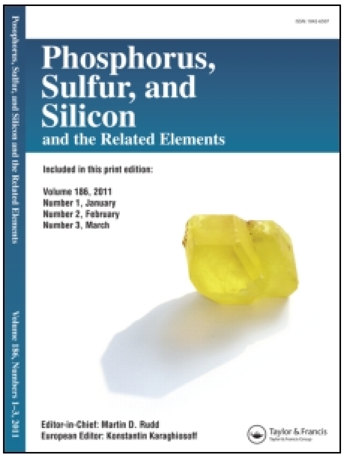

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Triphenyltellurium(IV) Diethyldithiocarbamate-Synthesis and Crystal Structure: A New Example Showing Sterically Sensitive Long Te—S Bonds

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To cite this Article Singh, Ajai K. , Srivastava, V. , Basumatary, J. K. , Singh, T. P. and Saxena, A. K.(1994) 'Triphenyltellurium(IV) Diethyldithiocarbamate-Synthesis and Crystal Structure: A New Example Showing Sterically Sensitive Long Te—S Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 31 — 37

To link to this Article: DOI: 10.1080/10426509408020429

URL: http://dx.doi.org/10.1080/10426509408020429

Phosphorus, Sulfur, and Silicon, 1994, Vol. 89, pp. 31–37
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TRIPHENYLTELLURIUM(IV) DIETHYLDITHIOCARBAMATE-SYNTHESIS AND CRYSTAL STRUCTURE: A NEW EXAMPLE SHOWING STERICALLY SENSITIVE LONG Te—S BONDS

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(Received February 4, 1994; in final form April 11, 1994)

Triphenyltellurium(IV) diethyldithiocarbamate has been synthesized and subjected to single crystal structure determination which indicates that in the solid state the molecule exists as a centrosymmetric dimer in which the diethyl dithiocarbamate ligand can be considered as acting as a bridge (through its two sulfur atoms) with long Te—S bonds. Each tellurium atom also becomes six coordinated by weakly interacting with another sulfur atom of the dithiocarbamate ligand. The coordination environment around each tellurium is a very distorted octahedral constituted by two facial sets, one consisting of three carbon atoms and the other of three sulfur atoms. The IR spectrum of $Ph_3Te(S_2CNEt_2)$ exhibits two ν(Te—S) bands at 285 and 185 cm^{-1}. The complete dissociation of $Ph_3Te(S_2CNEt_2)$ into Ph_3Te^+ and $Et_2NCS_2^-$ has not been evidenced even in DMF and DMSO at ~1 mM concentration level.

Key words: Triphenyltellurium(IV) diethyldithiocarbamate; crystal structure; dithiocarbamate; tellurium.

INTRODUCTION

The crystal structures of tellurium(II and IV)-sulfur donor complexes have attracted several research groups in the recent past.[1–4] We have observed recently that the crystal structures of triphenyltellurium(IV) alkylxanthates depend on the nature of the alkyl groups.[5,6] For bulky groups like *iso*-butyl, discrete monomeric units having a chelated xanthate ligand were observed in the crystals. A dimeric structure having bridging xanthate ligands[5] was observed for $Ph_3Te(S_2COMe)$. The structure[6] of $Ph_3Te(S_2COEt)$ has been found to be intermediate between these two extremes as the xanthate group chelates as well as makes a long Te—S bond with the tellurium atom of a neighbouring molecule. These results encouraged us to study the effect of the alkyl group on the crystal structures of triphenyltellurium(IV) dialkyldithiocarbamates. Drake and Wong[2] have reported the crystal structure of $Ph_3Te(S_2CN(i\text{-}Pr)_2)$. The molecule has been described as a dimer with both tellurium atoms as five coordinated. Thus we thought worthwhile to synthesize $Ph_3Te(S_2CNEt_2)$ and study its crystal structure. This molecule has also been found to be dimeric but both tellurium atoms become six coordinated due to the formation of long secondary Te—S bonds. These results are reported in the present paper.

