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The Molecular Structures of Trimethylarsenic, Trimethylantimony and Dimethyltellurium Determined by Gas Electron Diffraction

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The molecular structures of trimethylarsenic, trimethylantimony and dimethyltellurium have been determined by gas electron diffraction. The bond distances (r_a) are As–C=1.968(3) Å, Sb–C=2.163(3) Å, and Te–C=2.142(5) Å, the valence angles ∠CAsC=96.1(5)°, ∠CSbC= 94.1(5)° and ∠CTeC=94(2)°.

While making a survey of bond distances and valence angles in simple methyl derivatives of main group elements,[1] $El(CH_3)_k$, we discovered that accurate values were missing for $As(CH_3)_3$, $Sb(CH_3)_3$ and $Te(CH_3)_2$. The present study was undertaken in order to close the gap.

EXPERIMENTAL

Reagent grade $As(CH_3)_3$ (Strem Chemicals) and $Sb(CH_3)_3$ and $Te(CH_3)_2$ (Alpha/Ventron) were used without further purification.

The scattering patterns were recorded on Balzers Eldigraph KDG-2 with nozzle temperatures of about 20 °C and nozzle-to-plate distances of 50 and 25 cm. For the structure determination of $As(CH_3)_3$ we used six plates from each set, for $Sb(CH_3)_3$ we used six 50 cm and eleven 25 cm plates, and for $Te(CH_3)_2$ we used five 50 cm and four 25 cm plates. The scattering data were processed by standard procedures. The molecular intensity curves obtained for each nozzle-to-plate distance were averaged, but not connected. The curves extended from s=2.00 to 14.00 Å^{-1} with increment Δs=0.125 Å^{-1} (50 cm) and from s=4.00 to 28.00 Å^{-1} with increment Δs=0.250 Å^{-1}.

The complex atomic scattering factors of Sb were obtained by interpolation of tabulated values.[2] The scattering factors of As, Te, C and H were calculated from the atomic potentials[3] by the partial wave method.[4]

STRUCTURE ANALYSIS

Structure refinements of $As(CH_3)_3$ and $Sb(CH_3)_3$ were based on models of C_{3v} symmetry, structure refinement of $Te(CH_3)_2$ on a model of C_{2v} symmetry. The methyl groups in each molecule were assumed to have C_{3v} symmetry with the threefold axes coinciding with the El-C bonds. Finally, the orientation of the methyl groups was assumed to be staggered with respect to the bond(s) radiating from the heteroatom. See Figs. 1, 2 and 3. The structure of each molecule is then determined by four parameters; the bond distances El-C and C–H and the valence angles ∠CElC and ∠ElCH.

Simple valence force fields were adjusted to reproduce the normal modes of vibrations assigned for the three molecules,[5] and root-mean-square vibrational amplitudes, l, and the vibrational correction coefficients $D=r_\alpha-r_a$ calculated at T=293 K using a program written by Hilderbrandt.[6] The values obtained (Table 1) were similar to those reported by Beagley and Medwid.[5]

The molecular structures were refined under the constraints of geometrically consistent r_a structures by least squares calculations on the molecular intensities with non-diagonal weight matrices.[7] Those vibrational amplitudes which

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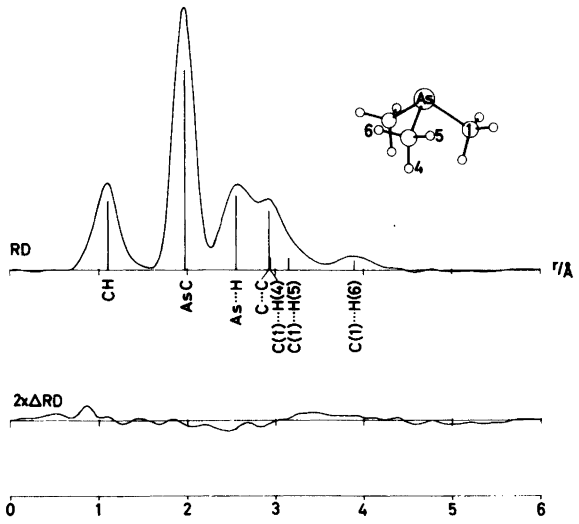

Fig. 1. Above: Experimental radial distribution curve for $As(CH_3)_3$. Artificial damping constant $k=0.003$ Å^2. Major interatomic distances are indicated by bars of height proportional to the *area* under the corresponding peak. *Below:* Difference between experimental curve and the theoretical curve calculated for the best model.

could not be refined were fixed at their calculated values. The refinements converged to yield the parameter values listed in Table 1. The estimated standard deviations have been expanded to include scale uncertainty of 0.1 %.

