Tetraphenylstibonium Dimesylaminide–Chloroform (1/1)

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Abstract. $[Sb(C_6H_5)_4][C_2H_6NO_4S_2].CHCl_3$, $M_r = 721\cdot74$, monoclinic, $P2_1/n$, $a = 8\cdot309$ (5), $b = 23\cdot484$ (9), $c = 15\cdot385$ (9) Å, $\beta = 93\cdot05$ (5)°, $V = 2998$ (3) Å^3, $Z = 4$, $D_x = 1\cdot599$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot36$ mm^{-1}, $F(000) = 1448$, $T = 291$ (1) K, final $R = 0\cdot045$ for 3671 unique observed $[F \geq 3\cdot0\sigma(F)]$ diffractometer data. The crystal structure of the title compound consists of Ph_4Sb cations, $N(SO_2CH_3)_2$ anions and chloroform as solvate molecules. The S—N bonds in the anion [bond angle S—N—S: $121\cdot4$ (3)°] are short, the S—N distances of $1\cdot576$ (5) and $1\cdot591$ (5) Å correlating with a bond order of about $1\cdot72$ to $1\cdot85$.

Introduction. Disulfonylamides $HN(SO_2R)_2$, which are strong protic compounds ($pK_a \leq 3$), form covalent derivatives $XN(SO_2R)_2$ and salt-like compounds with metal cations, with complex cations, and with onium ions (Helferich & Flechsig, 1942; Blaschette, Wieland, Seurig, Koch & Safari, 1983). A key to the better understanding of the behavior of such compounds is an improved knowledge of the bonding situation at the nitrogen atom. In this respect we are studying structures of covalent and ionic derivatives of dimesylamine $HN(SO_2CH_3)_2$ and report here on the preparation and solid-state structure of the title compound.

Experimental. $[Ph_4Sb][N(SO_2CH_3)_2].CHCl_3$ crystallizes from a solution of 5 mmol $Ph_5Sb.0\cdot5C_6H_{12}$ and 5 mmol dimesylamine in $CHCl_3$ after addition of petroleum ether. Crystal size $\sim 0\cdot34 \times 0\cdot10 \times 0\cdot13$ mm, $\omega/2\theta$ scan, scan speed $1\cdot8$–$3\cdot7°$ min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflections up to $2\theta = 24\cdot5°$; six standard reflections recorded every $2\cdot5$ h, only random deviations; 11247 reflections measured, $1\cdot0° \leq \theta \leq 25\cdot0°$, $-9 \leq h \leq 9$, $0 \leq k \leq 27$, $-18 \leq l \leq 18$; after averaging ($R_{int} = 0\cdot025$): 5284 unique reflections, 3671 with $F \geq 3\cdot0\sigma(F)$; Lorentz–polarization correction and

absorption correction *via* ψ scans, max./min. transmission $1\cdot00/0\cdot96$; systematic absences ($h0l$, $h+l = 2n+1$; $0k0$, $k = 2n+1$) conform to space group $P2_1/n$; structure solutions *via* direct methods, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms which were placed in geometrically calculated positions (C—H $0\cdot96$ Å); the phenyl groups were refined as rigid bodies (C—C $1\cdot395$ Å, angles 120°); refinement on F with 3671 reflections and 296 refined parameters; $w = 1\cdot00/[\sigma^2(F) + (0\cdot0005F^2)]$; $S = 1\cdot30$, $R = 0\cdot045$, $wR = 0\cdot043$, $(\Delta/\sigma)_{max} = 0\cdot04$, no extinction correction; largest peak in final ΔF map $\pm 0\cdot6$ (3) e Å^{-3}, atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974); programs: *Enraf–Nonius Structure Determination Package* (Frenz, 1985) for data reduction, *PARST* (Nardelli, 1983), *SHELXTL PLUS* (Sheldrick, 1987).