RESULTS AND DISCUSSION

Crystal Structure of $Ph_3Te(S_2CNEt_2)$

The molecular structure of a single molecule of triphenyltellurium(IV) diethyldithiocarbamate and the numbering scheme are shown in Figure 1 (Te—S(2) bond not shown for clarity). The selected bond lengths and bond angles are given in Table III with e.s.d's in parentheses. The phenyl rings in the structure appear normal (bond lengths 1.350(9)–1.415(14) Å, bond angles 118.6(6)–121.8(6)°). Details are available as supplementary material. The structure shown in Figure 1 does not give any indication of the dithiocarbamate bridge. The C(1), C(7), C(13) and S(1) together with the lone electron pair appear to provide a distorted trigonal bipyramidal environment around the tellurium atom (Figure 1). However, the Te—S(1) bond in $Ph_3Te(S_2CNEt_2)$ is considerably longer 3.017(2) Å than a Te—S single bond.[2] This suggests that the dithiocarbamate group as a whole provides the link[2] to the next molecule. Thus dithiocarbamate group acts as a bridge between tellurium atoms of neighbouring molecules and $Ph_3Te(S_2CNEt_2)$ is more correctly considered as a dimer as shown in Figure 2 (phenyl rings are omitted for clarity).

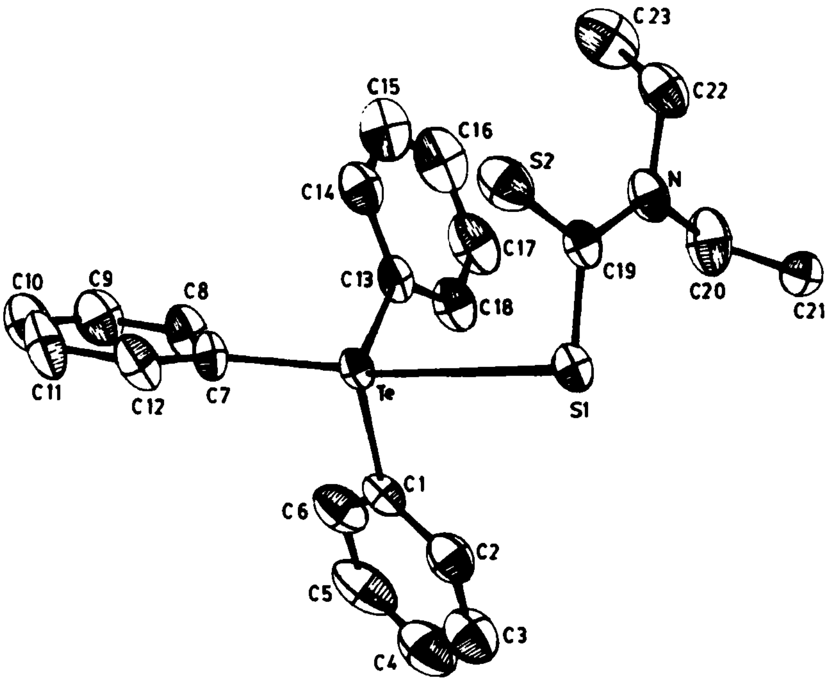

FIGURE 1 Molecular structure of $Ph_3Te(S_2CNEt_2)$ with atom labelling.

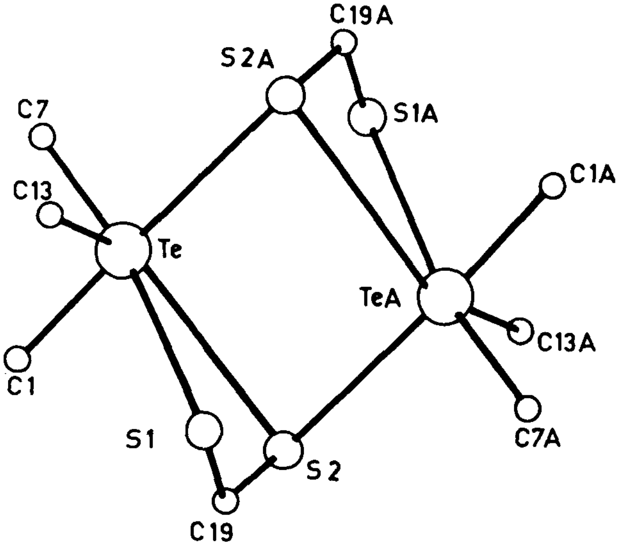

FIGURE 2 Core atoms in bridging unit of $Ph_3Te(S_2CNEt_2)$.

