Structure of Tetramethyltellurium(IV) Determined Experimentally in the Solid and Gas Phases and by *ab Initio* Calculations

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"Hypervalent" compounds of group 16 elements which violate the octet rule pose intriguing questions about bonding. Derivatives of S(IV) and S(VI) are, in general, stable only if at least one electronegative substituent is bonded to S. Thus SF_4, SF_6, SO_3, *etc.* are known compounds, but SH_4, $S(CH_3)_4$, and SH_6 are not. While compounds of selenium and tellurium in high oxidation states tend to be more stable than their sulfur counterparts (*e.g.*, *cf.* $TeCl_4$ and SCl_4) the successful preparation and spectroscopic characterization of tetramethyltellurium(IV) has been achieved only recently.[1] Although two limiting geometries, *viz.*, trigonal bipyramid with an equatorial lone pair or square pyramid with an apical lone pair, are possible, all well-characterized compounds EY_4 (E is a group 16 element; Y is a monodentate ligand) approximate to the former geometry. However, the proton-decoupled ^{13}C NMR spectrum of $Te(CH_3)_4$ at room temperature displays only a single resonance[1] so either pseudorotation rapidly interchanges axial and equatorial methyl groups, or the square-pyramidal geometry is favored.

The intriguing questions posed by $Te(CH_3)_4$ prompted three independent groups to investigate its structure. We present here the structure obtained by X-ray diffraction, electron diffraction, and *ab initio* theory.

Tetramethyltellurium(IV) was prepared[1] and purified by fractionation *in vacuo*: its purity was checked by reference to its IR and NMR spectra. A sample was condensed in a 0.28 mm i.d. Pyrex capillary, which was then mounted in the cold stream of an Oxford Cryosystems low-temperature device[2] attached to a Stoë Stadi-4 four-circle diffractometer. The polycrystalline matrix obtained on cooling the sample was warmed to give a single seed microcrystal from which a cylinder (of dimensions 0.28 × 0.28 × 0.50 mm) was obtained after slow cooling to 183 K. Details of the X-ray crystal structure are presented in ref 3. The molecular geometry in the crystal is based on a trigonal bipyramid, and dimensions are listed in Table 1; there is a crystallographic mirror plane which relates the equatorial methyl groups.

Electron-diffraction measurements for the vapor were made at 298 K using a Balzers Eldigraph KDG-2 with an all-glass inlet system;[4] details are presented in ref 5. A molecular model of $Te(CH_3)_4$ based on a trigonal bipyramid and in which the methyl groups are staggered with respect to the lone pair has C_{2v} symmetry and may be described by six independent structural parameters: the axial and equatorial bond lengths Te–C_{ax} and Te–C_{eq}, the C_{eq}–Te–C_{eq} and C_{ax}–Te–C_{ax} angles, a C–H bond length, and a Te–C–H valence angle. All six parameters refined, along with 11 vibrational amplitudes, to give a final overall *R*-factor of 0.054; the salient results are listed in Table 1. Refinements were also performed for models in which two or four methyl groups were eclipsed with respect to the lone pair. The *R*-factors were found to be marginally higher, and changes in other structural parameters were insignificant.

Table 1: Structural Parameters for $Te(CH_3)_4$

		theoretical dimens (r_e)		electron diffraction	
parameter[a]	X-ray dimens (r_α)	SCF	MP2	dimens (r_a)	vibrational amplitude
r(Te–C_{ax})	230.9(13) 227.5(17)	225.3	225.6	226.9(6)	6.8(8)
r(Te–C_{eq})	212.7(6)	213.2	214.2	213.8(5)	6.5(7)
∠(C_{eq}–Te–C_{eq})	109.1(3)	112.5	111.6	118(3)	
∠(C_{ax}–Te–C_{ax})	162.2(4)	160.8	158.7	153(2)	
r(C–H)	–[b]	108.6[c]	110.6[c]	110.4(3)	7.0(4)
∠(TeCH)	–[b]	110.1[c]	109.6[c]	110.6(9)	
∠(C_{ax}–Te–C_{eq})	84.9(3)	84.7	84.0	83.1(4)	
r(C_{ax}···C_{ax})	452.9(24)	444	443	441(2)	21(10)
r(C_{eq}···C_{eq})	346.4(16)	355	354	367(5)	39(22)
r(C_{ax}···C_{eq})	297.4–299.3(20)	295	294	293(1)	10(1)

[a] Bond lengths and vibrational amplitudes in picometers; angles in degrees; estimated standard deviations in parentheses in units of last digit (multiplied by 2 for electron-diffraction results). [b] Hydrogens not located. [c] Average value.

Structural parameters were also predicted by *ab initio* electronic structure calculations. A double-ζ valence basis was used for Te, in combination with a relativistic effective core potential.[6] Standard double-ζ bases were used for C and H atoms,[7] and a set of d-type polarization functions was added to Te (exponent 0.3) and C (exponent 0.75) atoms. Geometries were optimized at both SCF and MP2 levels of theory, using the program Gaussian 90.[8] Only minor differences between SCF and MP2 geometries were found, as expected, although the MP2 binding energies should be more reliable. The lowest energy structure has C_{2v} symmetry and is based on a trigonal bipyramid with the methyl groups all staggered with respect to the lone pair. Geometrical parameters are reported in Table 1.

