RUND, J. V. & HAZELL, A. C. (1980). *Acta Cryst.* B**36**, 3103–3105.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WIESNER, J. R. & LINGAFELTER, E. C. (1966). *Inorg. Chem.* **5**, 1770–1775.
ZAGORODNIKOV, V. P., KHODASHOVA, T. S., VARGAFTIK, M. N., MOISEEV, I. I. & PORAI-KOSHITS, M. A. (1985). *Koord. Khim.* **11**, 95–102.

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Structure of 2-Methyl-2-(2-pyridyl)propyl-*S*,*S*-dimethylsulfonium Hexafluorophosphate: an Intramolecular Non-Bonding S···N Interaction

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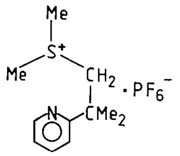
Abstract. $C_{11}H_{18}NS^+.PF_6^-$, $M_r = 341·29$, orthorhombic, $Pc2_1n$, $a = 17·725\,(1)$, $b = 10·580\,(1)$, $c = 8·314\,(1)$ Å, $V = 1559·2\,(3)$ Å^3, $Z = 4$, $D_x = 1·454$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1·5401$ Å, $\mu = 3·295$ mm^{-1}, $F(000) = 704$, $T = 296$ K, $R = 0·051$ for 1248 observed reflexions. A weak intramolecular interaction is observed between S and N with a length of 2·834 Å. This is longer than that of the typical N—S—N sulfurane but shorter than the van der Waals contact. The torsion angles N—C(2)—C(Me$_2$)—C(H$_2$) and C(2)—C(Me$_2$)—C(H$_2$)—S are 4·4 (6) and −60·6 (5)°, respectively, so that the conformation about the exocyclic chain is favourable for such an interaction.

Introduction. A variety of organic σ-sulfuranes has been synthesized and the structures have been determined by X-ray analysis (Baenziger, Buckles, Maner & Simpson, 1969; Paul, Martin & Perozzi, 1972; Kálmán, Sasvári & Kapvits, 1973; Perozzi, Martin & Paul, 1974; Adzima, Chiang, Paul & Martin, 1978). Every compound bears electron-withdrawing apical groups due to the electron-rich and polarizable nature of the apical three-centre four-electron bond. A series of *S*-substituted *N*-methyl-6,7-dihydro-5*H*,12*H*$^+$-dibenzo[*b*,*g*][1,5]thiazocinium salts was synthesized and their structures were determined by X-ray analysis (Iwasaki & Akiba, 1985). From the features of these structures these compounds were concluded to be a new type of σ-sulfurane with a strong transannular S···N interaction. The compound with X_{ap} = Me is the first example of a σ-alkylsulfurane with an apical alkyl group despite the electron-donating character of an alkyl group. The stability of such a structure may be attributed to ring formation. In order to investigate the S···N interaction for the noncyclic compound the structure determination of the title compound was carried out.



Experimental. Pale yellow prisms, 0·60 × 0·30 × 0·10 mm, unit-cell parameters by least squares from 25 reflexions (65 < 2θ < 75°), Rigaku AFC4 diffractometer, graphite monochromated, $2 \le 2\theta \le 130°$, $h = 0\to20$, $k = 0\to12$, $l = 0\to9$, ω–2θ scan, scan range $\Delta\omega = 1·2° + 0·5° \tan\theta$, scan speed 4° min^{-1} in 2θ, three reflexions monitored (040, 402, $\bar{3}02$) every 50 reflexions, variations within 2%. 1531 independent reflexions measured, 1248 observed, $|F_o| \ge 3\sigma(F)$. Two heavy atoms S and P were obtained by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Other non-H atoms were obtained from successive Fourier maps. Disordered PF_6^- ion with the occupancy factors estimated from the peak heights of a D map. H atoms were found from the D map. Block-diagonal least squares with anisotropic temperature factors for non-H and isotropic ones for H. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/(0·7194 + 0·0297|F_o| + 0·0006|F_o|^2)$. Three strong reflexions were omitted from the final refinement. $\Delta\rho(\max.) = 0·32$, $\Delta/\sigma(\max.) = 0·14$. $R = 0·049$ (0·051 for 1248