Discussion. The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit cell is in Fig. 2. Positional parameters and the equivalent isotropic values of the anisotropic tempera-
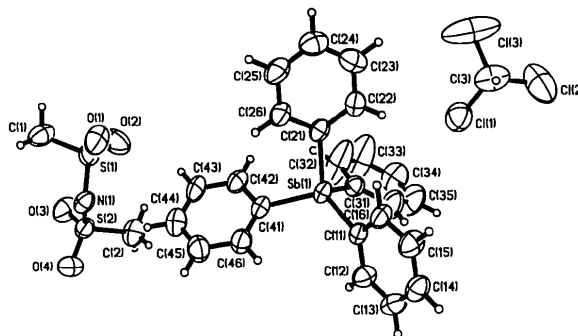

Fig. 1. The title molecule and numbering scheme.

ture factors for the non-H atoms are given in Table 1.*
Bond lengths and angles are given in Table 2. The
crystal structure contains one short $O(1)\cdots H(12)$-
$(1+x, y, z)$ distance [2·333 (6) Å] and one short
$N(1)\cdots H(3)(0·5-x, 0·5+y, 0·5-z)$ distance
[2·306 (9) Å].

The unit cell of the compound contains four Ph$_4$Sb
cations, four $(CH_3SO_2)_2N$ anions and four molecules of
chloroform. The Sb—C bond lengths [mean
2·076 (4) Å] of the distorted tetrahedral Ph$_4$Sb cations
[average C—Sb—C 109·4 (2)°, range of individual
C—Sb—C angles 102·2 (2)–116·5 (2)°] are shorter
than those found in five-coordinated tetraphenyl-
antimony compounds [Sb—C 2·108 (6)–2·218 (5) Å
(Rüther, Huber & Preut, 1985; Beauchamp, Bennett &
Cotton, 1969; Kopf, Vetter & Klar, 1974; Ferguson &
Hawley, 1974)].

The S—N—S angle [121·4 (3)°] in the $(CH_3SO_2)_2N$
anion is smaller than the appropriate angles found in
the comparable compounds $(C_2H_5SO_2)_2NH$ (I)
[125·3 (1)° (Blaschette, Wieland, Schomburg &
Adelhelm, 1986)] and $(CH_3SO_2)_2NH.H_2O$ (II)
[125·0 (1)° (Attig & Mootz, 1975)].

The S—N bond lengths [1·576 (5) and 1·591 (5) Å]
are significantly shorter than in compounds (I)
[1·642 (2) and 1·649 (2) Å], (II) [1·645 (1) Å] and
$(C_6H_5SO_2)_2NH$ [1·650 (5) Å (Cotton & Stokely,
1970)], and can be correlated with a bond order of
about 1·72 to 1·85 [calculation according to Pauling
(1968)]. S—N bond lengths similar to those in the title
compound have been found in $LiN(SO_2CH_3)_2.H_2O$
[1·599 (1) Å (Blaschette, Schomburg & Kassomenakis,
1988)], $[(CH_3)_3Sn(OH_2)_2]N(SO_2CH_3)_2$ [1·592 (3) Å
(Blaschette, Schomburg & Wieland, 1988a; Wieland,
1986)], $NaN(SO_2C_6H_5)_2$ [1·580 (5) Å (Cotton &
Stokely, 1970)] and $(CH_3)_3SnN(SO_2CH_3)_2$ [S—N
1·610 (3) Å (Blaschette, Schomburg & Wieland,
1988b)]. In the title compound as well as in the other

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* Lists of H-atom coordinates, anisotropic thermal parameters
and structure factor amplitudes have been deposited with the British
Library Document Supply Centre as Supplementary Publication
No. SUP 51711 (19 pp.). Copies may be obtained through The
Executive Secretary, International Union of Crystallography, 5
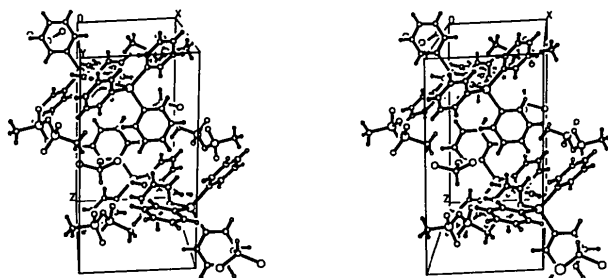Abbey Square, Chester CH1 2HU, England.

