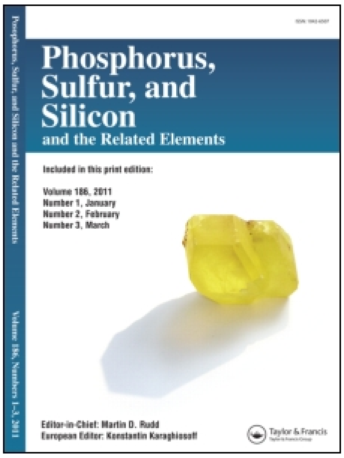

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Secondary Bonding, CH...O Hydrogen Bonding Assisted Supramolecular Associations and Charge Transfer (CT) Complexes of Organotelluriums and their Nonlinear Optical Properties

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Secondary Bonding, C—H· · ·O Hydrogen Bonding Assisted Supramolecular Associations and Charge Transfer (CT) Complexes of Organotelluriums and their Nonlinear Optical Properties

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A library of supramolecular assemblies of acyclic- and cyclic organotelluriums assisted by intermolecular Te· · ·X (X = Cl, Br, I, O, S) secondary bonds has been synthesized and X-ray characterized. In each case the immediate coordination geometry around the central Te atom is pseudotrigonal bipyramidal in which two methylene carbon atoms (attached to Te) in cyclic organotelluriums and methyl carbon atoms in acyclic organotelluriums and the stereochemically active electron lone pair occupy equatorial positions whereas the axial positions are occupied by halogen, oxygen or sulphur. They exists either as (a) ordered oligomers (trimeric, tetrameric, octameric aggregates) (b) cross linked chains, (c) zig-zag –2 dimensional ribbons and stairs, and (d) 3-dimensional supramolecular networks. It is observed that the supramolecular associations assisted by Te· · ·O and Te· · ·S secondary bonds are modified whereas those assisted by Te· · ·halogen remain more or less the same vis-à-vis the supramolecular associations present in their precursors in the solid state. The first detection of C—H· · ·O hydrogen bonds in organotellurium compounds has been done and their use in the synthesis of tellurium essential and ligand essential supramolecular assemblies is demonstrated. Tetraorganotelluroxanes obtained by easy and efficient routes represent the examples of cooperative participation of intermolecular and intramolecular Te· · ·O secondary bonds and C—H· · ·O hydrogen bonds. Hypervalent Te—I (formed through n → σ orbital interactions) bonds in cyclic telluranes act as potential synthons for the formation of CT complexes possessing unusual structures. The utility of organotelluriums in the serendipitous synthesis of the first triphenyl methyl phosphonium salts of* $[C_4H_8TeI_4]^{2-}$ *and* $[TeI_6]^{2-}$ *anions is shown. The second harmonic generation (SHG) efficiency of some of these new supramolecular assemblies of organotelluriums indicates that the presence of C—H· · ·O hydrogen bonds enhances their non linear optical (NLO) properties.*

Keywords Charge-transfer complexes; cyclic telluranes; hydrogen bonds; secondary bonds; second harmonic generation efficiency; supramolecular associations

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INTRODUCTION

The self-assembly by means of specific noncovalent interactions resulting in supramolecular structures by complexation chemistry utilizing metal ions and suitable ligands is one approach to new structures with unusual, useful and interesting properties.[1–6] Tellurium possesses inherent tendency to form Te···X (X = Cl, Br, I, O, S) noncovalent interactions termed as secondary bonds by Alcock[7] and C—Te···X as 3c—4e bonds by King et al.[8] and they are common place in organotellurium chemistry. However the use of Te···X secondary bonds in the synthesis of supramolecular associations in organotellurium complexes is only of recent origin. We, in this article, present our investigations during the last five years on organotellurium complexes bearing (i) supramolecular associations in acyclic and cyclic telluranes derivatives based on Te···X and C—H···O hydrogen bonds, (ii) synthesis of tetraoragnotelluroxanes through easy and efficient routes and their supramolecular associations through cooperative participation of Te···O and C—H···O hydrogen bonds, (iii) utility of hypervalent Te—I bond (formed through n → σ^* interaction) of cyclic telluranes to form charge transfer (**CT**) complexes with unusual structures, (iv) the first novel Te—C bond cleaved products from the reactions of cyclic telluranes with the salts of dithiocarbamates, (v) serendipitous synthesis of the first triphenyl methyl phosphonium salts of $[C_4H_8TeI_4]^{2-}$ and $[TeI_6]^{2-}$ anions defying VSEPR rules, and (vi) SHG efficiency (NLO properties) of select supramolecular associations of organotelluriums.

