

Bis(2,6-dimethoxyphenyl)tellurium dihalides (Cl, Br or I) and dithiocyanate: crystal structure and temperature-dependent NMR spectra

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Tris(2,6-dimethoxyphenyl)telluronium chloride hydrate, $[R_3Te]Cl \cdot nH_2O$ **1a** [$R = 2,6-(MeO)_2C_6H_3$, $n = 2-2.5$] was prepared by the reaction of RLi and $TeCl_4$. It decomposed in hot 0.1 M hydrochloric acid to give R_2TeCl_2 **3a**, exclusively, from which R_2TeX_2 ($X = Br$ **3b**, I **3c** or SCN **3d**) were derived by halogen exchange. The X-ray crystallographic analyses of **3a-3d** showed that these compounds have a twofold axis (except for **3d**) with essentially pseudo-trigonal bipyramidal co-ordination with two R groups and a lone pair of electrons occupying the equatorial sites and two halogen atoms the apical sites. The thiocyanate groups in **3d** bind to the tellurium atom *via* sulfur. No intermolecular $Te \cdots X$ secondary bond was observed for **3a-3d**. The $Te-C$ bond distances of **3a-3c** [2.09 ± 0.01 Å] are somewhat shorter than those reported for phenyl derivatives, and those of **3d** [2.042(3) and 2.073(2) Å] are the shortest ever reported. The $C-Te-C$ bond angle is much larger [$107.6(2)-104.37(9)^\circ$] than those reported. The $X-Te-X$ bond angles are very close to 180° . The $Te \cdots O$ distances of **3a-3d** [2.880–3.323 Å] are significantly shorter than the sum of the O and Te van der Waals radii [3.60 Å]. The 1H NMR spectra of **3a-3c** were halogen-, solvent-, and temperature-dependent showing that the rotation of $R-Te$ bonds was restricted due to the barrier between R groups and halogen atoms. The activation energies ΔG^\ddagger decreased in the order **3a** (90 kJ mol^{-1} in $DMSO-d_6$) $>$ **3b** (80 kJ mol^{-1} in $DMSO-d_6$) $>$ **3d** ($\geq 65 \text{ kJ mol}^{-1}$ in $CDCl_3$) $>$ **3c** (60 kJ mol^{-1} in $CDCl_3$) \geq **3d** (59 kJ mol^{-1} in CD_3CN).

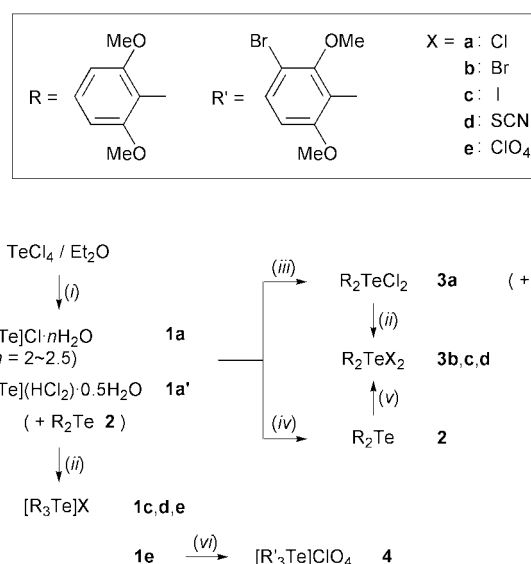
Owing to the electronic and positional effects of *ortho*-methoxy groups, 2,6-dimethoxyphenyl (R) derivatives often exhibit unusual properties. As a part of our systematic investigation on the chemistry of such derivatives of a variety of elements,¹⁻⁵ we have recently reported the preparations and some basic properties of 2,6-dimethoxyphenyl derivatives of Group 16 elements, such as R_2E and their oxides [$E = S, Se$ or Te].¹ We report here the preparations and properties of tris(2,6-dimethoxyphenyl)telluronium salts, $[R_3Te]X$, and bis(2,6-dimethoxyphenyl)tellurium dihalides, R_2TeX_2 (see Scheme 1), together with the crystal structures and the temperature-dependent 1H NMR spectra of R_2TeX_2 .

