Molecular Structure of Hexamethyltellurium by Gas-Phase Electron Diffraction

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While the syntheses of the first dialkyltellurium(II) compounds, diethyltellurium and dimethyltellurium, were published in 1840 and 1855, respectively,[1,2] the synthesis of the first tetraalkyltellurium(IV) compound, $(CH_3)_4Te$, was published only in 1989,[3] and the synthesis of the first hexaalkyltellurium(VI) compound, $(CH_3)_6Te$, in the following year.[4] Hexamethyltellurium was not only the first hexaalkyl derivative of Te but the first such derivative of any main group element, and the third such compound altogether, the two first being hexamethyltungsten[5] and hexamethylrhenium.[6]

The tellurium atom in $(CH_3)_6Te$ is surrounded by six bonding electron pairs, and according to the VSEPR model the coordination geometry should be octahedral.[7,8] Indeed, optimization of the structure by SCF MO calculations with a DZ basis led to a single minimum in the potential energy surface with close to octahedral symmetry.[9] (An equilibrium model with static methyl groups cannot have perfect O_h symmetry.) Finally, the octahedral structure of the isoelectronic molecule TeF_6 has been demonstrated by a gas electron diffraction study.[10]

At first glance, therefore, it might appear unnecessary to seek experimental confirmation of the octahedral structure of $(CH_3)_6$-Te. However, we have recently shown that the coordination geometry of the closely related compound $(CH_3)_6W$[11] is *trigonal prismatic* even though the coordination geometries of WF_6,[12] $W(OMe)_6$,[13] $W(NMe_2)_6$,[14] and WCl_6[15] are all octahedral.

Hexamethyltellurium was synthesized and characterized as described in ref 4. $(CH_3)_6Te$ is thermally very stable: a 10% solution in C_6D_6 gave no indication of decomposition after 4.5 h at 140 °C.[4] The gas electron diffraction data were recorded on our Baltzers Eldigraph KDG 2 unit[16,17] with a glass inlet system at room temperature. Exposures were made with nozzle to photographic plate distances of about 50 and 25 cm; structure refinements were based on data from six plates from the 50 cm set and five plates from the 25 cm set. The plates were photometered and the data processed by a program written by T. G. Strand. Atomic scattering factors were taken from ref 18. Backgrounds were drawn as least-squares adjusted tenth (50 cm) or eighth (25 cm) degree polynomials to the difference between total experimental and calculated molecular intensity curves. Least-squares refinements of the molecular structure to the modified molecular intensity curves were carried out with the program KCED26, which was written by G. Gundersen, S. Samdal, H. M. Seip, and T. G. Strand.

Structure refinements were based on a molecular model where the TeC_6 frame has O_h symmetry and the $TeCH_3$ fragments C_{3v} symmetry. The orientations of the methyl groups were chosen so as to yield a molecular model of D_{3h} symmetry as indicated in Figure 1. The barriers restricting internal rotation of the methyl groups must have 12-fold symmetry. Such barriers are expected to be much smaller than the thermal energy available at room temperature, $RT = 2.5$ kJ mol^{-1}, and the methyl groups are expected to rotate freely. The distance from the methyl group H atoms to the *trans* C atom are, of course, independent of the rotational angle. The methyl group orientation shown in the figure leads to six different H to *cis* C atom distances spaced with dihedral angles ϕ(CTeCH) ranging from 15° to 165° in steps of 30°. Such a model is expected to provide satisfactory modeling of free rotation of the methyl groups.

The molecular model in Figure 1 is determined by only three independent structure parameters, the Te−C and C−H bond distances and the ∠TeCH valence angle. These were refined along with 13 rms vibrational amplitudes to yield the best values listed in Table 1. Since the least-squares refinements had been carried out with diagonal weight matrices, the estimated standard deviations listed in the table have been multiplied by a factor of 2.0 to include the uncertainty due to data correlation[20] and further expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated intensity curves and radial distribution functions are compared in Figures 2 and 3, respectively.

Rms vibrational amplitudes (l) and vibrational correction terms, $D = r_\alpha - r_a$, for the TeC_6 frame were then calculated by fitting a diagonal force field to the vibrational frequencies calculated by Schaefer and co-workers.[9] The vibrational amplitudes thus obtained were in good agreement with those listed in Table 1. Introduction of the vibrational correction terms and new least-squares refinements did not improve the fit, and the best values obtained for the structure parameters differed from those in Table 1 by less than 1/2 esd.