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Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms* (*occupancy factor of* F *atoms is* 0·75)

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	1093 (1)	2017 (2)	5761 (2)	4·2
N	993 (3)	4690 (5)	5741 (5)	4·5
C(2)	1419 (3)	4813 (5)	4443 (7)	4·2
C(3)	1841 (4)	5901 (7)	4166 (11)	6·7
C(4)	1825 (4)	6876 (8)	5303 (14)	8·4
C(5)	1400 (4)	6745 (7)	6651 (11)	7·3
C(6)	986 (4)	5624 (7)	6848 (9)	5·9
C(7)	1436 (3)	3724 (6)	3270 (7)	4·4
C(8)	876 (3)	2675 (6)	3791 (7)	4·2
C(9)	205 (4)	2025 (8)	6746 (9)	6·0
C(10)	1227 (5)	379 (8)	5331 (10)	7·4
C(71)	2233 (3)	3140 (7)	3204 (8)	5·6
C(72)	1183 (4)	4134 (7)	1576 (8)	6·0
P	1279 (1)	−452 (2)	358 (2)	5·3
F(1)	709 (3)	−711 (7)	−1025 (7)	7·5
F(2)	1871 (4)	−166 (13)	1635 (8)	13·7
F(3)	1918 (3)	−781 (7)	−880 (7)	7·4
F(4)	638 (3)	−197 (9)	1588 (8)	10·3
F(5)	1298 (5)	960 (7)	−267 (13)	12·4
F(6)	1289 (5)	−1862 (7)	913 (12)	12·9

reflexions), $wR = 0{\cdot}057$, $S = 0{\cdot}755$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a HITAC M180 computer of the Data Processing Center of the University of Electro-Communications with the programs *UNICS*III (Sakurai & Kobayashi, 1979), *MULTAN*78 and *ORTEP*II (Johnson, 1976). The final atomic parameters are given in Table 1.*

Discussion. The molecular structure with the atom numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. The N atom deviates from the plane defined by the five C atoms of the pyridine ring by 0·021 (3) Å. The deviations of five C atoms from this plane are within 0·002 (2) Å. The C—C lengths in the propyl chain show normal C(sp^3)—C(sp^3) and C(sp^3)—C(sp^2) lengths. S—C lengths are within the range of normal S—C single bonds (Pauling, 1960).

There is a weak interaction between S and N, with a length of 2·834 (5) Å. This is much longer than the S—N apical length (1·89 Å) for the typical N—S—N sulfurane (Adzima *et al.*, 1978) and S···N lengths for N—S···N asymmetric thiathiophthene analogues (2·2–2·6 Å) (Butler, Glidewell & Liles, 1978; Iwasaki & Akiba, 1981), but shorter than the van der Waals contact (3·35 Å). The angles C(10)—S···N, C(9)—S···N and C(8)—S···N are 167·4 (3), 86·7 (3) and 66·4 (2)°, respectively. The angle between the S···N vector and the C(8)—S—C(9) plane is 64·7 (5)°, and that between S···N and the pyridine plane is 27·8 (6)°. The torsion angles about the propyl chain are listed in Table 3. C(8) is *cis* to N about the C(7)—C(2) bond and S is *gauche* to C(2) about the C(8)—C(7) bond. These conformations are favourable to the S···N interaction. The structural features of the S···N contact show partial formation of σ-sulfurane. The net charge of each atom was calculated by the CNDO/2 method based on the determined structure, and the values for S (+0·400) and N (−0·275) indicate the presence of an electrostatic

