phys.* **1979**, *36*, 1. Bock, H.; Dammel, D.; Lenta, D. *Inorg. Chem.* **1984**, *23*, 1535.

(19) Huisgen, R. In *1,3-dipolar cycloaddition chemistry*; Padwa, A., Ed.; Wiley: New York, 1984.

**Table III.** Cationic Bond Distances (Å) and Angles (deg) in (1)$AsF_6$

| | | | |
|---|---|---|---|
| S(1)–S(2) | 2.057 (5) | C(1)–C(2) | 1.55 (1) |
| S(1)–N(1) | 1.652 (10) | C(2)–F(21) | 1.32 (1) |
| S(2)–S(3) | 1.997 (5) | C(2)–F(22) | 1.33 (1) |
| S(3)–C(1) | 1.717 (10) | C(2)–F(23) | 1.33 (1) |
| N(1)–C(1) | 1.26 (1) | | |
| S(2)–S(1)–N(1) | 101.1 (4) | C(1)–C(2)–F(21) | 107.9 (8) |
| S(1)–S(2)–S(3) | 97.5 (2) | C(1)–C(2)–F(22) | 108.9 (8) |
| S(2)–S(3)–C(1) | 97.1 (4) | C(1)–C(2)–F(23) | 113.6 (8) |
| S(1)–N(1)–C(1) | 117.9 (7) | F(21)–C(2)–F(22) | 107.6 (8) |
| S(3)–C(1)–N(1) | 126.3 (8) | F(21)–C(2)–F(23) | 106.3 (9) |
| S(3)–C(1)–C(2) | 116.0 (7) | F(22)–C(2)–F(23) | 112.3 (9) |
| N(1)–C(1)–C(2) | 117.7 (8) | | |

completely consistent with the given formulation, which is confirmed by its X-ray structure.

The mass spectrum of (1)$AsF_6$ shows features similar to those of the spectrum of $CF_3CSSSCCF_3AsF_6$,[6] although the parent molecular ion is much weaker (14.4% compared to 100%). The usual mode of volatilization of $AsF_6^-$ salts[24a] is via an initial fluoride ion transfer (eq 2), which is supported in this case by the

$$(1)AsF_6 \rightarrow (1)F + AsF_5 \qquad (2)$$

peak at *m/z* 151 (100%, $AsF_4^+$). However, a peak at *m/z* 229 (*I* = 3.0%) implies that the alternative process in eq 3 may compete

$$(1)AsF_6 \rightarrow (1)F_3 + AsF_3 \qquad (3)$$

with eq 2, leading to a (1)$F_2^+$ fragment. This process is significantly less important than in the mass spectrum of $CF_3CSSSCCF_3AsF_6$, in which the $CF_3C(F)SSSC(F)CF_3^+$ fragment has an intensity of 46.2%, presumably because it requires the formation of weaker N–F or S–F bonds (bond energies: C–F 485, N-F 283, S-F 320 kJ·mol$^{-1}$).[24b]

**Crystal Structure and Magnetic Properties of (1)$AsF_6$.** The unit cell of (1)$AsF_6$ consists of planar, monomeric **1** cations (see Figure 3) (maximum deviation from planarity: S(2), 0.018 (8) Å) and $AsF_6^-$ anions. There is significant disorder in the positions of the anionic fluorine atoms, which has been modeled with two sets of six F positions in a 55:45 occupancy ratio. This precludes any detailed discussion of the geometry of the $AsF_6^-$ anions or contacts to the cation, although the As–F bond distances are between 1.66 and 1.76 Å and F–As–F angles are all around 90°. Cationic bond distances and angles are given in Table III.