The Te–C bond lengths obtained from the three studies are in excellent agreement with one another and with those obtained

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(3) Crystal data for $Te(CH_3)_4$: $P2_1/m$, $a = 5.9413(19)$ Å, $b = 7.2618(21)$ Å, $c = 8.528(5)$ Å, $\beta = 108.881(21)°$, $V = 348.1$ Å^3, $D_{calc} = 1.791$ g cm^{-3}, $Z = 2$, $\mu = 4.14$ mm^{-1}. Data were collected at 183 K on a Stoë Stadi-4 four-circle diffractometer with graphite-monochromated Mo K_α X-radiation; 1816 absorption-corrected reflections ($5° \le 2\theta \le 45°$; $-6 \le h \le 6$, $-7 \le k \le 7$, $-9 \le l \le 9$), 498 unique (R_{int} 0.042), of which 476 with $F \ge 4\sigma(F)$ were used in all calculations. Te and C atoms located by direct methods (SHELXS-86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467) and then refined anisotropically. Hydrogen atom positions identified from a ΔF synthesis were used to derive idealized positions (SHELXTL/PC version 4.2, Siemens Analytical X-ray Instrumentation, Inc., Madison, WI) at which the hydrogen atoms were fixed. Weighting scheme [$w^{-1} = \sigma^2(F) + 0.0031F^2$] led to final convergence with R, R_w = 0.0384, 0.0553, respectively, S = 0.96 for 29 refined parameters. Maximum peak and minimum trough in the final ΔF synthesis were 2.5 and –0.68 e/Å^3, respectively.

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from crystallographic studies of the related compounds $(CH_3)_2TeCl_2$ [r(Te–C_{eq}) = 211.6(1) pm][9] and $TePh_4 \cdot {}^1/_8C_6H_6$ [r(Te–C_{eq} = 213.0(0), r(Te–C_{ax}) = 227(1)–231(1) pm].[10] The Te–C_{eq} bond lengths are very similar to those in $Te(CH_3)_2$ [214.2(5) pm],[11] but the Te–C_{ax} bonds are significantly longer; similar structural patterns are found in SF_4[12] and SeF_4.[13] Although the values of the C_{eq}–Te–C_{eq} and C_{ax}–Te–C_{ax} angles predicted by theory agree reasonably well with those determined in the X-ray study, the results of the gas-phase study give corresponding values which are appreciably different. Furthermore, these angles have unusually large uncertainties and the vibrational amplitudes associated with the $C_{ax} \cdots C_{ax}$ and $C_{eq} \cdots C_{eq}$ pairs are both large and uncertain. Preliminary analysis of the vibrational spectra also indicates that there are large vibrational amplitudes associated with these atom pairs. All attempts to fit the scattering data to a model based on the solid-state structure resulted in significantly poorer R-factors. This suggests therefore that in the electron-diffraction experiment we are witnessing a dynamic process involving interconversion of two trigonal-bipyramidal structures *via* Berry pseudorotation. *The barrier to pseudorotation is so low that the apparent structure we observe represents a Boltzmann-weighted superposition of all geometries between the equilibrium and transition-state structures.* This interpretation implies that the barrier height is in the order of the thermal energy which is available at the temperature of the experiment. Further evidence for this remarkable observation comes from the theoretical calculations. A further stationary point was located with C_{4v} symmetry, and this was found to be a first-order transition state at the SCF level (one imaginary vibrational frequency, 80i cm^{-1}). All carbon atoms are equivalent in this structure, and it represents the transition state for the Berry pseudorotation process in which axial and equatorial methyl groups interchange. The Te–C bond length is 219.1 (SCF) or 220.0 (MP2) pm, and the angle between the C_4 axis and a Te–C bond is 109.8° (SCF) or 110.1° (MP2). The relationships between the calculated C_{2v} equilibrium structure, the apparent structure from the electron-diffraction study, and the calculated C_{4v} transition state for Berry pseudorotation are illustrated in Figure 1. At the SCF level the transition state lies 8.2 kJ mol^{-1} above the C_{2v} ground state, but at the MP2 level this barrier is only 4.2 kJ mol^{-1}. Calculations have also been performed on $S(CH_3)_4$ and $Se(CH_3)_4$ to arrive at MP2 pseudorotation barriers of 20 and 14 kJ mol^{-1}, respectively.[14] The decrease in barrier height in the series $S(CH_3)_4 > Se(CH_3)_4 > Te(CH_3)_4$ is in line with qualitative arguments based on steric considerations. The barrier for axial–equatorial exchange in SF_4 has been determined by gas-phase NMR studies to be 50.7(30) kJ mol^{-1}.[15] To test whether calculations which employ larger bases would predict an even lower barrier, we performed calculations on both C_{2v} and C_{4v} isomers using the previously described basis to which a set of f-functions (exponent 0.35) was added to Te. The energy difference between the C_{2v} and C_{4v} isomers with geometries as optimized previously was found to be 2.8 kJ mol^{-1} at the QCISD (T) level of theory (2.6 kJ mol^{-1} at the MP2 level).

Figure 1. Diagram illustrating the relationship between the various geometries of the TeC_4 fragment of $Te(CH_3)_4$: calculated C_{2v} structure (solid circles), apparent structure from electron diffraction of the vapor (hatched circles), and calculated C_{4v} transition state (open circles).

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Supplementary Material Available: Crystallographic tables for $Te(CH_3)_4$ and molecular scattering intensity and radial distribution curves (6 pages); observed and calculated structure factors (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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