The octahedral molecular model is characterized by 12 nonbonded C- -C distances spanning a valence angle of 90° and three nonbonded C- -C distances spanning an angle of 180°. The former 12 distances give a prominent peak a little above $r = 300$ pm in the radial distribution curve, and the latter three distances give a small peak at about $r = 435$ pm. A trigonal prismatic model would lead to two closely spaced peaks representing a total of nine nonbonded C- -C distances spanning valence angles of about 82°, and a third peak representing six C- -C distances spanning an angle of about 136°. Such a model

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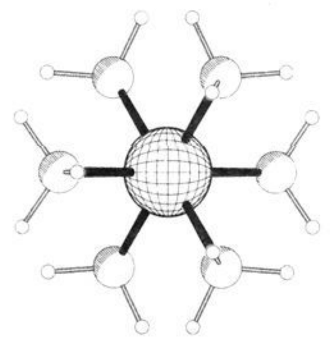

Figure 1. Molecular model (Pluton[19]) $(CH_3)_6Te$. Molecular symmetry D_{3d}.

Table 1. Interatomic Distances (r_a), Root Mean Square Vibrational Amplitudes (l), and Valence Angle in $(CH_3)_6Te^a$

	r_a	l	valence angle
Te−C	219.3(3)	5.8(3)	
C−H	110.2(3)	6.8(4)	
	nonbonded distances		
Te- -H	277.5(14)	17.1(36)	
C- -C_{cis}	310.1(4)	12.6(13)	
C- -C_{trans}	438.6(6)	9.1(20)	
C- -H_{trans}	487.9(17)	15.9(19)	
C- -H_{cis}	285−411	13(2)−58(26)	
∠TeCH			110.3(9)
R factors^b (%)	1.8 (50 cm)	11.8 (25 cm)	3.9 (total)

^{a} Distances and vibrational amplitudes in pm, angles in deg. Estimated standard deviations in parentheses in units of the last digit. ^{b} $R = [\Sigma W(I_{obs}-I_{calc})^2/\Sigma W(I_{obs})^2]^{1/2}$.

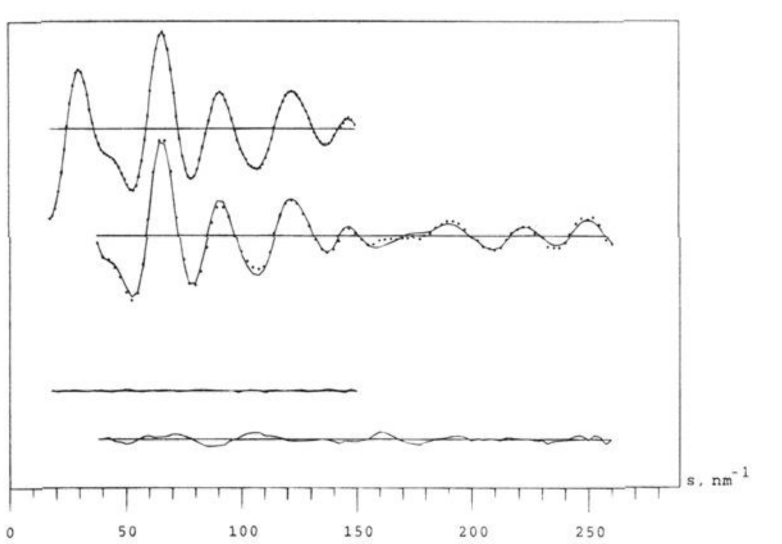

Figure 2. Experimental (dots) and calculated (lines) modified molecular intensity curves for $(CH_3)_6Te$. Below: Difference curves.