The structure is composed of layers containing both cations and anions (Figure 4) roughly perpendicular to the *b* axis (although the As atoms are displaced by 0.357 (14) Å from the planes of the cations). There is an incipient (or noncrystallographic) inversion center at ($^1/_2$, $^1/_2$, $^1/_2$) so that each cation or anion is surrounded by six anions or cations (four in plane, one above, and below), the structure being related to that of NaCl.[25] A related packing regime exists in the structures of $SNSSNAsF_6$[26] and $CF_3CSSSCCF_3AsF_6$[6] (which respectively contain monomeric $S_3N_2^+$ and $CF_3CSSSCCF_3^+$ radical cations), although in the case of $S_3N_2AsF_6$ the anions are 1.46 Å from the planes of the cations. The minimum interradical S–S distance is 5.04 Å (S(1)–S(2)), and the observed lack of dimerization of **1** is consistent with the very weak dimerization observed for $CF_3CSNSCCF_3^•$ (which dimerizes through the sulfur atoms, with S–S bond lengths of 3.27 (7) and 3.07 (7) Å; Δ*H*(dimerization) is zero or positive).[2] Formation of weak dimers will be electrostatically opposed by the positive charge on **1**, which consistently remains monomeric.

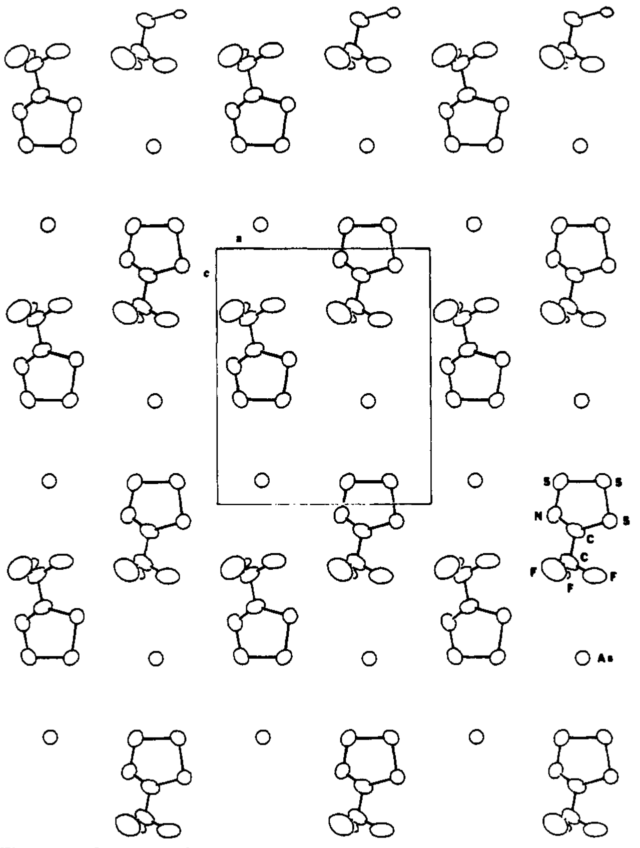

**Figure 4.** Contents of plane at *b* = 0.25, showing monomeric cations and anions in the crystal structure of (1)$AsF_6$. The fluorine atoms are not included; O = As.

Consistent with the lack of dimerization, (1)$AsF_6$ is paramagnetic, but although a planar array of radical cations is potentially capable of giving rise to unusual magnetic properties, (1)$AsF_6$ exhibits ordinary Curie–Weiss behavior (see Figure 1). The magnetic moment of (1)$AsF_6$ (1.65 $\mu_B$ between 25 and 200 K) is similar to that of $CF_3CSSSCCF_3AsF_6$ (1.68 $\mu_B$ over the same range),[6] implying weak spin coupling between cations. Similar magnetic behavior is shown by a variety of related 7$\pi$ sulfur–nitrogen-containing heterocyclic radicals, e.g. $RCSNSCR^•$ ($\mu$ = 1.52 $\mu_B$, R = $CF_3$, neat liquid at room temperature), $RCNSNS^•$ ($\mu$ = 1.41 $\mu_B$, R = ${}^tBu$, neat liquid at room temperature), and $RCNSSN^•$ ($\mu$ = 1.40 $\mu_B$, R = $CF_3$, after melting).[2,3] Weak interactions between the unpaired electrons are responsible for reducing $\mu$ below the ideal spin-only value (1.73 $\mu_B$). In