Supramolecular associations of organotelluriums [cyclic telluranes: 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene($C_4H_8TeI_2$); 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane($C_5H_{10}TeI_2$); 1,3-dihydro-2λ^4–benzo tellurole-2,2-diyl diiodide($C_8H_8TeI_2$)] and their derivatives formed through Te···I, Te···Cl, Te···Br, Te···O and Te···S secondary bonds and C—H···O hydrogen bonds have been synthesised and characterised through single crystal X-ray diffraction studies.

(a) Te···X (X = Cl, Br, I) Secondary Bonds Based Supramolecular Assemblies

Te···I secondary bonds induced (i) ribbons (Figure 1), (ii) ordered oligomers (trimeric molecular aggregates) (Figure 2), and (iii) three dimensional polymeric (Figure 3) supramolecular associations of cyclic telluranes [$C_4H_8TeI_2$, $C_5H_{10}TeI_2$, $C_8H_8TeI_2$] have been obtained. Te···I bond distances [3.697, 3.738, 3.796, 3.999 Å] (**1**); [3.900, 3.870 Å] (**2**); and [3.660, 3.670 Å] (**3**) are shorter than the sum of vander Waals radii (4.35 Å) and longer than the sum of covalent radii (2.70 Å) of Te and

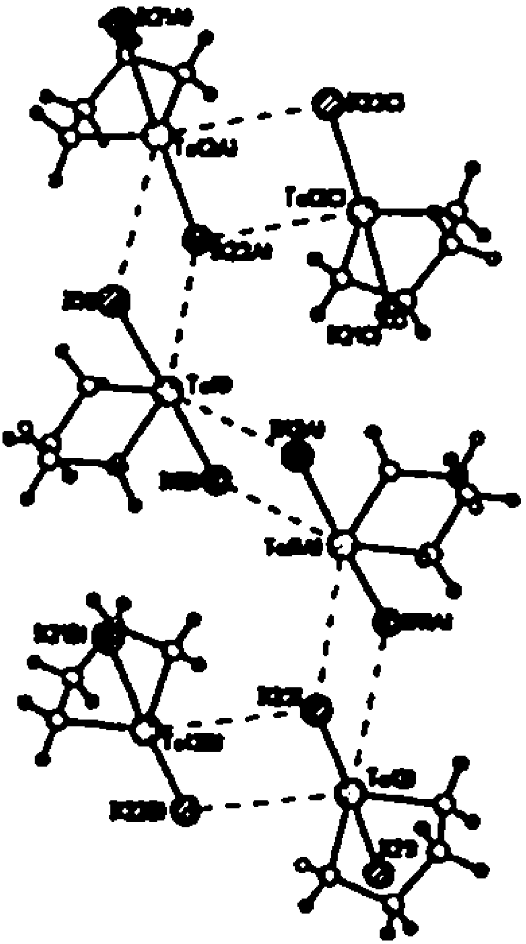

FIGURE 1 Molecular structure of $C_4H_8TeI_2$.

I and therefore correspond to secondary bonds. The primary geometry around each tellurium atom is distorted trigonal bipyramidal with stereochemically active electron lone pair. The study also accounts for the first X-ray structural study of telluracyclohexane ring which exists in chair conformation. The part of the ring is flattened and a part is considerably puckered. The effect of change of I^- with Cl^- and Br^- in these supramolecular associations has been studied and it is observed that with these changes there is no change in the conformation of the heterocycle and also the nature of supramolecular associations remains the same.[9]

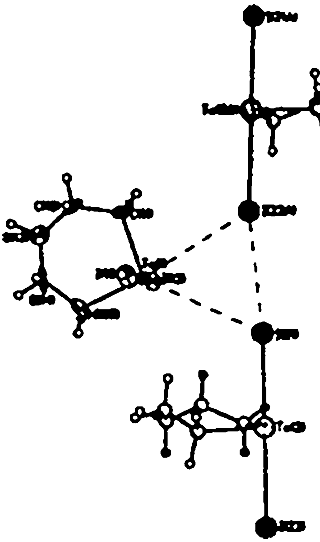

FIGURE 2 Molecular structure of $C_5H_{10}TeI_2$.

When these supramolecular associations are compared with the supramolecular associations present in the simplest acyclic telluranes [α-Me_2TeCl_2 (*zig-zag* chains), α-Me_2TeBr_2 (tetra nuclear species), α-Me_2TeI_2(corrugated sheets)] it is evident that supra-molecular associations of cyclic telluranes are drastically changed.[10]

(b) Te···O Secondary Bonds Based Supramolecular Assemblies

The transformation of supramolecular associations **1–3** into Te···O directed supramolecular associations [$C_4H_8Te(OCOC_6H_5)_2$, $C_5H_{10}Te(OCOC_6H_5)_2$, $C_8H_8Te(OCOC_6H_5)_2$] leads to the change of (i) the zig-zag ribbon based supramolecular associations in **1** into polymeric zig-zag chain based supramolecular associations, (ii) trimeric supramolecular aggregates in **2** into polymeric (zig-zag chains) supramolecular associations, and (iii) the polymeric supramolecular association in **3** into tetrameric (stair like) supramolecular association (Figure 4) where primary geometry (distorted TBP) is retained at each tellurium atom while the coordination around tellurium varies. The Te···O secondary bond distances are 3.083 Å(1), 3.307 Å(2), and 3.376(3).[11,12]