Results and discussion

Preparation of tris(2,6-dimethoxyphenyl)telluronium salts and bis(2,6-dimethoxyphenyl)tellurium dihalides

The reaction of an excess of 2,6-dimethoxyphenyllithium with $TeCl_4$ gave a tris(2,6-dimethoxyphenyl)telluronium derivative. It could be extracted into water, from which salts such as $[R_3Te]Cl \cdot nH_2O$ **1a** ($n = 2-2.5$) and $[R_3Te][HCl_2] \cdot 0.5 H_2O$ **1a'** were obtained as crystals depending on the method of isolation. The amount of water was estimated from the elemental analyses. From the organic layer, a small amount of bis(2,6-dimethoxyphenyl) telluride, R_2Te **2**,¹ was obtained. Anion exchanges of **1a** or **1a'** in water easily occurred to give $[R_3Te]X$ [$X = I$ **1c**, SCN (monohydrate) **1d**, or ClO_4 **1e**], which were less soluble in water than **1a**.

When compound **1a** or **1a'** was heated in 0.1 M hydrochloric acid, it easily decomposed to give bis(2,6-dimethoxyphenyl)tellurium dichloride, R_2TeCl_2 **3a**, together with 1,3-dimethoxybenzene, a product expected to be formed by protonolysis at the *ipso*-carbon of an R group. Compound **3a** was identical with that obtained by reaction of the oxide $R_2TeO \cdot (0.67)H_2O$ ¹ with



Scheme 1 (i) RLi(excess)– Et_2O ; (ii) $+X^-$ –water; (iii) in aq. HCl, $80^\circ C$, 20 h; (iv) $+NaBH_4$ –water; (v) $+Br_2$ or I_2 , $CHCl_3$; (vi) $+NBS$ –acetone.

hydrochloric acid. When **1a'** was treated in D_2O containing a catalytic amount of hydrochloric acid, the 1H NMR spectrum of the product **3a** showed a decrease in intensity of the 3,5-proton resonance and appearance of a new doublet for the 4-proton, indicating the presence of H–D exchange of 3,5-protons during the decomposition from **1a'** to **3a**.

Compound **3a** was soluble in water and reacted with sodium bromide, potassium iodide, and sodium thiocyanate to give R_2TeX_2 **3b-3d** ($X = Br, I$ or SCN), which were less soluble in water than **3a**.

Table 1 ^1H NMR spectral data for 2,6-dimethoxyphenyltellurium derivatives^a

Compound	Solvent	$T/^\circ\text{C}$	4-H ^b	3,5-H ^c	O-Me ^d
1a $[\text{R}_3\text{Te}]\text{Cl}\cdot n\text{H}_2\text{O}$	CDCl_3	25	7.51	6.68	3.67
1a' $[\text{R}_3\text{Te}][\text{HCl}_2]\cdot 0.5\text{H}_2\text{O}$	CDCl_3	25	7.51	6.68	3.68
1c $[\text{R}_3\text{Te}]\text{I}$	CDCl_3	25	7.51	6.68	3.68
1d $[\text{R}_3\text{Te}]\text{SCN}\cdot\text{H}_2\text{O}$	CDCl_3	25	7.51	6.68	3.68
1e $[\text{R}_3\text{Te}]\text{ClO}_4$	CDCl_3	25	7.49	6.67	3.66
3a R_2TeCl_2	CDCl_3	25	7.41	6.68, 6.65	4.01, 3.67
	$\text{DMSO}-d_6$	30	7.52	6.87, 6.84	3.94, 3.58
	$\text{DMSO}-d_6$	120	7.50	6.85	3.79
	D_2O	25	7.63	6.88	3.79
3b R_2TeBr_2	CDCl_3	25	7.42	6.64 ^e	4.02, 3.68
	$\text{DMSO}-d_6$	30	7.53	6.84 ^e	3.95, 3.60
	$\text{DMSO}-d_6$	80	7.52	6.83	3.79
3c R_2TeI_2	CDCl_3	25	7.43	6.58	3.84
	CDCl_3	-50	7.50	6.62	4.04, 3.71
3d $\text{R}_2\text{Te}(\text{SCN})_2$	CDCl_3	25	7.49	6.74, 6.64 ^e	4.14, 3.58 ^e
	$\text{DMSO}-d_6$	25	7.55	6.86	3.76
4 $[\text{R}'_3\text{Te}]\text{ClO}_4$	CDCl_3	25	7.70	6.76	3.85, 3.66

^a 270.17 MHz; δ . ^b A triplet with $J_{\text{H-H}} = 8-9$ Hz. ^c A doublet with $J_{\text{H-H}} = 8-9$ Hz except for compound **3d** in CDCl_3 . ^d Singlet. ^e Broad.