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(20) (a) The intense absorptions at 1200, 700, and 394 cm$^{-1}$ in the infrared spectrum of (1)$AsF_6$ are clearly associated with the $CF_3$ substituents[20b] and the $AsF_6^-$ anions.[21] The IR and Raman bands at 1551 cm$^{-1}$ are assigned to $\nu$(CN) by analogy with the CC stretch in $CF_3CSSSCCF_3^{•+}$ at 1549 cm$^{-1}$.[6] The higher frequency of this vibration than of $\nu$(CN) in the isovalent $CF_3CNSSN^•$ radical (1412 cm$^{-1}$ [2a]) is consistent with the shorter CN bond length in **1** (cf. 1.258 (11) Å in **1**[4a] and 1.318 (6) Å in $CF_3CNSSN^•$ [4a]). The IR band at 850 cm$^{-1}$ is assigned to $\nu$(SN) on the basis of Banister's SN bond length–stretching frequency correlation,[22] while the vibrations at 542 and 449 cm$^{-1}$ are assignable to $\nu$(SS) on the basis of their strong Raman and weak IR intensities and Steudel's correlation for SS bonds.[23] (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric identification of organic compounds*; 4th ed.; Wiley: New York, 1981.

(21) Begun, G. M.; Rutenberg, A. C. *Inorg. Chem.* **1967**, *6*, 2212.

(22) $\lambda(SN) = 0.1941D(SN) - 20.66$, where *D*(SN) is the SN bond length in pm and λ(SN) is the stretching wavelength. See: Banister, A. J.; Durrant, J. A.; Gorrell, I. B.; Roberts, R. S. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1771.

(23) $D(SS) = 2.53 - 1.041 \times 10^{-3}\nu_{SS}$, where *D*(SS) is the SS bond length in Å and $\nu_{SS}$ is the stretching frequency in cm$^{-1}$. See: Steudel, R. *Angew. Chem., Int. Ed Engl.* **1975**, *14*, 655.

(24) (a) The mass spectra of related $RCSNSCRAsF_6$ and $RCNSNSAsF_6$ can generally be interpreted as arising from the neutral fluoride of the cation and $AsF_5$ given by fluoride ion transfer on volatilzation of the salt. E.g. see: Maclean, G. K.; Passmore, J.; Rao, M. N. S.; Schriver, M. J.; White, P. S.; Bethall, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1405. (b) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983.

(25) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, England, 1984.

(26) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784.