Fig. 2. A stereoview of the unit cell.

Table 1. *Atomic coordinates and equivalent isotropic
thermal parameters* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = (1/3)(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Sb(1)	0.03502 (4)	0.08244 (2)	0.25587 (2)	41
S(1)	0.8533 (2)	0.24847 (7)	0.1350 (1)	51
S(2)	0.7083 (2)	0.35365 (7)	0.1126 (1)	52
O(1)	0.8620 (5)	0.2067 (2)	0.2036 (3)	76
O(2)	0.7799 (7)	0.2299 (2)	0.0539 (3)	89
O(3)	0.8079 (6)	0.3658 (2)	0.0419 (3)	75
O(4)	0.6793 (6)	0.4001 (2)	0.1698 (4)	85
N(1)	0.7723 (6)	0.3029 (2)	0.1736 (3)	50
C(1)	1.0533 (8)	0.2674 (3)	0.1170 (5)	72
C(2)	0.5196 (8)	0.3320 (3)	0.0655 (4)	68
C(12)	-0.2372 (5)	0.1273 (1)	0.3618 (2)	52
C(13)	-0.3547 (5)	0.1237 (1)	0.4231 (2)	58
C(14)	-0.3608 (5)	0.0762 (1)	0.4771 (2)	58
C(15)	-0.2494 (5)	0.0322 (1)	0.4700 (2)	62
C(16)	-0.1319 (5)	0.0358 (1)	0.4087 (2)	53
C(11)	-0.1258 (5)	0.0834 (1)	0.3546 (2)	40
C(22)	0.1206 (4)	-0.0432 (2)	0.2489 (3)	52
C(23)	0.2216 (4)	-0.0906 (2)	0.2535 (3)	67
C(24)	0.3848 (4)	-0.0842 (2)	0.2777 (3)	65
C(25)	0.4469 (4)	-0.0302 (2)	0.2974 (3)	65
C(26)	0.3459 (4)	0.0172 (2)	0.2928 (3)	54
C(21)	0.1827 (4)	0.0108 (2)	0.2686 (3)	43
C(32)	-0.0265 (4)	0.0727 (3)	0.0612 (3)	141
C(33)	-0.1177 (4)	0.0653 (3)	-0.0167 (3)	161
C(34)	-0.2844 (4)	0.0583 (3)	-0.0157 (3)	84
C(35)	-0.3597 (4)	0.0587 (3)	0.0631 (3)	98
C(36)	-0.2685 (4)	0.0661 (3)	0.1411 (3)	79
C(31)	-0.1019 (4)	0.0731 (3)	0.1401 (3)	46
C(42)	0.3125 (5)	0.1495 (2)	0.1916 (2)	54
C(43)	0.4326 (5)	0.1911 (2)	0.1940 (2)	60
C(44)	0.4413 (5)	0.2311 (2)	0.2610 (2)	62
C(45)	0.3300 (5)	0.2296 (2)	0.3257 (2)	69
C(46)	0.2099 (5)	0.1880 (2)	0.3234 (2)	56
C(41)	0.2012 (5)	0.1480 (2)	0.2563 (2)	44
Cl(1)	-0.2969 (3)	-0.0853 (1)	0.1057 (2)	92
Cl(2)	-0.4909 (4)	-0.1844 (1)	0.0823 (2)	143
Cl(3)	-0.1485 (5)	-0.1917 (2)	0.0742 (2)	189
C(3)	-0.304 (1)	-0.1581 (4)	0.1228 (5)	89

Table 2. *Bond distances* (Å) *and angles* (°)