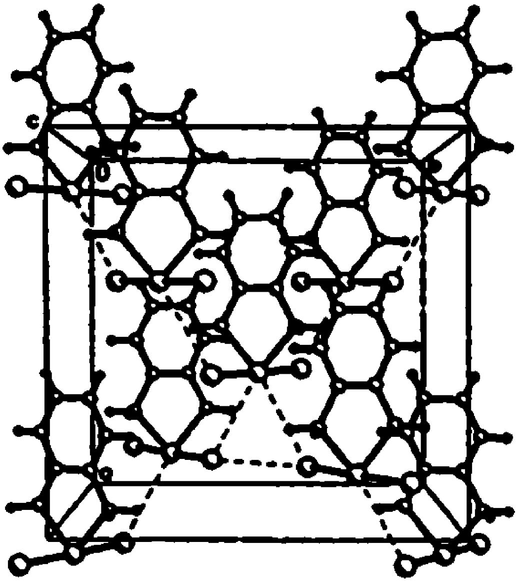

FIGURE 3 Molecular structure of $C_4H_8TeI_2$.

(c) Te···S Secondary Bonds Based Supramolecular Assemblies

Te···S (3.583, 3.684 Å) secondary bonds based supramolecular assemblies of organotellurium iodo di-thiocarbamates [C_4H_8TeIX (X = morpholine dithiocarbamate, piperidine dithiocarbamate) exist as

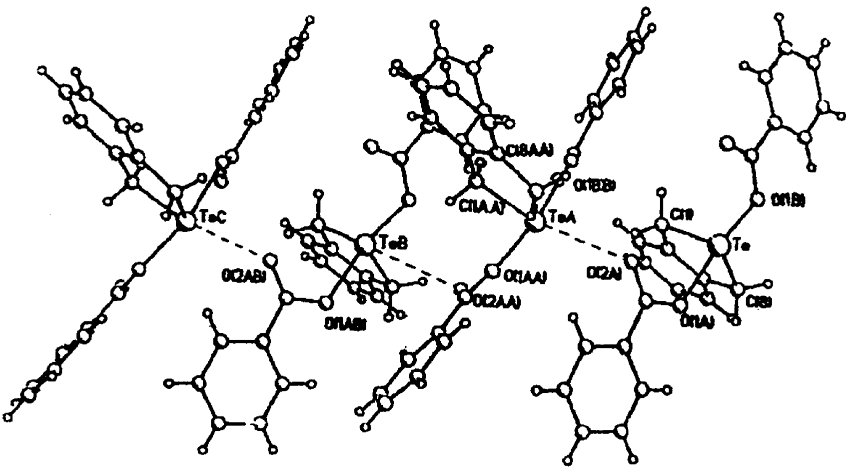

FIGURE 4 Molecular structure of $C_8H_8Te(OCOC_8H_5)_2$.