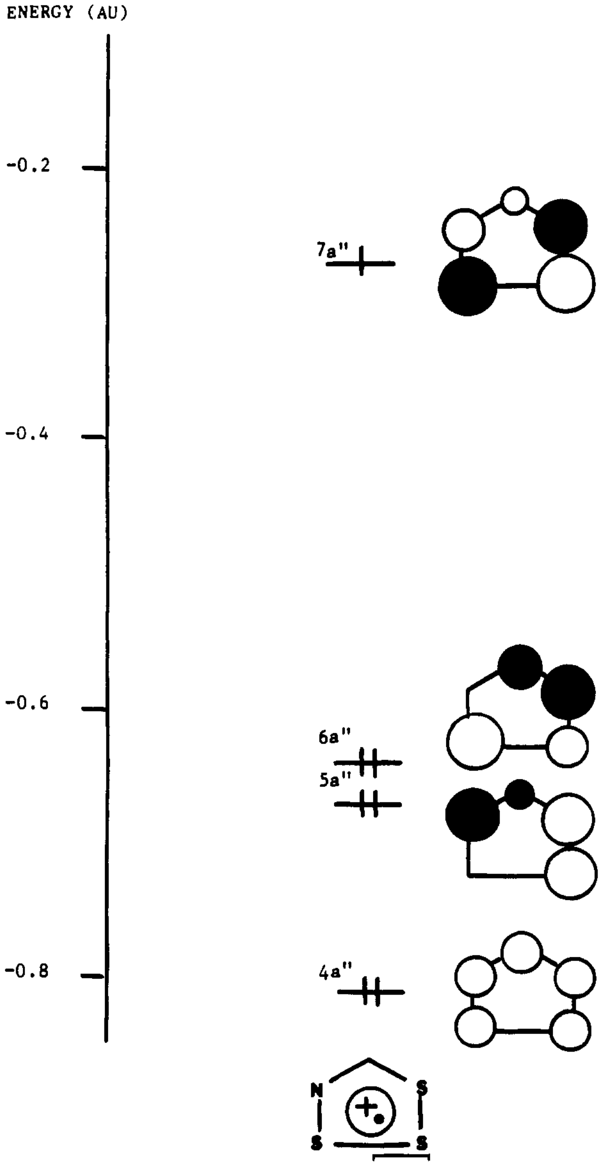

**Figure 5.** π-Electronic structure of $\overline{\mathrm{HCNSSS}}^{\bullet+}$, obtained at the ROHF/3-21G* level. SOMO coefficients: S(1) 3pπ inner (I) −0.40, outer (O) −0.37; S(2) 3pπ (I) 0.42, (O) 0.41; S(3) 3pπ (I) −0.29, (O) −0.32; N(1) 2pπ (I) 0.14, (O) 0.19; C(1) 2pπ (I) 0.10, (O) 0.14. The SOMO calculated by the UHF method using the same basis set did not differ significantly from that shown here.

contrast to $\mathrm{R\overline{CSNSC}R}^{\bullet}$, $\mathrm{R\overline{CNSNS}}^{\bullet}$, and $\mathrm{R\overline{CNSSN}}^{\bullet}$, which are "paramagnetic liquids" (i.e. diamagnetic in the solid state but paramagnetic as liquids), (1)$AsF_6$ can be described as a paramagnetic solid.[3] Other examples of this class of compounds are well-known (e.g. $O_2$, $O_2AsF_6$, and $I_2Sb_2F_{11}$), although they tend to be rare among the heavier main group elements, especially in cases where there is no steric hindrance to dimerization.[27] In addition, (1)$AsF_6$ undergoes short-range antiferromagnetic ordering at about 4 K (see Figure 2) remarkably similar to that found for the related $\mathrm{CF_3\overline{CSSSC}CF_3(AsF_6)}$.

The bond orders[28] in **1** (CN, 2.3; CS, SN, 1.3; SS, ca. 0.9, 1.1) indicate that π bonding is strongest in the CN bond, weaker in the CS and SN bonds, and weakest of all in the SS bonds. The trend in the CN, CS, and SN bond orders is reflected by the π electronic structure of **1** shown in Figure 5 (ROHF/3-21G*). However, this MO model predicts the SS bonds to have significant π character, but this is not the case (average bond order 1.04). SS bonds are often found to be longer than anticipated from a simple π MO treatment (e.g.: $S_4^{2+}$, 2.014 (3) Å;[29] $\mathrm{CF_3\overline{CNSSN}}^{\bullet}$, 2.113 (6) Å;[4a] $\mathrm{\overline{SNSNS}}^{2+}$, 2.093 (5)[30] Å), and this effect may be ascribable to the electrostatic repulsion between adjacent, positively charged sulfur atoms. The π MO model predicts that S(1)–S(2) should be shorter than S(2)–S(3), contrary to what is observed (S(1)–S(2) = 2.056 (4), S(2)–S(3) = 1.998 (4) Å); the origin of the observed difference in the SS bond lengths in **1** is unclear. An electrostatic explanation seems to be unlikely on the basis of the sums of the occupancy-weighted fluorine contact valencies[31] to S(1), S(2), and S(3) (0.18, 0.32, and 0.23 vu (vu = valency units), respectively), which reflect the magnitude of the positive charge residing on a given sulfur atom.