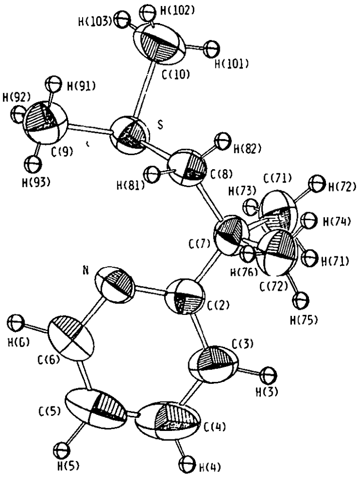

Fig. 1. *ORTEP*II (Johnson, 1976) drawing with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the non*-H *atoms*

S—C(8)	1·821 (6)	C(3)—C(4)	1·399 (14)
S—C(9)	1·775 (9)	C(4)—C(5)	1·358 (15)
S—C(10)	1·786 (9)	C(5)—C(6)	1·404 (12)
N—C(2)	1·324 (8)	C(7)—C(8)	1·551 (9)
N—C(6)	1·350 (9)	C(7)—C(71)	1·544 (10)
C(2)—C(3)	1·391 (11)	C(7)—C(72)	1·540 (10)
C(2)—C(7)	1·510 (9)	P—F(4)	1·552 (10)
P—F(1)	1·555 (7)	P—F(5)	1·582 (11)
P—F(2)	1·523 (14)	P—F(6)	1·562 (11)
P—F(3)	1·569 (7)		
C(8)—S—C(9)	103·0 (3)	C(4)—C(5)—C(6)	118·2 (9)
C(8)—S—C(10)	102·7 (4)	N—C(6)—C(5)	122·3 (7)
C(9)—S—C(10)	102·4 (4)	C(2)—C(7)—C(8)	110·7 (5)
C(2)—N—C(6)	119·3 (5)	C(2)—C(7)—C(71)	110·2 (5)
N—C(2)—C(3)	121·5 (6)	C(2)—C(7)—C(72)	111·7 (5)
N—C(2)—C(7)	117·5 (5)	C(8)—C(7)—C(71)	108·0 (5)
C(3)—C(2)—C(7)	121·0 (6)	C(8)—C(7)—C(72)	105·8 (5)
C(2)—C(3)—C(4)	119·2 (8)	C(71)—C(7)—C(72)	110·3 (6)
C(3)—C(4)—C(5)	119·5 (10)	S—C(8)—C(7)	112·9 (4)
F(1)—P—F(2)	176·5 (6)	F(2)—P—F(6)	88·6 (7)
F(1)—P—F(3)	86·8 (4)	F(3)—P—F(4)	177·1 (5)
F(1)—P—F(4)	92·4 (5)	F(3)—P—F(5)	88·8 (5)
F(1)—P—F(5)	86·4 (5)	F(3)—P—F(6)	88·5 (5)
F(1)—P—F(6)	93·3 (5)	F(4)—P—F(5)	93·9 (5)
F(2)—P—F(3)	90·3 (6)	F(4)—P—F(6)	88·8 (5)
F(2)—P—F(4)	90·6 (7)	F(5)—P—F(6)	177·3 (6)
F(2)—P—F(5)	91·6 (7)		

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* Lists of structure factors, anisotropic temperature factors for non-hydrogen atoms, atomic parameters of F atoms with occupancy factor of 0·25 and of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44205 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°) *about the exocyclic chain*

C(9)–S–C(8)–C(7)	132·5 (4)	N–C(2)–C(7)–C(8)	4·4 (6)
C(10)–S–C(8)–C(7)	−121·4 (4)	N–C(2)–C(7)–C(71)	−115·1 (5)
S–C(8)–C(7)–C(2)	−60·6 (5)	N–C(2)–C(7)–C(72)	122·0 (5)
S–C(8)–C(7)–C(71)	60·2 (5)	C(3)–C(2)–C(7)–C(71)	64·6 (7)
S–C(8)–C(7)–C(72)	178·2 (4)	C(3)–C(2)–C(7)–C(72)	−58·3 (7)