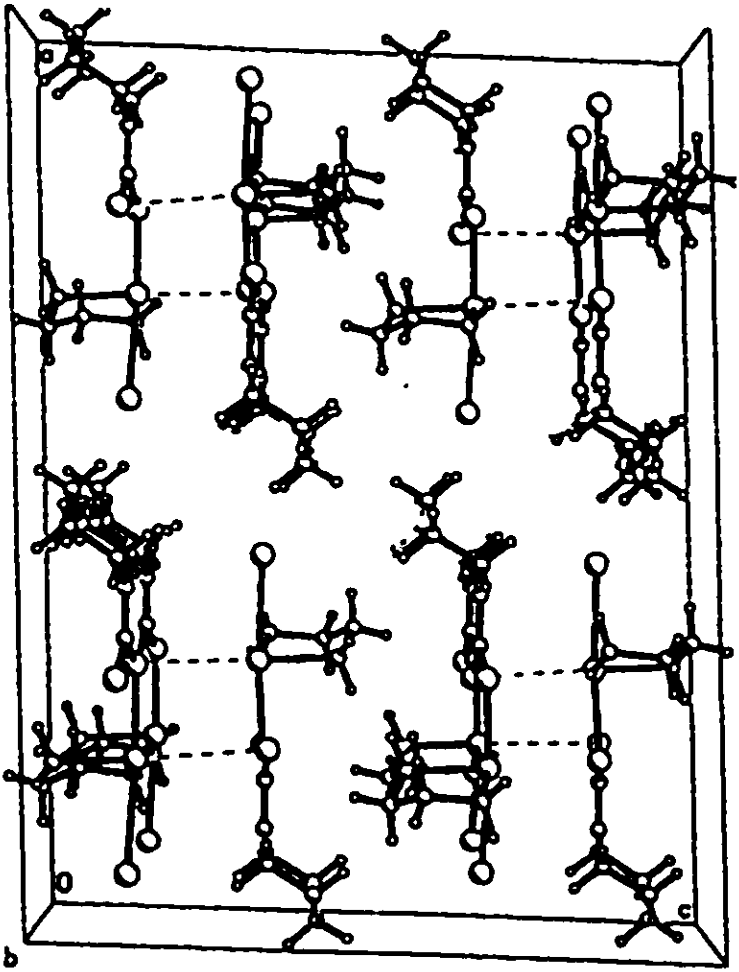

FIGURE 5 Crystal structure of $C_5H_{10}TeI(dtc)$.

dimers which self assemble to form ordered tetrameric oligomers (Figure 5) whereas trimeric molecular aggregates are present in case of $C_5H_{10}TeIX$ (X = diethyldithiocarbamate (dtc)). The supramolecular association of organotellurium xanthate [C_4H_8Te (isopropylxanthate)$_2$] exists as *zig-zag* ribbons.[13]

(d) The First Te—C Bond-Cleaved Products in the Reaction of Cyclic Telluranes with the Salts of Dithiocarbamates

The more interesting aspect of the reaction of (cyclic tellurane) $C_4H_8TeI_2$ with ammonium anilinedithiocarbamate is the formation of

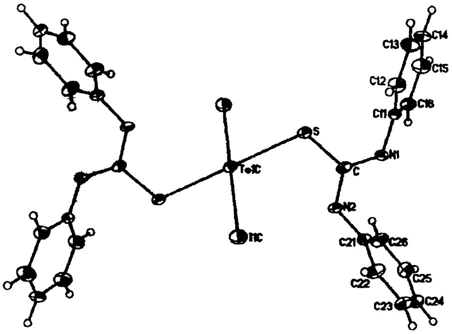

FIGURE 6 Molecular structure of $(^{-}C_{13}H_{12}N_2S)_2TeI_2$.

unusual product (Figure 7) consisting of two complete $[C_4H_8TeI_2]$ moieties and one molecule of $[(C_{13}H_{12}N_2S)_2TeI_2]$ (Figure 6) interlinked by Te···I (3.660, 3.884 Å) and CH···I interactions.

The first Te—C bond cleaved product Te(II) (piperidine dithiocarbamate)$_2$ (Figure 8), is obtained by the reaction of $C_8H_8TeI_2$ with ammonium piperidine dithiocarbamate which exists as a dimer.[13]

(e) C—H···O Hydrogen Based Supramolecular Assemblies

For the first time, C—H···O hydrogen bonds (FT-IR, solid state NMR, X-ray evidence) have been detected in organotelluriums. acyclic- and cyclic telluranes: $(CH_3)_2Te(OCOC_6H_5)_2$ (Figure 9), and $C_4H_8Te(OCO\text{-}4\text{-}NO_2C_6H_4)_2$, and $C_4H_8Te(OCOCH{=}CHC_6H_5)_2]$. These C—H···O hydrogen bonds act as crystal structure directors and through C(sp^3)H···O hydrogen bonds [C···O = 3.169, 3.318 Å ; H···O = 2.510, 2.618 Å, ∠C—H···O = 175.6,152.9°] (—CH group is of —CH_3 or —CH_2-group

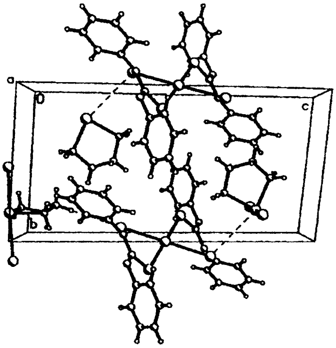

FIGURE 7 Crystal structure of **7**.

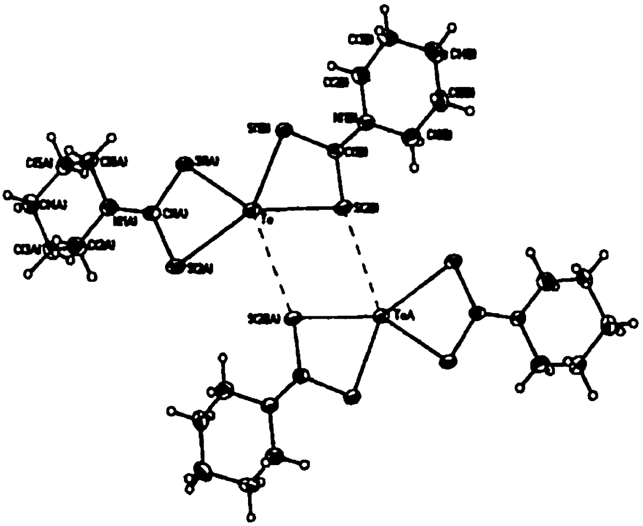

FIGURE 8 Crystal structure of Te (piperdine dithiocarbamate)$_2$.

