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Intermolecular interactions in cyanodimethylarsine and cyanodimethylstibine

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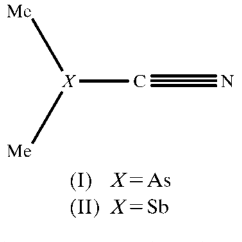
Cyanodimethylarsine, [As(CH$_3$)$_2$(CN)], and cyanodimethylstibine, [Sb(CH$_3$)$_2$(CN)], have closely related, but not isomorphous, crystal structures containing XCN···XCN··· chains. The N···As distance of 3.185 (3) Å is slightly shorter than the expected van der Waals distance of 3.5 Å, while the N···Sb distance of 2.862 (9) Å, compared with the expected value of 3.7 Å, is much shorter. This is consistent with Sb being a stronger Lewis acid than As.

Comment

After it was recognised that there were significant CN···X intermolecular interactions in (CH$_3$)$_2$AsCN (Camerman & Trotter, 1963), As(CN)$_3$ (Emerson & Britton, 1963), P(CN)$_3$ (Emerson & Britton, 1964), and CH$_3$As(CN)$_2$ (Schlemper & Britton, 1966), we attempted to extend this series to the corresponding Sb compounds.



(I) X=As
(II) X=Sb

Schlemper (1964) prepared (CH$_3$)$_2$SbCN, but found it invariably to be twinned and could only partially solve the structure. [Schlemper also prepared Sb(CN)$_3$, but all attempts to prepare single crystals led to amorphous solids. In addition, when he attempted to prepare CH$_3$Sb(CN)$_2$ from CH$_3$SbBr$_2$ and AgCN, the product was again (CH$_3$)$_2$SbCN.] With the more powerful techniques now available, we decided to return to this problem and report here the structure of (CH$_3$)$_2$SbCN, (II). We have also redetermined the structure of (CH$_3$)$_2$AsCN, (I), for comparison.

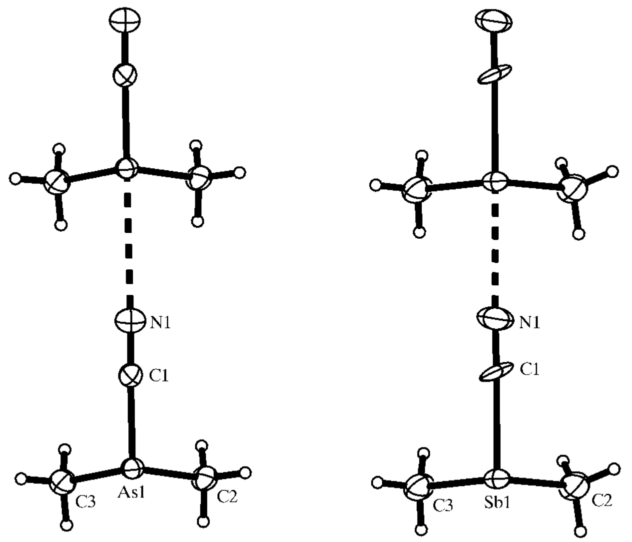


Figure 1
Views of the molecules of (I) (the As compound) and (II) (the Sb compound). Displacement ellipsoids are shown at the 50% probability level. In both cases, the N···X intermolecular interaction to a second molecule is shown.

The atom labeling and displacement ellipsoids for both compounds are shown in Fig. 1, and the bond lengths and angles are compared in Table 1. The differences in the bond lengths and angles are as would be expected when Sb replaces As. The one unusual feature is that the Sb—C1 distance appears to be larger than the Sb—C2 and Sb—C3 distances; the difference is about eight s.u.'s, which is marginally significant. This is in contrast to the expected shortening when Csp^3 is replaced by Csp.

The most significant intermolecular interactions are the N···As and N···Sb contacts, which result in the molecules being arranged in linear chains in both cases (see Fig. 1). The N···As distance of 3.2 Å is slightly shorter than the distance of 3.5 Å that would be expected from the usual van der Waals radii (Pauling, 1960), but the N···Sb distance of 2.9 Å is much shorter than the van der Waals distance of 3.7 Å. This trend is as would be expected, since Sb should be a stronger Lewis acid than As. The strong N···Sb interaction is also consistent with the greater length of the Sb—C1 bond.