An interesting observation is that Te—S(2) is 3.607(4) Å and little shorter than the sum of vander Waal's radii 3.86 Å[7] for Te and S. This long Te—S bond increases the coordination number of tellurium to six and the arrangement of C(1), C(7), C(13), S(1), S(2), S(2A) around tellurium appears to form an octahedron distorted partly by the lone electron pair on tellurium. The structure[2] of $Ph_3Te(S_2CN(i\text{-}Pr)_2)$ does not exhibit such additional long Te—S interactions. This indicates that the structure of triphenyltellurium(IV) dialkyldithiocarbamates is also affected by the size of the alkyl group. The C(1) C(7) and C(13) carbon atoms form one facial set of the coordination octahedron and S(1), S(2) and S2(A) another. The lone pair appears to be located between the three Te—S bonds. In the structure of an analogous xanthate[7] $Ph_3Te(S_2COEt)$ each sulfur ligand chelates asymmetrically with tellurium as well as forms a bridge to the tellurium atom of another molecule through long Te—S bonds. Such chelation also occurs in the structure of $Ph_3Te(S_2CNEt_2)$. It was not noticed in the structure[2] of $Ph_3Te(S_2CN(i\text{-}Pr)_2)$ probably due to steric influence of the larger *iso*-propyl group. Thus the weak Te—S bonds are sterically sensitive as observed for triphenyltellurium(IV) xanthates.[5] The shortest Te—S bond length of $Ph_3Te(S_2CNEt_2)$ is also longer than single covalent Te—S bond length,[8] supporting its weak nature. However, the shortest Te—S bond length in $Ph_3Te(S_2CNEt_2)$ is somewhat shorter than those of triphenyltellurium(IV) xanthates.[9] This may be attributed to the greater ligand strength of dithiocarbamates in comparison to xanthates.[9] One of the three C—N bonds of the dithiocarbamate ligand (N—C(19)) is much shorter than the other two such bonds. This is because the mesomeric shift of electron density from N towards S imparts partial double bond character to this C—N bond. The *trans*-influence of the Te—C bonds on the Te—S bond is reflected by the weak Te—S bonds in the present structure. The distortion in the arrangement of ligands around Te in its six coordination in the present structure is probably caused by this *trans* influence and by the presence of the lone pair of electrons on tellurium atom.

Solution Behaviour and IR Spectra

The molecular weight of $Ph_3Te(S_2CNEt_2)$ in chloroform was found in the range 406–495 at concentration levels 7.35 to 29.80 mg kg^{-1}. On comparing it with the calculated value of 506.6, significant association between dithiocarbamate and Ph_3Te^+ ion may be inferred. The ΔM values of $Ph_3Te(S_2CNEt_2)$ in DMSO and DMF at 25°C and concentration ~1 mM were found to be 26 and 48 ohm^{-1} cm^2 mol^{-1}. Both are less than the expected values (30 and 80 ohm^{-1} cm^2 mol^{-1}, respectively) for a 1:1 electrolyte. This suggests that even in DMSO/DMF the dissociation of $Ph_3Te(S_2CNEt_2)$ into Ph_3Te^+ and $Et_2NCS_2^-$ is only partial. It is probable that this is due to the Te—S interactions depicted by the crystal structure.

The Far-IR spectrum of $Ph_3Te(S_2CNEt_2)$ exhibits two bands at 285 and 185 cm^{-1} which may be assigned to the Te—S interactions. The second band is somewhat weak in nature. It appears that two Te—S bonds having bond lengths 3.294(2) and 3.017(2) Å exhibit overlapping IR absorptions, as the band at 285 cm^{-1} is somewhat broad.