attached to Te): (a) zig-zag chain or ring type supramolecular associations are formed while through C(sp^2)H$\cdots$O hydrogen bonds [C$\cdots$O = 3.297 Å; H$\cdots$O = 2.449 Å, $\angle$C—H$\cdots$O = 166.3°] (—CH group is of phenyl ring of the ligand) (b) only ring type supramolecular associations are obtained; the former are termed as (i) tellurium essential whereas latter

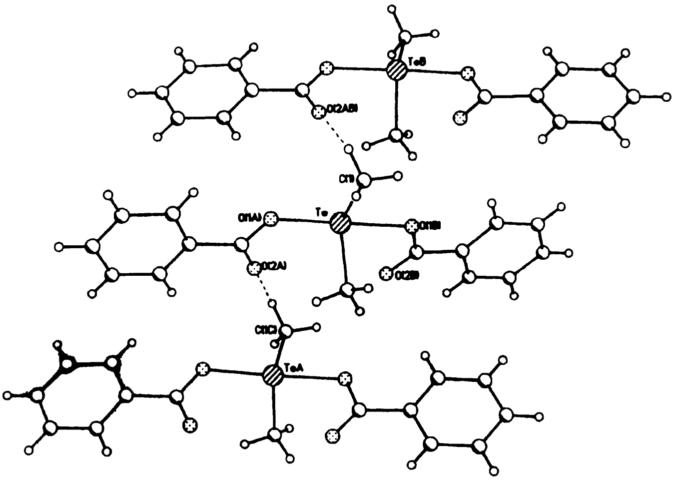

FIGURE 9 Crystal structure of (CH$_3$)$_2$Te(OCOC$_6$H$_5$)$_2$.

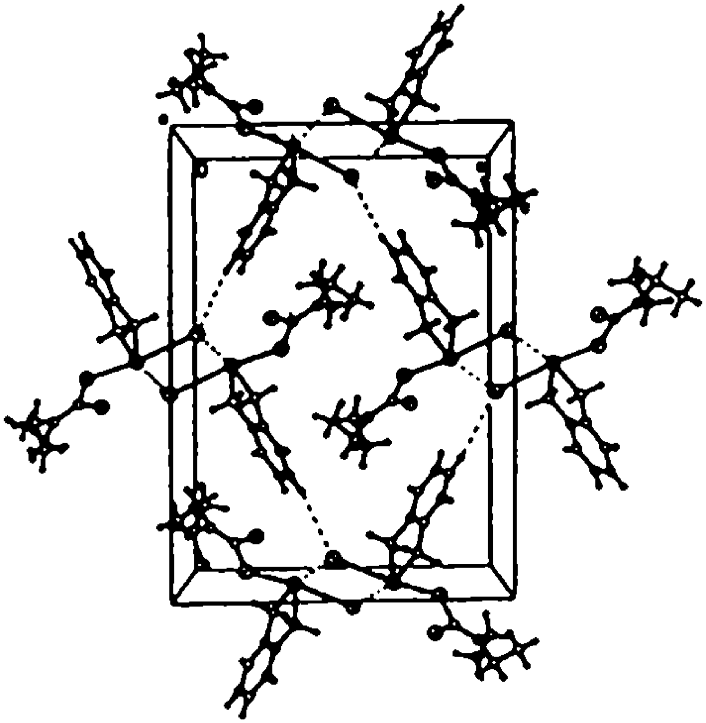

FIGURE 10 Crystal structure of **10**.

are termed as (ii) ligand essential supramolecular associations. Both type of supramolecular associations are of relatively smaller complexity than their precursors.[14]

(f) C—H· · ·I Hydrogen-Based Supramolecular Assemblies

The supramolecular assemblies based on organotellurium iodo dithiocarbamates exists as dimers formed through Te· · ·I secondary bonds and these dimers are joined through C—H· · ·I hydrogen bonds resulting in octanuclear complex **9** with large cavity. **9** is reacted with 1,10-phenanthroline to yield its adduct indicating the possibility of the use of metal-directed-self assembly to form host macrocycle capable of binding neutral substrates.