**Characterization of (1)$AsF_6$ in Solution.** ESR spectra of (1)$AsF_6$ in $SO_2$ consisted of a singlet at *g* = 2.016, whether the sample was prepared in situ (from $S_8$, $AsF_5$, and $CF_3CN$) or prepared by redissolving solid (1)$AsF_6$ in $SO_2$. The magnitude of the *g* value is similar to that of $\mathrm{CF_3\overline{CSSSC}CF_3}^{\bullet+}$ in $SO_2$ (2.014)[6] but larger than those of $\mathrm{\overline{SNSNS}}^{\bullet+}$ (2.0111),[32] $\mathrm{CF_3\overline{CNSNS}}^{\bullet}$ (2.0057), $\mathrm{CF_3\overline{CNSSN}}^{\bullet}$ (2.0112), and $\mathrm{CF_3\overline{CSNSC}CF_3}^{\bullet}$ (2.005),[1a,2,3] consistent with a larger spin–orbit coupling associated with the interaction of the unpaired electron with three (instead of two) sulfur centers.

Although the ESR spectrum of **1** was expected to consist of a 1:1:1 triplet ($^{14}N$, $I = 1$) of 1:3:3:1 quartets ($^{19}F$, $I = {}^1/_2$), no such hyperfine splittings could be resolved, even at −70 °C, with a low modulation amplitude (0.8 G). An attempt to improve the spectral resolution, by reducing the spin-exchange contribution to $T_2$ by means of a controlled reduction of the concentration of the radical by 5-min periods of UV irradiation, did not reveal any further hyperfine structure. This result implies that the unpaired electron densities on N and F are negligibly small. This is reflected in the $^{19}F$ NMR spectrum of **1**, which shows a broad singlet at −45 ppm; $CF_3$ resonances are normally observed at about −60 ppm, and the very small homomolecular contact shift[33] in **1** also implies low unpaired electron density at the $^{19}F$ nuclei. UHF 3-21G* calculations on $\mathrm{H\overline{CNSSS}}^{\bullet+}$ revealed a π* SOMO located primarily on the $S_3$ moiety, with much smaller contributions from the N and C pπ AOs (see Figure 5), consistent with the lack of hyperfine coupling to nitrogen.

The ESR spectrum of **1** is similar to that of $\mathrm{CF_3\overline{CN'SN''S}}^{\bullet}$, which only exhibits coupling to N'' (11.2 G), with none to N' or $^{19}F$, even though the spectra of other derivatives of the $\mathrm{\overline{CN'SN''S}}^{\bullet}$ ring show small *a*(N') values of 0.5–1.5 G. This has similarly been ascribed to the π* SOMO residing mostly on the SN''S moiety.[2a,3,34]

Two weak, broad $^{33}S$ satellites (*a* = 8.3 G) can be resolved on either side of the main singlet under conditions of high microwave

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(27) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984.

(28) Bond order = $10^{(D_1-D_n)/0.71}$, where $D_1$ = length of a formal single bond (CC 1.54, CS 1.79, SN 1.77, and SS 2.04 Å) and $D_n$ = observed bond length. See: Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(29) Passmore, J.; Sutherland, G.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1980**, 330.

(30) Brooks, W. V. F.; Cameron, T. S.; Grein, F.; Parsons, S.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.*, in press.

(31) Since the fluorine atoms in the $AsF_6^-$ anions are disordered over two orientations, the number of valence units corresponding to a given S–F contact distance, *R*, is given by $k(R/1.550)^{-3.8}$, where *K* is the site occupancy factor for the F atom (0.55 for F, 0.45 for F′). See: Brown, I. D. In *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: London, 1981; Vol. 2.

(32) Preston, K. F.; Charland, J. P.; Sutcliffe, L. H. *Can. J. Chem.* **1988**, *66*, 1299.

(33) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Longman: Harlow, England, 1986.