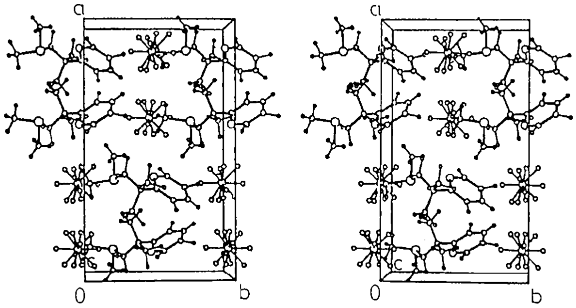

Fig. 2. Stereoscopic view of the crystal structure.

interaction between S and N. It is interesting that the weak S···N interaction has been found for such an open chain system which is able to rotate around the single bonds, C(2)–C(7) and C(7)–C(8).

Fig. 2 shows the molecular packing viewed along the *b* axis. There is no special intermolecular contact shorter than the van der Waals contact.

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References

Adzima, L. J., Chiang, C. C., Paul, I. C. & Martin, J. C. (1978). *J. Am. Chem. Soc.* **100**, 953–962.

Baenziger, N. C., Buckles, R. E., Maner, R. J. & Simpson, T. D. (1969). *J. Am. Chem. Soc.* **91**, 5749–5755.

Butler, A. R., Glidewell, C. & Liles, D. C. (1978). *Acta Cryst.* B**34**, 2570–2574.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Iwasaki, F. & Akiba, K. (1981). *Acta Cryst.* B**37**, 180–185.

Iwasaki, F. & Akiba, K. (1985). *Acta Cryst.* B**41**, 445–452.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kálmán, A., Sasvári, K. & Kapvits, I. (1973). *Acta Cryst.* B**29**, 355–357.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Paul, I. C., Martin, J. C. & Perozzi, E. F. (1972). *J. Am. Chem. Soc.* **94**, 5010–5017.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Perozzi, E. F., Martin, J. C. & Paul, I. C. (1974). *J. Am. Chem. Soc.* **96**, 6735–6744.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–74. (In Japanese.)

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Structure of 1-(2-Hydroxyethyl)-3,4-bis(trimethylsilyl)-8-oxabicyclo[4.3.0]nonadien-6-ol

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Abstract. $C_{16}H_{30}O_3Si_2$, $M_r = 326{\cdot}59$, triclinic, $P\bar{1}$, $a = 6{\cdot}857\ (1)$, $b = 10{\cdot}090\ (1)$, $c = 14{\cdot}477\ (2)$ Å, $\alpha = 81{\cdot}54\ (1)$, $\beta = 89{\cdot}51\ (1)$, $\gamma = 73{\cdot}71\ (1)°$, $V = 950{\cdot}4\ (3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}12$, $D_x = 1{\cdot}141$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}873$ cm^{-1}, $F(000) = 356$, $T = 298$ K, $R = 0{\cdot}036$, $wR = 0{\cdot}048$, 1940 observed reflections [$I \geq 3\sigma(I)$]. The steric crowding caused by the vicinal trimethylsilyl groups distorts the six-membered ring as compared with unsubstituted 1,3-cyclohexadiene. Each molecule is hydrogen-bonded to one translationally related neighbor *via* the hydroxyl groups. The resulting chains are in turn hydrogen-bonded to one neighboring chain by means of two symmetrically equivalent hydrogen bonds between pairs of molecules. The double chains thus formed are oriented along the *a* axis, the direction of most rapid growth of the crystal.

Introduction. The title compound was prepared by D. Harvey and K. P. C. Vollhardt of this department as part of an ongoing investigation of [2+2+2] cycloadditions mediated by (η^5-C_5H_5)Co(CO)$_2$. The reaction involved furyl propargyl ether and bis(trimethylsilyl)ethyne in the presence of (η^5-C_5H_5)Co(CO)$_2$, sub-

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