2. CT Complexes of Cyclic Telluranes Involving Hypervalent Te· · ·I Bonds

Use of hypervalent Te· · ·I bonds (formed through n → σ^* orbital interaction) has been demonstrated to form the first charge transfer (CT)

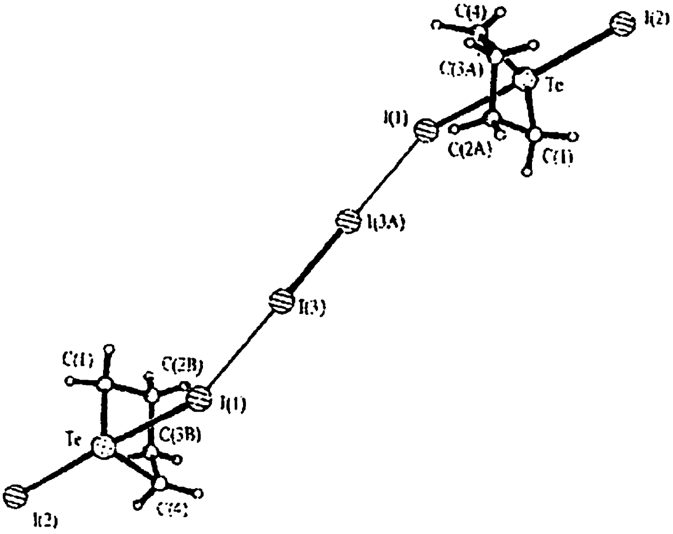

FIGURE 11 Molecular structure of $C_4H_8TeI_{21}I_2$.

complexes of organotelluriums containing cyclic telluranes with unusual structures (X-ray evidence).[15]

$C_4H_8TeI_2$ reacts with I_2/ICl to yield the **CT** complex $C_8H_{16}Te_2I_6$[$IC_4H_8TeI\cdots I—I\cdots ITeC_4H_8I$] (Figure 10); an unusual dinuclear species. The I(3)—I(3A) bond is lengthened and it is 2.77 Å. The $I(1)\cdots I(3A) = 3.39$ Å while the covalent radius of I—I is 2.67 Å. The elongation of I—I bond in **10** can be attributed to the donation of electron density from filled nonbonding orbitals of **10** to the antibonding LUMO of diiodine molecule which is an antibonding σ^* orbital lying along the main axis of diiiodine ($n \rightarrow \sigma^*$ orbital interaction). The overall extended structure **11** is hexanuclear species containing Te_2I_2 square (Figures 11 and 12). In **11** the weak [$C(sp^3)—H\cdots I$ contacts [$H—I = 3.21$ Å, $C—I = 4.16$ Å, $C—H = 0.97$ Å, and $\angle C—H\cdots I = 167.9°$] are also seen.

The UV/Vis spectrum of **10** in CH_2Cl_2 shows bands at 336 and 271 nm [cf. UV-Vis spectrum of $C_4H_8TeI_2$ in CH_2Cl_2 (330 and 270 nm)]. I_2 in CH_2Cl_2 absorbs at 501 nm. The absence of free I_2 in solution of the **CT** complex **10** appears to suggest that **10** remains intact in solution.

The reaction of another cyclic tellurane $C_5H_{10}TeI_2$ with I_2 yields $C_5H_{10}TeI_4$, possessing different structural motif than **10**. In $C_5H_{10}TeI_4$, the iodine molecules are on both sides bonded to iodine atom of hypervalent Te—I bond of $C_5H_{10}TeI_2$.

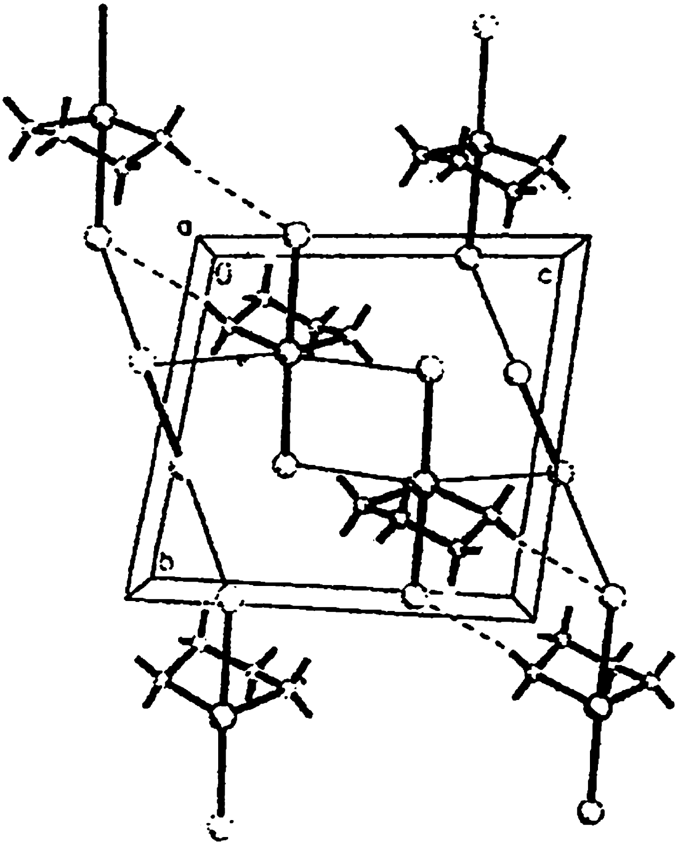

FIGURE 12 Packing diagram of $C_4H_8TeI_{21}I_2$.