(34) SOMO coefficients for the model $\mathrm{H\overline{CN'S'N''S''}}^{\bullet}$ calculated at the ROHF/3-21G* level: C 2pπ inner (I) 0.05, outer (O) 0.09; N′ 2pπ (I) 0.06, (O) 0.09; S′ (I) −0.25, (O) −0.27; N″ (I) 0.49, (O) 0.69; S″ (I) −0.23, (O) −0.28. A model geometry was taken from ref 3c for *p*-$\mathrm{(\overline{CNSNS}^{\bullet})_2C_6H_4}$, C–H bond length 1.09 Å.

power, low modulation amplitude (0.08 G), low temperature (−70 °C), and high signal gain. The asymmetry of the satellites implies that they consist of overlapping resonances, although we were unable to resolve them into their components. The magnitude of $a(^{33}S)$ (8.3 G) is similar to that in $CF_3\overline{CSSSC}CF_3^{\bullet+}$ (8.6 G) and $MeO_2\overline{CCSSSC}CO_2Me^{\bullet+}$ (8.0 and 8.9 G)[6] and is consistent with the uniform distribution of the SOMO over the $S_3$ moiety (see above).

**Acknowledgments.** We thank Mr. E. G. Awere, Mr. D. Drummond, and Dr. G. Schatte (UNB) for the mass and FT Raman spectra, respectively, and Mrs. S. Mulholland for valuable experimental help. Financial assistance by the NSERC (Canada) and a graduate fellowship from the Canadian Commonwealth Scholarship and Fellowship Committee are gratefully acknowledged.

**Registry No.** $AsF_5$, 7784-36-3; S, 7704-34-9; $CF_3CN$, 353-85-5; $CF_3\overline{CNSSS}AsF_6$, 140462-71-1.

**Supplementary Material Available:** IR, Raman, mass, and ESR spectra and an extended mass spectral listing with assignments for (**1**)-$AsF_6$, a tabular summary of other reactions performed with the aim of preparing (**1**)$AsF_6$, an extended table of crystal data and a listing of anisotropic thermal parameters for (**1**)$AsF_6$, and tables of bond distances and angles for the $AsF_6^-$ anion and torsional angles for the $\overline{CNSSS}$ ring in (**1**)$AsF_6$ (12 pages); a listing of observed and calculated structure factors for (**1**)$AsF_6$ (10 pages). Ordering information is given on any current masthead page.

# Notes

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## Deriving Chemical Parameters from Electrostatic Potential Maps of Molecular Anions

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*Received August 21, 1991*

The shapes and sizes of ions are of considerable interest in many diverse areas of chemistry.[1-3] There is indeed a long history of the idealized concept of "ionic radius", beginning as early as the 1920s, with the pioneering works[4] of Landé, Wasastjerna, Yatsimirskii, and Goldschmidt (see Pauling[1] for a lucid discussion on ionic radii). In particular, a clear-cut rigorous treatment of sizes and shapes of polyatomic ions is found to be lacking in the chemical literature. The measure of spatial extent of these ions is normally provided in terms of their "spherical" radii. The latter are calculated by a variety of methods;[5] for example, the so-called thermochemical radii are obtained via a Born–Haber calculation of the lattice energy of the crystal. That the assumption of sphericity is rather inadequate for the treatment of polyatomic ions is generally recognized in the literature. For example, as Huheey[3] has remarked, "In many cases, the fact that the ions (such as $CO_3^{2-}$, $CNS^-$, $CH_3CO_2^-$) are markedly nonspherical, limits the use of these radii". Yet another instance of desirability of a nonspherical anion may be seen from the intuitive picture of $CN^-$ in the NaCN crystal and that of $OH^-$ in $Ca(OH)_2$ as given in the standard treatise of Wells.[2] The subject of anisotropy in ionic interactions is also of current interest in thermochemistry.[6] Of particular interest are the statements regarding near sphericity of $NH_4^+$ and $CN^-$ ions in situations where electrostatic interactions predominate. Thus, the need of a rigorous yet simple and practical definition of shapes and sizes of polyatomic anions can hardly be overemphasized.