Experimental radial distribution (RD) curves calculated by Fourier inversion of experimental modified molecular intensity curves, are shown in Figs. 1, 2 and 3 along with the difference between the experimental RD curves and their theoretical counterparts calculated for the best model.

Table 1 shows that the structure of $Te(CH_3)_2$ has been determined with lower accuracy than expected from studies of this kind. We feel that

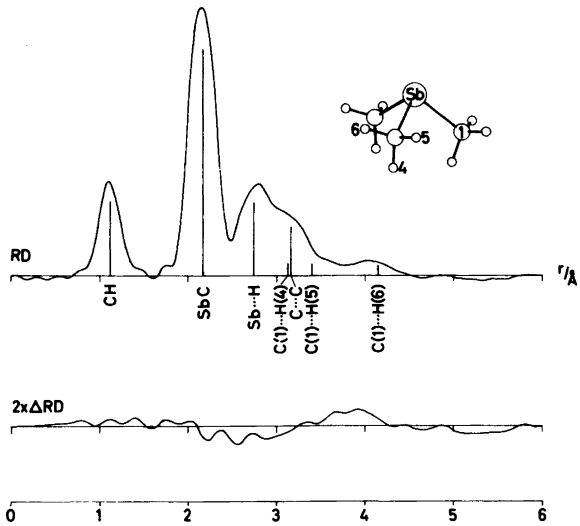

Fig. 2. Experimental radial distribution curve for $Sb(CH_3)_3$. $k=0.002$ Å^2.

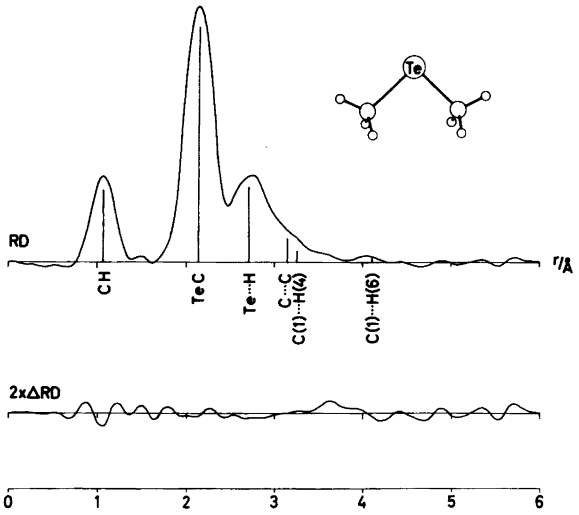

Fig. 3. Experimental radial distribution curve for $Te(CH_3)_2$. k=0.003 Å^2.

Table 1. Internuclear distances (r_a), valence angles, and root mean square vibrational amplitudes (l) of $As(CH_3)_3$, $Sb(CH_3)_3$ and $Te(CH_3)_2$ obtained by least squares refinement on gas electron diffraction (GED) data. Estimated standard deviations in parentheses in units of the last digit. Root mean square vibrational amplitudes and vibrational correction terms ($D=r_a-r_a$) calculated from a molecular force field (FF).

	r_a (Å)	l (Å) (GED)	l (Å) (FF)	D (Å) (FF)
$As(CH_3)_3$				
As–C	1.968(3)	0.062(3)	0.050	−0.0012
C–H	1.100(6)	0.080(6)	0.078	−0.0316
As···H	2.54	0.119(6)	0.118	−0.0111
C···C	2.92	0.100(8)	0.103	0.0018
$C_1\cdots H_4$	2.93	(0.204)	0.204	0.0022
$C_1\cdots H_5$	3.15	0.22(7)	0.208	0.0034
$C_1\cdots H_6$	3.89	0.14(3)	0.126	−0.0061
∠CAsC(°)	96.1(5)			
∠AsCH(°)	109.0(6)			
$Sb(CH_3)_3$				
Sb–C	2.163(3)	0.051(1)	0.053	−0.0017
C–H	1.113(6)	0.080(6)	0.078	−0.0363
Sb···H	2.74	0.122(9)	0.122	−0.0126
C···C	3.16	0.13(1)	0.117	0.0022
$C_1\cdots H_4$	3.15	(0.226)	0.226	0.0031
$C_1\cdots H_5$	3.40	(0.227)	0.227	0.0038
$C_1\cdots H_6$	4.15	0.16(3)	0.138	−0.0067
∠CSbC(°)	94.1(5)			
∠SbCH(°)	110.1(8)			
$Te(CH_3)_2$				
Te–C	2.142(5)	0.06(2)	0.055	−0.0003
C–H	1.07(2)	0.07(2)	0.078	−0.0388
Te···H	2.71	(0.119)	0.119	−0.0121
C···C	3.14	(0.114)	0.114	0.0035
C···H	3.25	(0.229)	0.229	0.0055
C···H	4.10	(0.131)	0.131	−0.0055
∠CTeC(°)	94(2)			
∠TeCH(°)	112(2)			