Sb(1)–C(11)	2·076 (4)	S(2)–O(3)	1·430 (5)
Sb(1)–C(21)	2·086 (4)	S(2)–O(4)	1·430 (6)
Sb(1)–C(31)	2·073 (4)	S(2)–N(1)	1·591 (5)
Sb(1)–C(41)	2·068 (4)	S(2)–C(2)	1·767 (7)
S(1)–O(1)	1·440 (5)	Cl(1)–C(3)	1·732 (9)
S(1)–O(2)	1·427 (5)	Cl(2)–C(3)	1·751 (9)
S(1)–N(1)	1·576 (5)	Cl(3)–C(3)	1·72 (1)
S(1)–C(1)	1·756 (7)		

C(31)–Sb(1)–C(41)	114·7 (2)		
C(21)–Sb(1)–C(41)	102·2 (2)	O(3)–S(2)–O(4)	116·0 (3)
C(21)–Sb(1)–C(31)	106·8 (2)	S(1)–N(1)–S(2)	121·4 (3)
C(11)–Sb(1)–C(41)	116·5 (2)	Sb(1)–C(11)–C(16)	118·3 (3)
C(11)–Sb(1)–C(31)	106·5 (2)	Sb(1)–C(11)–C(12)	121·4 (3)
C(11)–Sb(1)–C(21)	109·8 (2)	Sb(1)–C(21)–C(26)	119·7 (3)
N(1)–S(1)–C(1)	106·3 (3)	Sb(1)–C(21)–C(22)	120·2 (3)
O(2)–S(1)–C(1)	107·7 (4)	Sb(1)–C(31)–C(36)	120·2 (3)
O(2)–S(1)–N(1)	114·0 (3)	Sb(1)–C(31)–C(32)	119·8 (3)
O(1)–S(1)–C(1)	106·1 (3)	Sb(1)–C(41)–C(46)	120·9 (3)
O(1)–S(1)–N(1)	106·4 (3)	Sb(1)–C(41)–C(42)	119·0 (3)
O(1)–S(1)–O(2)	115·8 (3)	Cl(2)–C(3)–Cl(3)	110·9 (5)
N(1)–S(2)–C(2)	106·8 (3)	Cl(1)–C(3)–Cl(3)	110·6 (5)
O(4)–S(2)–C(2)	107·3 (4)	Cl(1)–C(3)–Cl(2)	109·4 (5)
O(4)–S(2)–N(1)	105·6 (3)		
O(3)–S(2)–C(2)	106·4 (3)		
O(3)–S(2)–N(1)	114·2 (3)		

above-mentioned disulfonylamide derivatives the S—N
bonds are appreciably shorter than the S—N single-
bond distance found in H_3NSO_3 [1·7714 (3) Å (Bats,
Coppens & Koetzle, 1977)] or than 1·73 Å, the
corrected sum of the covalent bond radii (Schomaker &
Stevenson, 1941). The contraction of the S—N bond

lengths can be attributed to increased $(p-d)$ $\pi S-N$ bonding effected by the high electron density of the deprotonated negative nitrogen atom.

The mean S=O bond length of 1·432 (6) Å is not significantly different from the values found in (I) [mean 1·422 (2) Å] and (II) [mean 1·427 (1) Å]. However, a comparison of the $\bar{\nu}SO_2$ values of $[Ph_4SbN][(SO_2-CH_3)_2].CHCl_3$ (1194 cm⁻¹) and of (I) and (II) (ca 1250 cm⁻¹) infers a decrease of the S=O bond order. A very weak H bond is indicated by the short N···H—CCl₃ distance [2·306 (9) Å]. The orientation of the chloroform molecule agrees with this assumption (Fig. 2).

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References

ATTIG, R. & MOOTZ, D. (1975). Acta Cryst. B31, 1212–1214.

BATS, J. W., COPPENS, P. & KOETZLE, T. F. (1977). Acta Cryst. B33, 37–45.

BEAUCHAMP, H. L., BENNETT, M. J. & COTTON, F. A. (1969). J. Am. Chem. Soc. 91, 297–301.

BLASCHETTE, A., SCHOMBURG, D. & KASSOMENAKIS, S. (1988). Unpublished.