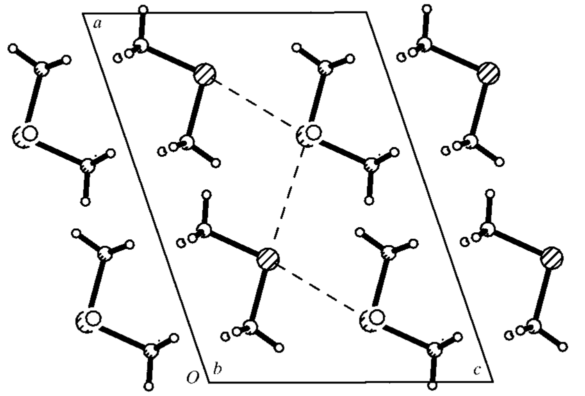


Figure 2
The packing of (I) viewed along the b axis. The intermolecular As···As contacts are shown as dashed lines.

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† Deceased.

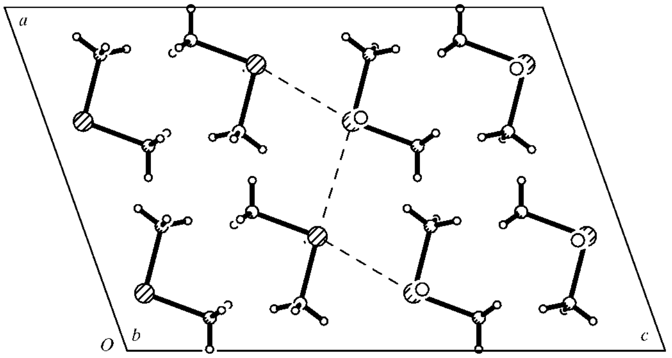

Figure 3
The packing of (II) viewed along the *b* axis. The intermolecular Sb$\cdots$Sb contacts are shown as dashed lines.

The linear chains formed by the N$\cdots$$X$ interactions are combined into double layers by $X\cdots X$ interactions (Figs. 2 and 3; Table 2). The As$\cdots$As distances of 3.7 and 4.0 Å can be compared with the 4.0 Å van der Waals distance and the 3.1 Å distance found in elemental As (Donohue, 1982; the As—As single-bond distance is 2.517 Å). The Sb$\cdots$Sb distances of 3.8 and 4.1 Å can be compared with the 4.4 Å van der Waals distance and the 3.4 Å distance found in elemental Sb (the Sb—Sb single-bond distance is 2.908 Å). These $X\cdots X$ interactions are weaker than in the pure elements but still appear to be an important part of the packing.

The crystals of the two compounds are not isomorphous but, as can be seen from Figs. 2 and 3, they are closely related. The chains parallel to the *b* axes and the double layers parallel to (001) are virtually the same in both structures. In both cases, the two halves of the double layers are related by centers of symmetry. The difference between the two lies in the stacking of adjacent double layers, which are related by a center of symmetry in the As compound, (I), but by a 2_1 axis in the Sb compound, (II).

Experimental

Compound (I) was prepared from $(CH_3)_2AsI$ and AgCN, as described by Camerman & Trotter (1963). Compound (II) was prepared in a similar manner. $(CH_3)_2SbBr$ and excess AgCN were allowed to react in benzene for 24 h. The benzene was evaporated and (II) was separated from the AgCN/AgBr residue by sublimation. The compound melted at 385–388 K. Both samples were prepared by Elmer Schlemper in 1963 and stored under vacuum since then.

Compound (I)

Crystal data

$[As(CH_3)_2(CN)]$
$M_r = 131.01$
Triclinic, $C\bar{1}$
$a = 10.738$ (2) Å
$b = 6.253$ (2) Å
$c = 7.875$ (2) Å
$\alpha = 98.30$ (3)°
$\beta = 108.39$ (3)°
$\gamma = 90.68$ (3)°
$V = 495.6$ (2) Å^3

$Z = 4$
$D_x = 1.756$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2568 reflections
$\theta = 2.8$–27.5°
$\mu = 6.68$ mm^{-1}
$T = 173$ (2) K
Needle, colorless
0.50 × 0.15 × 0.10 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.28$, $T_{max} = 0.51$
2927 measured reflections

1125 independent reflections
1058 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.05$
1125 reflections
46 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.11P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.66$ e Å^{-3}
$\Delta\rho_{min} = -1.33$ e Å^{-3}

Compound (II)

Crystal data

$[Sb(CH_3)_2(CN)]$
$M_r = 177.84$
Monoclinic, $C2/c$
$a = 11.313$ (7) Å
$b = 6.175$ (4) Å
$c = 16.701$ (11) Å
$\beta = 109.673$ (9)°
$V = 1098.6$ (12) Å^3
$Z = 8$

$D_x = 2.150$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2092 reflections
$\theta = 2.6$–25.0°
$\mu = 4.86$ mm^{-1}
$T = 173$ (2) K
Irregular, colorless
0.4 × 0.3 × 0.2 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.20$, $T_{max} = 0.38$
1063 measured reflections

968 independent reflections
959 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 25.1°$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 19$

Table 1
Comparison of bond distances and angles in (I) (X = As) and (II) (X = Sb) (Å, °).