the poor result is due to a combination of several effects; the background of atomic scattering is high, the beat-out corresponding to $\Delta\eta_{TeC}=\pi/2$ occurs somewhat below $s=20$ Å^{-1}, and the multiplicity of the C–C distance is unity as compared to three in $Sb(CH_3)_3$. The refinement of the latter was based on eleven 25 cm plates, the refinement of $Te(CH_3)_2$ on four. It would clearly have been advantageous to include a larger number of 25 cm plates for $Te(CH_3)_2$, but when this became clear, we had already destroyed the sample.

RESULTS AND DISCUSSION

The structure parameters of $As(CH_3)_3$, $Sb(CH_3)_3$ and $Te(CH_3)_2$ are listed in Table 1. The results for $As(CH_3)_3$ are in agreement with an early gas electron diffraction study which yielded R(As–C)=1.98(2) Å and ∠CAsC=95(5)°.[8] Later, Lide determined the principal moment of inertia, which together with an assumed value for ∠CAsC=96°, gave R(As–C)=1.96(1) Å.[9] We are not aware of any previous gas phase studies of $Sb(CH_3)_3$ or $Te(CH_3)_2$.

We have already made use of the results of the present study when discussing period and group variations of main-group-element-to-carbon, -hydrogen and -chlorine bond distances in homoleptic compounds $El(CH_3)_k$, ElH_k and $ElCl_k$.[1] It was then noted that the bonding radius of a fourth period element between Cd and I appears to be 0.19±0.01 Å greater than the third period element in the same group. The El–C bond distances reported here conform to the rule; R(Sb–C) $-R$(As–C)=0.195(4) Å; combination with the published Se–C bond distance in $Se(CH_3)_2$[10] gives R(Te–C)$-R$(Se–C)= 0.202(6) Å.

In our discussion of the periodic variation of El–C bond distances, we limited ourselves to trivalent compounds of group VB elements and divalent compounds of group VI B elements. In Table 2 we compare the bond distances in triorganyl-derivatives of P, As and Sb with equatorial and axial bond distances in corresponding pentaorganyl-derivatives with trigonal bipyramid structure: It is seen that the equatorial bond distances in the pentavalent compounds are very similar to the bond distances in the trivalent compounds, while the axial bonds are 0.10 to 0.15 Å longer. The bond distances, therefore, are in good agreement with the view that the equatorial bonds may be regarded as normal single bonds while the $C_{ax}ElC_{ax}$-fragment is held together by a three-center, four electron bond.[23]

Very recently Titus, Zialo and co-workers have reported the crystal and molecular structure of the first tetraorganyl Te(IV) compound, tetraphenyltellurium 1/8 benzene.[24] The structure is that of a distorted trigonal bipyramid with an electron pair occupying an equatorial site. The mean equatorial Te–C bond distance, 2.13(0) Å, is indistinguishable from the bond distance in $Te(CH_3)_2$, while the mean Te–C_{ax} bond distance is 2.29(1) Å.

Table 2. El-C bond distances in homoleptic compounds of type ElR_3 and equatorial and axial bond distances in ElR_5 compounds of trigonal bipyramid symmetry.[a] El=P, As and Sb.

Compound	R (Å)	Ref.	Compound	R_{eq} (Å)/R_{ax} (Å)	Ref.
$P(CH_3)_3$	1.85	11			
PPh_3	1.83	12	PPh_5	1.85/1.99	18
$PMes_3$	1.84	13			
$As(CH_3)_3$	1.97				
$AsPh_3$	1.96	14	$AsPh_5$[b]	1.96/2.11	19
$AsTol_3$	1.95	15			
$Sb(CH_3)_3$	2.16		$Sb(CH_3)_5$	2.15/2.25	20
$SbTol_3$	2.14	16	$SbPh_5$	2.13/2.25	21
$SbXyl_3$	2.19	17	$SbTol_5$	2.16/2.26	22

[a] Ph = phenyl, Tol=*p*-tolyl, Xyl = 2,6-dimethylphenyl, Mes = mesityl. [b] Crystallized with 0.5 mol cyclohexane.

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