TABLE I

Crystal data, details of intensity measurement and refinement of $Ph_3Te(S_2CNEt_2)$

Formula	$C_{26}II_{25}NS_2Te$
Molecular weight	507.16
Crystal dimensions (mm^3)	1.50 × 0.08 × 0.07
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.635 (2)
b (Å)	10.502 (4)
c (Å)	12.901 (2)
α (°)	68.81 (2)
β (°)	77.32 (1)
γ (°)	65.98 (2)
V ($Å^3$)	1107.7 (6)
Z	2
Dc	1.1698
F(000)	254
2θ (°)	1–140
λ (Cu-K_α) (Å)	1.5418
μ (cm^{-1})	209.200
Electron density in final difference map ($e^-/Å^3$)	
Maximum	0.8077
Minimum	−1.2972
Measured reflections	5081
Unique reflections	4021
Agreement between equivalent reflections (R_{merge})	0.025
Reflections used in refinement [$I > 3\sigma(I)$]	3940
Weighting Scheme	Unit weights
R	0.0414
R_w	0.0414

TABLE II

Final atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms (estimated standard deviations are given in parentheses) of $Ph_3Te(S_2CNEt_2)$

Atom	*X/a*	*Y/b*	*Z/c*	U_{eq} (Å^2)
Te	1.0340 (1)	0.3586 (0)	0.1674 (0)	0.0107 (1)
S1	1.1938 (1)	0.2592 (1)	−0.0581 (1)	0.0149 (8)
S2	1.2803 (1)	0.5124 (1)	−0.0880 (1)	0.0134 (6)
N	1.4623 (5)	0.2793 (5)	−0.1491 (3)	0.0174 (23)
C1	0.8985 (5)	0.4089 (5)	0.3119 (3)	0.0149 (23)
C2	0.7864 (6)	0.3572 (7)	0.3662 (5)	0.0204 (30)
C3	0.7021 (8)	0.3967 (9)	0.4598 (5)	0.0275 (39)
C4	0.7282 (8)	0.4939 (8)	0.4933 (5)	0.0331 (38)
C5	0.8379 (8)	0.5495 (8)	0.4384 (6)	0.0301 (39)
C6	0.9251 (6)	0.5087 (6)	0.3454 (5)	0.0178 (30)
C7	1.2379 (5)	0.2661 (6)	0.2563 (4)	0.0144 (26)
C8	1.3709 (7)	0.2752 (7)	0.1928 (5)	0.0167 (32)
C9	1.5014 (7)	0.2311 (8)	0.2442 (7)	0.0232 (42)
C10	1.4981 (8)	0.1793 (7)	0.3589 (6)	0.0176 (40)
C11	1.3667 (8)	0.1710 (7)	0.4219 (5)	0.0213 (34)
C12	1.2386 (6)	0.2142 (7)	0.3704 (4)	0.0209 (30)
C13	1.0038 (6)	0.1547 (5)	0.2051 (4)	0.0093 (24)
C14	0.9381 (6)	0.1394 (6)	0.1271 (5)	0.0146 (29)
C15	0.9118 (8)	0.0103 (8)	0.1501 (6)	0.0173 (40)
C16	0.9512 (9)	−0.0993 (7)	0.2468 (7)	0.0123 (46)
C17	1.0181 (10)	−0.0856 (8)	0.3228 (7)	0.0125 (48)
C18	1.0470 (8)	0.0435 (7)	0.3025 (5)	0.0153 (36)
C19	1.3240 (5)	0.3444 (5)	−0.1026 (4)	0.0141 (24)
C20	1.5766 (7)	0.3484 (8)	−0.1927 (5)	0.0251 (36)
C21	1.6810 (9)	0.3127 (10)	−0.1072 (7)	0.0426 (50)
C22	1.5105 (7)	0.1321 (6)	−0.1619 (5)	0.0168 (32)
C23	1.4822 (10)	0.1410 (8)	−0.2744 (6)	0.0223 (44)

EXPERIMENTAL

Published methods were used to synthesize Ph_3TeCl[10] and sodium diethyldithiocarbamate.[11] The C, H and N analyses were caried out with a Perkin Elmer elemental analyzer 240C. Tellurium was determined by a standard method.[12] The ^1H NMR were recorded on a JEOL FX-100 FT-NMR spectrometer at 99.55 Hz. The FAR-IR spectra in polyethylene were recorded on a Perkin Elmer 1700X FT-FAR IR spectrometer. The conductivities in DMSO and DMF were measured with a Pye conductivity bridge. The molecular weights in $CHCl_3$ were determined with a Knauer Vapour Pressure Osmometer.