A beginning in this direction has recently been made by Sen and Politzer,[7] by defining the radii of *atomic anions* on the basis of the behavior of their electrostatic potential. They show that[7] a monoatomic negative ion *must* have a negative-valued minimum in its electrostatic potential $V(r)$, at a radial distance of $r_m$. The value of $r_m$ has been identified by them with the anionic radius. It may be noted the ions $F^-$, $Cl^-$, $Br^-$, and $I^-$ generally turn out to be smaller in their treatment,[7] as compared to the respective crystal radii. It is the purpose of this note to provide a completely general yet practical treatment of anisotropies of molecular anions.

Our definition stems from general topographical features exhibited by the molecular electrostatic potential (MESP) maps of such systems. The MESP $V(\vec r)$ at a point $\vec r$ due to a molecular species (with nuclear charges $\{Z_A\}$ located at $\{\vec r_A\}$ and electron density $\rho(\vec r)$) is given by (in au)

$$V(\vec r) = \sum_A Z_A/|\vec r - \vec r_A| - \int \rho(\vec r\,')d^3r'/|\vec r - \vec r\,'| \qquad (1)$$

In the above equation, the first term represents the nuclear contribution and the second one corresponds to the electronic part. A reciprocal relation to (1) is furnished by the Poisson equation, viz.

$$\nabla^2 V(\vec r) = 4\pi\rho(\vec r) - 4\pi\sum_A Z_A\delta(\vec r - \vec r_A) \qquad (2)$$

This relation has recently been exploited by Gadre et al.[8,9] to explore the maximal and minimal characteristics of MESP maps. The topography of these maps is indeed very distinctive, since it can exhibit no nonnuclear maxima[8,9] at any point in space. The minima in such maps are invariably joined via saddle points. In the same spirit, it can be readily proven that an anionic MESP must attain[8,9] a negative-valued minimum along any ray emanating from within the nuclear framework. Thus, for every anion, there

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† Universität Karlsruhe.
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(1) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(2) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, England, 1975; pp 521 and 751. A pictorial description of anisotropies for the $OH^-$ and $CN^-$ ions is given.
(3) Huheey, J. *Inorganic Chemistry*, 3rd ed., Harper: New York, 1983; pp 77–78.
(4) Landé, A. *Z. Phys.* **1920**, *191*, 1. Wasastjerna, J. A. *Soc. Sci. Fenn. Comm. Phys. Math.* **1923**, *38*, 1. Yatsimirskii, K. B. *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk.* **1947**, 453. Goldschmidt, V. M. *Geochemische Verteilungsgestetze der Elemente*; Skrifter Norske Videnskaps-Akad.: Oslo, 1926; I, Mat.-Naturv., Kl, Vol. No. 2.
(5) (a) Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Educ.* **1979**, *56*, 576. (b) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.
(6) Liebman, J. F.; Romm, M. J.; Meot-Ner (Mautner), M.; Cybulski, S. M.; Scheiner, S. *J. Phys. Chem.* **1991**, *95*, 112. Meot-Ner (Mautner) M.; Cybulski, S. M.; Scheiner, S.; Liebman, J. F. *J. Phys. Chem.* **1988**, *92*, 2738 and references therein.
(7) Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989**, *90*, 4370. Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989**, *91*, 5123.
(8) Pathak, R. K.; Gadre, S. R. *J. Chem. Phys.* **1990**, *93*, 1770. Gadre, S. R.; Pathak, R. K. *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **1990**, *102*, 18.
(9) Gadre, S. R.; Shrivastava, I. H. *J. Chem. Phys.* **1991**, *94*, 4384. Note that the surface, $\underset{\sim}{S}$, computed in the present work is a good approximation to a $\vec\nabla V\cdot d\vec S = 0$ surface.