3. Tetraorgano Telluroxanes (Supramolecular Associations Through Cooperative Participation of Te···O Secondary Bonds and C—H···O Hydrogen Bonds)

New tetraorgano telluroxanes have been synthesized through easy and efficient methods (by the reactions of $(CH_3)_2Te(OH)_2$, $C_4H_8Te(OH)_2$, $C_5H_{10}Te(OH)_2$ with 2,4,6-trinitrophenol) and are X-ray characterized (Figures 13 and 14). The supramolecular associations **12** are achieved through cooperative participation of intermolecular (Te···O = 3.136 Å) and intramolecular (Te···O = 3.059 Å) secondary bonds and C—H···O hydrogen bonds (C—H = 0.99 Å, H···O = 2.54 Å, C···O = 3.453 Å, ∠C—H···O = 153.7°).[16]

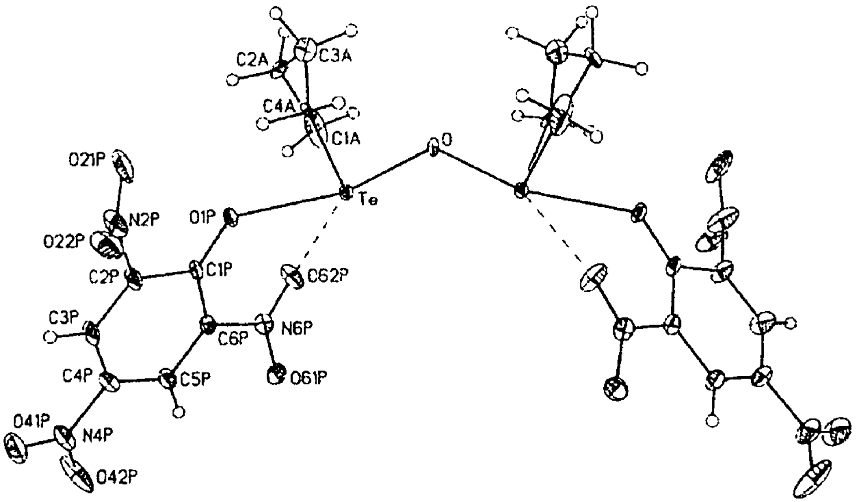

FIGURE 13 Molecular structure $[\{C_4H_8TeOC_6H_2(NO_2)_3{}^{-2,4,6}\}_2O]$.

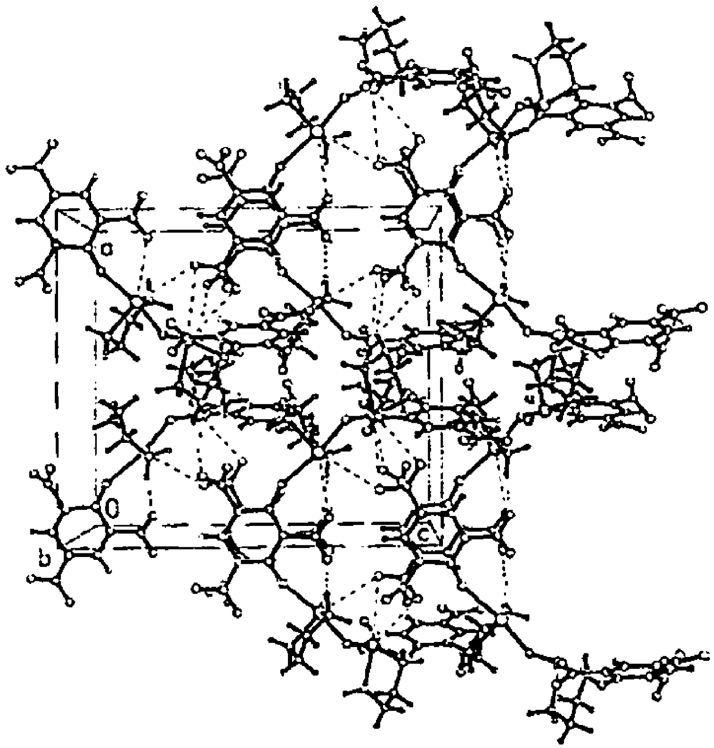

FIGURE 14 Packing diagram of $[\{C_4H_8TeOC_6H_2(NO_2)_3{}^{-2,4,6}\}_2O]$.