BLASCHETTE, A., SCHOMBURG, D. & WIELAND, E. (1988a). Unpublished.

BLASCHETTE, A., SCHOMBURG, D. & WIELAND, E. (1988b). Z. Anorg. Allg. Chem. 566, 103–110.

BLASCHETTE, A., WIELAND, E., SCHOMBURG, D. & ADELHELM, M. (1986). Z. Anorg. Allg. Chem. 533, 7–17.

BLASCHETTE, A., WIELAND, E., SEURIG, G., KOCH, D. & SAFARI, F. (1983). Z. Anorg. Allg. Chem. 506, 75–86.

COTTON, F. A. & STOKELY, P. F. (1970). J. Am. Chem. Soc. 92, 294–302.

FERGUSON, G. & HAWLEY, D. M. (1974). Acta Cryst. B30, 103–111.

FRENZ, B. A. (1985). Enraf–Nonius Structure Determination Package (SDP-PLUS, V3.0). Enraf–Nonius, Delft, The Netherlands.

HELFERICH, B. & FLECHSIG, H. (1942). Ber. Dtsch. Chem. Ges. 75, 532–536.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KOPF, J., VETTER, G. & KLAR, G. (1974). Z. Anorg. Allg. Chem. 409, 285–298.

NARDELLI, M. (1983). Comput. Chem. 7, 95–98.

PAULING, L. (1968). The Nature of the Chemical Bond, 3rd ed., p. 235. Ithaca, NY: Cornell Univ. Press.

RÜTHER, R., HUBER, F. & PREUT, H. (1985). J. Organomet. Chem. 295, 21–28.

SCHOMAKER, V. & STEVENSON, D. P. (1941). J. Am. Chem. Soc. 63, 37–40.

SHELDRICK, G. M. (1987). SHELXTL PLUS (Release 2) for Nicolet R3m/V. Crystallography from Diffraction Data. Univ. of Göttingen, Federal Republic of Germany.

WIELAND, E. (1986). Dissertation, TU Braunschweig, Federal Republic of Germany.

Structure of Nitrato(triphenylphosphine)gold(I), Au(PPh₃)(NO₃)

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Abstract. $[AuNO_3(C_{18}H_{15}P)]$, $M_r = 2081\cdot1$, monoclinic, $P2_1/c$, $a = 8\cdot922$ (6), $b = 10\cdot131$ (8), $c = 19\cdot592$ (15) Å, $\beta = 97\cdot33$ (6)°, $V = 1756\cdot4$ (22) Å³, $Z = 4$, $D_x = 1\cdot97$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0\cdot71073$ Å, $\mu = 84\cdot1$ cm⁻¹, $F(000) = 992$, $T = 295$ K. Final $R = 0\cdot0336$ for 1603 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$. The coordination of Au^I is linear [P—Au—O = 179·2 (2)°]. The short Au—P bond, 2·208 (3) Å, is attributed to the *trans* influence of the covalently bonded oxygen atom from the nitrate ligand with Au—O(1) = 2·074 (8) Å. Short, identical Au···O(3) and Au···N intramolecular distances [2·84 (1) Å] are observed.

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Introduction. Au(PPh₃)(NO₃) has been widely used as a starting material for the synthesis of binuclear and polynuclear gold compounds (Khan, Wang, Heinrich & Fackler, 1988; Heinrich, Khan, Fackler & Porter, 1988; Steggerda, Bour & van der Velden, 1982). Only a few gold(I)–oxygen compounds have been structurally characterized (Jones, 1984, 1985; Hohbein, Jones, Meyer-Base, Schwarzmann & Sheldrick, 1985). The structure of the title compound was reported (Barron, Engelhardt, Healy, Oddy & White, 1987) along with structures of Au(PPh₃)X, where X = Br, I, and SCN. The abstract of this paper contains a reported Au—O distance for the title compound of 2·02 (1) Å while the text reports 2·199 (5) Å with R = 0·077. Examination of the coordinates suggests textual error and gross