Synthesis of $Ph_3Te(S_2CNEt_2)$.[13] Triphenyltellurium(IV) chloride (0.5 g, 1.25 mmol) dissolved in water (25 cm^3) was stirred with sodium diethyldithiocarbamate (0.22 g, 1.25 mmol) solution made in 25 cm^3 water for 0.5 h at 60–70°C. The yellow precipitate was filtered, washed with hot water, dried and recrystallized from acetonitrile, yield 72%; m.p. 158–160°C.

Analyses: Found C, 53.81; H, 4.72; N, 2.55; Te 24.50%. Calcd. for $C_{20}H_{25}NS_2Te$: C, 54.48; H, 4.93; N, 2.76; Te, 25.19%. NMR (^1H, $CDCl_3$, 25°C); δ, 1.16 (t, 6H, CH_3), 3.96 (q, 4H, CH_2), 7.27–7.78 (m, 15H, ArH).

Crystal structure of $Ph_3Te(S_2CNEt_2)$. Single crystals of $Ph_3Te(S_2CNEt_2)$ suitable for X-ray work were grown from acetonitrile. X-ray diffraction data were collected on an Enraf Nonius CAD-4 diffractometer in the ω-2θ scan mode with $1 < 2\theta < 140$; h, $0 \rightarrow 11$, k, $0 \rightarrow 12$, 1, $0 \rightarrow 15$ and CuK_α radiation. Data were corrected[14] for Lorentz polarization and absorption effect. A semiempirical ψ-scan technique[14] was used to correct for absorption (the maximum and minimum correction factors were 0.85 and 0.35, respectively). The structure was solved by direct methods using SHELX 86[15] and a full matrix least square refinement procedure on $|F|$ for non-hydrogen atoms with anisotropic thermal parameters. Using SHELX 76[16] hydrogen atoms located from a difference Fourier map, were given the isotropic thermal

TABLE III

Selected bond lengths (Å) and bond angles (°) of $Ph_3Te(S_2CN(C_2H_5)_2)$

Bond Lengths (Å)

Te	—	S(1)	3.017 (2)
Te	—	S(2)	3.607 (4)
Te	—	S(1A)	3.865 (2)
Te	—	S(2A)	3.294 (2)
Te	—	C(1)	2.130 (5)
Te	—	C(7)	2.178 (5)
Te	—	C(13)	2.145 (5)
C(19)	—	N	1.344 (6)
C(19)	—	S(1)	1.711 (5)
C(19)	—	S(2)	1.711 (5)
C(20)	—	N	1.463 (10)
C(20)	—	N	1.483 (9)

Bond Angles (°)

C(1)	—	Te	—	C(7)	89.6 (2)
C(1)	—	Te	—	C(13)	94.7 (2)
C(7)	—	Te	—	C(13)	95.5 (2)
S(1)	—	Te	—	S(2)	48.3 (4)
S(1)	—	Te	—	C(7)	169.2 (2)
S(1)	—	Te	—	C(13)	77.1 (2)
S(1)	—	Te	—	C(1)	98.1 (2)
S(2)	—	Te	—	C(1)	85.4 (2)
S(2)	—	Te	—	C(7)	140.6 (2)
S(2)	—	Te	—	C(13)	124.7 (2)
S(2A)	—	Te	—	S(1)	90.6 (3)
S(2A)	—	Te	—	C(13)	91.9 (2)
S(2A)	—	Te	—	C(1)	174.6 (1)
S(2A)	—	Te	—	C(7)	77.6 (3)
S(1)	—	C(19)	—	S(2)	120.6 (4)
S(1)	—	C(19)	—	N	120.1 (5)
S(2)	—	C(19)	—	N	119.3 (5)

parameters of the atoms to which they are attached and were included in the structure factor calculation but not refined. The literature values of the atomic scattering factors of hydrogen[17] and non-hydrogen atoms[18] were used. All calculations were performed on a MicroVAX II system. Experimental data of the crystal and refinement conditions are given in Table I. Final coordinates are listed in Table II. All reflections were given unit weights during the refinement.

ACKNOWLEDGEMENT

The authors thank CSIR (India) for financial support and for the award of a Research Associateship to one of them (VS).

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