	(I)	(II)		(I)	(II)
X—C1	1.943 (3)	2.230 (9)	C1—X—C2	94.51 (15)	90.3 (4)
X—C2	1.948 (4)	2.150 (10)	C1—X—C3	94.99 (14)	90.4 (4)
X—C3	1.950 (3)	2.172 (9)	C2—X—C3	98.36 (16)	95.8 (4)
C1—N1	1.139 (4)	1.112 (12)	X—C1—N1	176.3 (3)	176.8 (10)

Table 2
Distances and angles in the $X\cdots Y$ contacts in (I) and (II) (Å, °).

C(X)	X	Y	C(Y)	C(X)—$X\cdots Y$	$X\cdots Y$	$X\cdots Y$—C(Y)
(I)						
C1	N1	As1^{i}	C1^{i}	174.9 (2)	3.185 (3)	171.6 (2)
C2	As1	As1^{ii}	C2^{ii}	172.7 (2)	3.671 (1)	172.7 (2)
C3	As1	As1^{iii}	C3^{iii}	136.5 (2)	4.003 (1)	136.5 (2)
(II)						
C1	N1	Sb1^{i}	C1^{i}	171.1 (9)	2.862 (9)	168.0 (10)
C2	Sb1	Sb1^{ii}	C2^{ii}	169.4 (9)	3.847 (4)	169.4 (9)
C3	Sb1	Sb1^{iii}	C3^{iii}	142.9 (9)	4.062 (4)	142.9 (9)

Symmetry codes: (i) $x, y-1, z$; (ii) $2-x, -y, 1-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.097$
$S = 1.06$
968 reflections
49 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 3.19P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 2.19$ e Å^{-3}
$\Delta\rho_{\min} = -1.62$ e Å^{-3}

The As compound, (I), has a conventional cell, with $a = 6.181$ (2), $b = 6.245$ (2) and $c = 7.875$ (2) Å, and $\alpha = 78.52$ (1), $\beta = 69.69$ (1) and $\gamma = 60.43$ (1)°. The matrix $(110/1\bar{1}0/00\bar{1})$ converts this to the cell given in the *Crystal data*. The change was made to facilitate comparison with the Sb structure, (II). [The matrix $(010/001/\bar{1}00)$ converts the conventional cell to the orientation used by Camerman & Trotter (1963).] Schlemper (1964) examined 20 crystals of the Sb compound and found 18 obviously multiple from the diffraction patterns obtained from precession photographs (Mo $K\alpha$ radiation). The remaining two crystals appeared to be orthorhombic, with $a = 32.04$ (5), $b = 11.58$ (2) and $c = 6.21$ (1) Å. With $Z = 16$, the calculated density (2.05 Mg m^{-3}) agreed reasonably with the experimental density determined by flotation in a CCl_4–CBr_4 mixture [2.15 (1) Mg m^{-3}]. However, the extinctions (for *hkl* reflections $h+k$, $k+l$, $h+l$ all odd, and for $hk0$ reflections $h+k \neq 4n$) did not fit any space group and twinning was suspected even for these two crystals. At this point, Weissenberg photographs were taken with Cu $K\alpha$ radiation where, with the greater resolution, some split spots could be detected. These data fit a twinned monoclinic cell with $a = 11.58$ (2), $b = 6.21$ (1) and $c = 17.03$ (3) Å, and $\beta = 109.8$ (2)°; the extinctions were now appropriate for *Cc* or *C*2/*c*. The Sb atoms, but not all of the light atoms, could be located, and the problem was abandoned.

The new data for (II) could be indexed as a *C*-centered monoclinic cell (the one reported in the *Crystal data*) or as an *F*-centered orthorhombic cell, which can be obtained from the monoclinic cell using the matrix (100/010/102). As found in the earlier work, the Sb positions could be found readily in the monoclinic cell, but only some of the light atoms could be found. Rotating the monoclinic cell by 180° around the *a* axis produces a pseudo-merohedral twin related by the twin law $(\bar{1}00/0\bar{1}0/101)$. Continuing the solution and refinement treating the crystal as a merohedral twin led to a chemically reasonable solution with a twin fraction of 0.475 (3).

Crystals of both (I) and (II) were too irregular in shape to allow face-indexed absorption corrections. While the *SADABS* (Sheldrick, 1996) absorption corrections were significant, they were not completely adequate. This problem led to large peaks in the final difference maps. In both cases, all of the large peaks were close to the heavy atom. Problems with the absorption corrections were also the most likely reason for the elongated displacement ellipsoid for atom C1 in (II). H atoms were placed geometrically, with C—H = 0.98 Å, and refined as riding atoms, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1648). Services for accessing these data are described at the back of the journal.

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