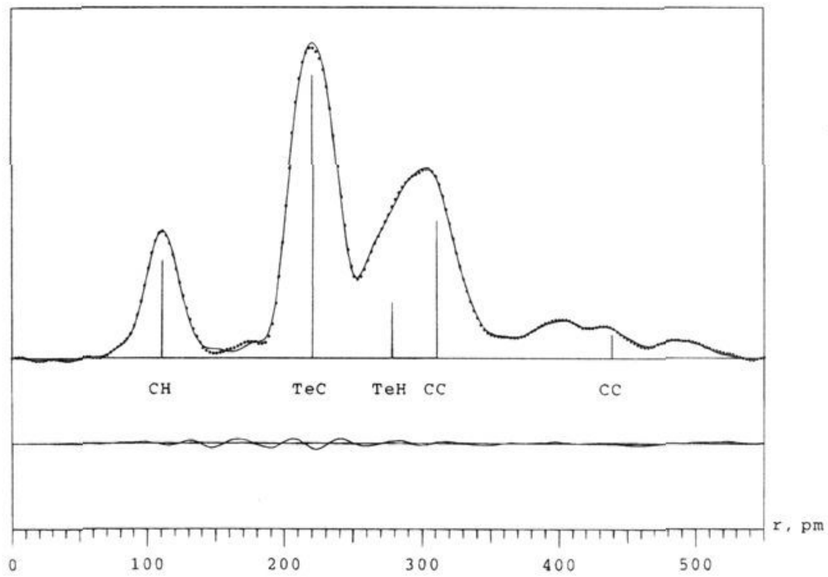

Figure 3. Experimental (dots) and calculated (line) radial distribution curves of $(CH_3)_6Te$. The vertical scale is arbitrary. Below: Difference curve. Artificial damping constant k = 25 pm^2.

could not be brought into agreement with the electron diffraction data and may be ruled out with confidence.

Since trigonal prismatic coordination leeds to shorter nonbonded C- -C distances than octahedral, and since the Te−C bond distance in $(CH_3)_6Te$ is about 5 pm longer than the W−C bond distance in $(CH_3)_6W$, 214.6(3) pm,[11] it appears unlikely that the different coordination geometries in the two compounds are due to ligand−ligand interactions.

The trigonal prismatic structure of $(CH_3)_6W$ has been rationalized in terms of metal atom hybridization and two center molecular orbitals: if the valence shell d orbitals have lower energy and are less diffuse than the valence shell p orbitals, spd^4 hybrid orbitals which are pointing toward the corners of a trigonal prism[21] would presumably lead to stronger σ bonds to the six ligands than the well-known octahedral sp^3d^2 hybrids.[22] The prismatic structure may also be rationalized in terms of a second-order Jahn−Teller distortion of an octahedral model: In an octahedral molecule the delocalized MOs containing the six bonding electrons are (in order of increasing energy) a_{1g}, which is a symmetrical combination of the metal 6s orbital with a suitable σ orbital on each ligand, the doubly degenerate e_g orbitals formed by the $5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals on the metal with an appropriate combination of ligands σ orbitals, and finally the triply degenerate t_{1u} orbitals, which are formed from the three 6p orbitals on the metal with an appropriate combination of ligand σ orbitals. The LUMO has t_{2g} symmetry. It is triply degenerate and consists of the metal atom $5d_{xz}$, $5d_{yz}$, and $5d_{xy}$ orbitals. These orbitals are optimal for π interactions to the ligand, but are unable to interact with ligand σ orbitals for symmetry reasons. If the coordination geometry is changed from octahedral to trigonal prismatic, two out of the three LUMO 5d orbitals interact with with two of the HOMO t_{1u} orbitals. If the interaction is sufficiently large, the trigonal prismatic coordination will be the more stable.[23]

Since the t_{2g} orbitals are optimal for π bonding to the ligands, π-bonding ligands will stabilize octahedral coordination. Since ligand−ligand distances are maximized in the octahedral configuration, steric or Coulombic repulsion between the ligands will destabilize the trigonal prismatic configuration. The trigonal prismatic configuration is therefore only expected with pure σ-bonding ligands which are small and not too electronegative. Aside from the methyl or n-alkyl ligands, these requirements may only be satisfied by ligating H atoms.[24]

Since both of the above rationalizations for the prismatic structure of $(CH_3)_6W$ rest on the availability of vacant valence shell d orbitals, it is very gratifying that $(CH_3)_6Te$, where the valence shall d orbitals on the central atom are filled, proves to prefer octahedral coordination.

Comparison of Te−C bond distances in $(CH_3)_2Te$, $(CH_3)_4$-Te, and $(CH_3)_6Te$ show that the variation of bond distances with increasing valence is irregular: The bond distance in $(CH_3)_2Te$ is 214.2(5) pm,[25] about 5 pm shorter than in $(CH_3)_6Te$. The structure of the tetramethyl compound may be described as trigonal bipyramidal with an equatorial nonbonding electron pair. Two equatorial Te−C bonds at 213.8(5) pm are indistinguishable from the bonds in the dimethyl.[26] The two axial bonds at 226.9(6) pm are much longer than in $(CH_3)_6Te$.[26] As a consequence the *average* bond distance in $(CH_3)_4Te$ becomes slightly larger than in $(CH_3)_6Te$.

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