Table 2 ^{13}C and ^{125}Te NMR spectral data for 2,6-dimethoxyphenyltellurium derivatives^a

Compound	$^{13}\text{C}^b$	$^{125}\text{Te}^c$
1a	97.6, 161.5, 104.8, 135.0, 56.6	554
1c	97.7, 161.6, 104.9, 135.1, 56.8	552
1d	97.8, 161.6, 104.9, 135.0, 56.5; 130.7 ^d	553
1e	97.4, 161.4, 104.6, 134.8, 56.3	552
2	Reported in ref. 1	236
3a	114.0, 161.9 and 159.8, 105.2 and 104.7, 133.9, 57.0 and 55.9	789
3b	109.9, 162.2 and 159.7, 105.0 and 104.6, 133.9, 56.9 and 55.7	729
3c	102.7, 160.9, 104.5, 133.8, 56.0	^e
3d	106.9, 161.0 and 159.4, 104.6 and 104.2, 134.8, 56.9 and 55.7; 117.2 ^d	713
4	106.2, 161.2 and 158.4, 109.5 and 106.2, 139.1, 62.3 and 57.0	621

^a δ in CDCl_3 . ^b At 125.8 MHz. In the order 1-C, 2,6-C, 3,5-C, 4-C, O-CH₃; others. ^c At 158.3 MHz. ^d SCN. ^e Not observed.

N-Bromosuccinimide (NBS) has been known to react with 2,6-dimethoxyphenyl derivatives in a variety of ways.²⁻⁵ It reacted with **1e** to give 3-brominated derivative $[\text{R}'_3\text{Te}]\text{ClO}_4$ **4**.

The ^1H , ^{13}C , and ^{125}Te NMR spectral data are summarized in Tables 1 (^1H) and 2 (^{13}C and ^{125}Te), respectively.

Crystal structures of bis(2,6-dimethoxyphenyl)tellurium dihalides **3a–3d**

Among the three series of organotellurium halides, R_3TeX , R_2TeX_2 and RTeX_3 , examples of the first series have been found to occur essentially as ionic species, $[\text{R}_3\text{Te}]\text{X}$.⁶ Structures of second series compounds have been reported for Ph_3TeX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I),⁷⁻¹⁰ $\text{Ph}(4\text{-BrC}_6\text{H}_4)_2\text{TeCl}_2$,¹¹ $(4\text{-ROC}_6\text{H}_4)_2\text{TeCl}_2$ ($\text{R} = \text{Me}$ or Ph),^{12,13} $(4\text{-ClC}_6\text{H}_4)_2\text{TeI}_2$,¹⁴ $(4\text{-HO-3-MeC}_6\text{H}_3)_2\text{TeCl}_2$,¹⁵ $(2\text{-C}_{10}\text{H}_7)_2\text{TeI}_2$,¹⁶ and phenoxatellurin 10,10-dichloride.¹⁷ The Te atom in these monomers is in a pseudo-trigonal bipyramidal co-ordination with two Te–C bonds and a lone pair of electrons occupying the equatorial sites and with two halogen atoms occupying the apical sites. In many cases the Te atoms are further linked by secondary $\text{Te}\cdots\text{X}$ interactions. The structures of $\text{Ph}_2\text{Te}(\text{NO}_2)_2$,¹⁸ $(4\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{OAc})_2$,¹⁹ and $\text{Ph}_2\text{Te}(\text{S}_2\text{CNR}_2)_2$ ²⁰ have also been reported, and these include intramolecular chelation of the anionic group to give highly co-ordinated tellurium atoms.

Great interest has been paid to the effect of *ortho*-substituents in diaryltellurium dihalides.²¹⁻²⁵ The X-ray crystallographic analyses of ArPhTeX_2 ($\text{Ar} = 2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$; $\text{X} = \text{Br}$ or I) were indicative of an ionic structure, $[\text{ArPhTeX}]\text{X}$, with the $2\text{-Me}_2\text{NCH}_2$ nitrogen atom co-ordinated to the tellurium atom forming a five-membered ring.^{21,26} The crystal structure of 4-ethoxyphenyl(2-benzylideneamino-5-methylphenyl)tellurium dichloride showed that the geometry around

tellurium could be considered as essentially pseudo-octahedral with lone pair electrons occupying the fourth equatorial site.²² The $\text{Te}\cdots\text{N}$ distance of 2.905(2) Å is shorter than the sum of the van der Waals radii of Te and N (about 3.7 Å), indicating substantial secondary intramolecular co-ordination between Te and N.