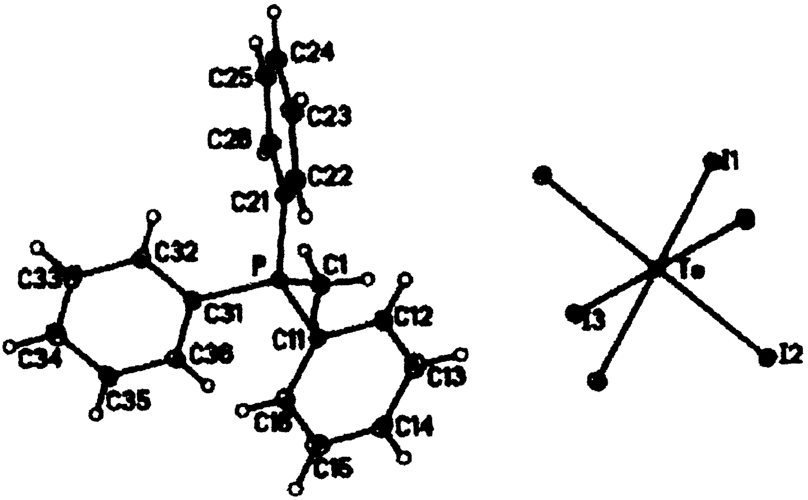

FIGURE 15 Molecular structure of **13**.

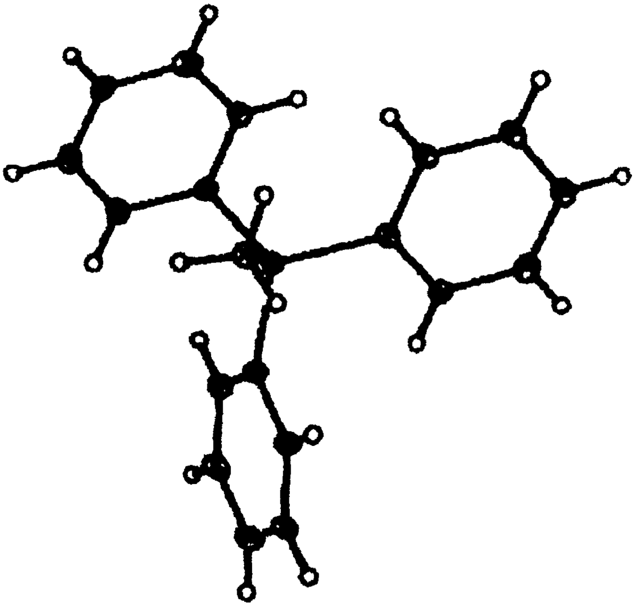

FIGURE 16 Molecular structure of [Ph$_3$MeP]$^+$.

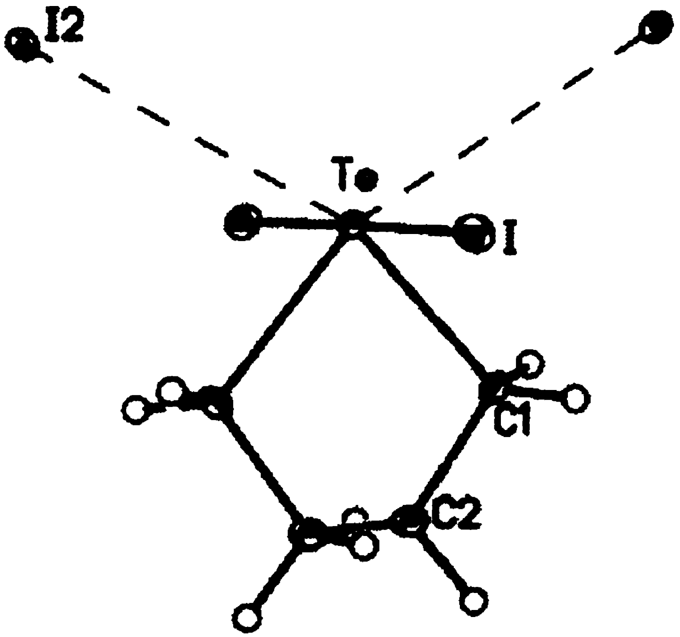

FIGURE 17 Molecular structure of **14**.

4. Serendipitous Synthesis of Triphenylmethyl Phosphonium Salts Containing $[C_4H_8TeI_4]^{2-}$ and $[TeI_6]^{2-}$ Anions

Utility of telluranes in the oxidation of phosphines has been observed. For example PPh_3 reacts with $C_4H_8TeI_2$ to form $[Ph_3MeP]_2^{2+}TeI_6^{2-}$ **13.** Coincidently **13** is also the first triphenyl methyl phosphonium salt containing discrete TeI_6^{2-} regular octahedron which contains stereochemically inactive electron-lone pair (such examples are rare in organotellurium chemistry) and thus defies conventional VSEPR rules.[15]

5. Synthesis of organotellurium dianion

Utility of telluranes in the synthesis of hitherto unknown organotellurium dianion containing cyclic telluranes **14** has been demonstrated.[15]

6. SHG Efficiency

Preliminary measurements have indicated that the supramolecular associations containing C—H···O hydrogen bonds exhibit weak SHG efficiency.

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