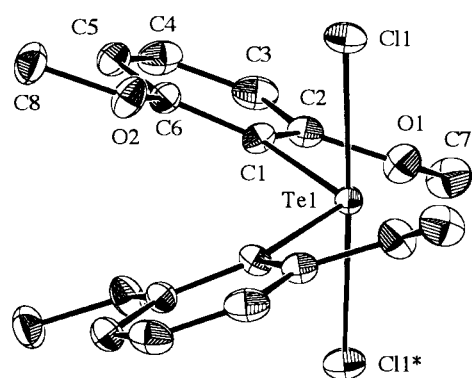
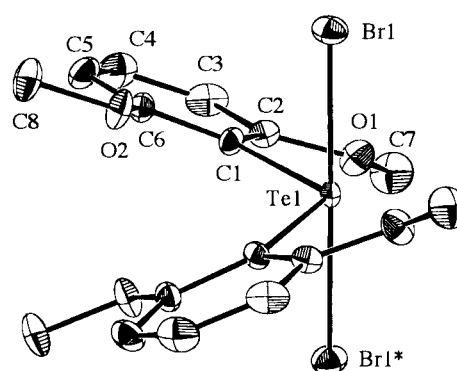
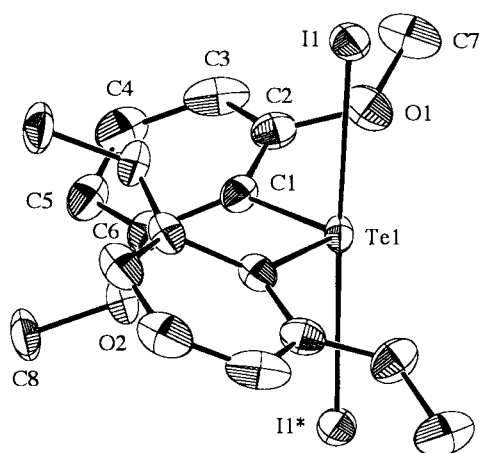
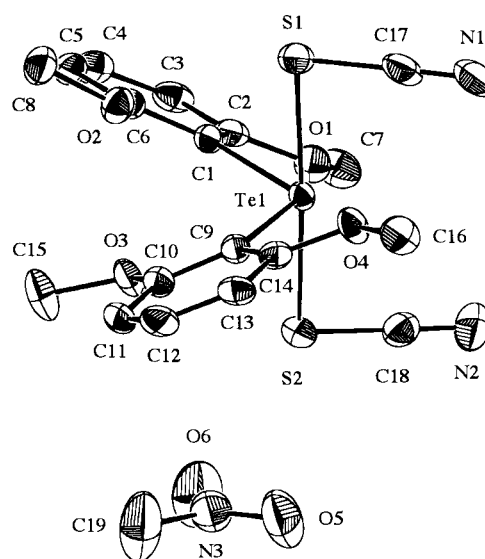
The structures of compounds **3a–3d** are shown in Fig. 1. Selected interatomic distances and angles are given in Table 3. The structures of **3a–3c** in the solid state show a twofold rotation axis. The co-ordination around the tellurium atom can also be considered as essentially pseudo-trigonal bipyramidal with two R-groups and a lone pair of electrons occupying the equatorial sites and two halogen atoms occupying the apical sites. The crystals of **3d** contained one molecule of nitromethane per **3d** molecule. The thiocyanate groups bind to tellurium atom *via* the sulfur atom.

Characteristic is the observation that no intermolecular $\text{Te}\cdots\text{X}$ secondary bond is observed for compounds **3a–3d**, while the co-ordination polyhedra in many Ar_2TeX_2 compounds are completed by such secondary bonds to halogen atoms as mentioned above. The nearest intermolecular $\text{Te}\cdots\text{X}$ distances are 5.886(1) Å [**3a**, $\text{Te}\cdots\text{Cl}$], 5.9789(4) Å [**3b**, $\text{Te}\cdots\text{Br}$], 5.7380(5) Å [**3c**, $\text{Te}\cdots\text{I}$], and 5.598(3) Å [**3d**, $\text{Te}\cdots\text{N}$], respectively.

Very interestingly, in spite of the steric bulkiness of the R groups, the Te–C bond distances in compounds **3a–3c** [2.100(2), 2.092(3), 2.111(5) Å, respectively] are somewhat shorter than those reported for phenyl derivatives,⁷⁻¹⁷ and those of **3d** [2.042(3) and 2.073(2) Å] may be the shortest ever reported. It is likely that these results reflect the unique role of 2,6-dimethoxyphenyl groups, as mentioned below. The Te–X bond lengths in **3a–3c** are similar to those found for reported Ar_2TeX_2 compounds in spite of the absence of

Table 3 Selected interatomic distances (Å) and angles (°) of compounds **3a–3d**

	3a	3b	3c	3d
Te(1)–X(1)	2.513(1)	2.6746(3)	2.9362(4)	2.7300(9)
Te(1)–S(2)				2.7361(8)
Te(1)–C(1)	2.100(2)	2.092(3)	2.111(5)	2.073(2)
Te(1)–C(9)				2.042(3)
Te(1)···O(1)	2.880(2)	2.878(2)	2.906(5)	3.051(2)
Te(1)···O(2)	3.278(2)	3.262(2)	3.255(4)	3.323(2)
Te(1)···O(3)				3.013(2)
Te(1)···O(4)				3.074(2)
Te(1)···X(1)′	5.886(1)	5.9789(4)	5.7380(5)	5.598(3)N(2)*
X(1)···X(1)′	3.886(2)	3.8335(7)	5.229(1)	—
X(1)–Te(1)–X(1)*	177.57(3)	179.36(1)	177.60(2)	177.17(2)
C(1)–Te(1)–C(1)*	107.6(2)	107.5(2)	106.2(3)	104.37(9)
X(1)–Te(1)–C(1)	87.27(8)	87.83(8)	88.2(1)	88.80(8)
S(1)–Te(1)–C(9)				81.61(9)
Te(1)–C(1)–C(2)	113.4(2)	113.7(2)	114.4(4)	113.7(2)
Te(1)–C(1)–C(6)	125.9(2)	125.6(2)	124.3(4)	121.2(2)
Te(1)–C(9)–C(10)				117.9(2)
Te(1)–C(9)–C(14)				119.2(2)

**3a****3b****3c****3d****Fig. 1** Crystal structures of compounds **3a–3d** drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

intermolecular secondary bonds. Compound **3d** is the first example of a crystal structural analysis for compounds of the type $\text{Ar}_2\text{Te}(\text{SCN})_2$. A variety of tellurium compounds having Te–S bonds have been studied by crystal structure analysis,

and the Te–S bond lengths have been reported, *e.g.* for $\text{Ph}_2\text{Te}(\text{S}_2\text{CNR}_2)_2$ [2.588 and 2.649 Å, the shortest Te–S for each ligand],²⁰ $\text{Ph}_2\text{Te}[\text{S}_2\text{P}(\text{OMe})_2]_2$ [2.619 and 2.625 Å],²⁷ and $\text{Ph}_2\text{Te}(\text{S}_2\text{COEt})_2$ [2.607 and 2.629 Å].²⁸ Some others include

Te(SPh)₂ [2.406(2) Å],²⁹ Te(SCPh)₂ [2.379(2) Å],³⁰ Me₂Te(S₂CNR)₂, Me₂TeX(S₂CNR)₂, Me₂TeX[S₂P(OR)₂], and Me₂-Te(S₂COMe)₂ (X = Cl, Br or I) [2.484–2.649 Å, the shortest Te–S for each ligand],^{31–33} Ph{2,6-(PhS)₂C₆H₃}TeX₂,³⁴ and [Cu(S₆)₂(TeS₃)₂]^{6–}, [Mn(TeS₃)₂]^{2–}, [Cu(TeS₃)][–], [Ag(TeS₃)][–], and [Au(TeS₃)₂]^{2–} [2.327–2.395 Å].^{35–38} The Te–S bonds of **3d** are apparently longer than the reported ones, due to the three-center four-electron bond character of the X–Te–X bonds in Ar₂TeX₂. The X–Te–X (X = Cl, Br, I, or SCN) bond angles are very close to 180°. It is generally accepted that the d-orbital contribution in these elements is negligible. The Te–halogen bonds in Ar₂TeX₂ also cannot be dp-hybrid orbital bonds.

The C–Te–C bond angle in compounds **3a–3d** is narrower than the ideal of 120° for trigonal bipyramidal, as expected from VSEPR theory, but it is much wider [107.6(2)–104.37(9)°] than those reported for Ar₂TeX₂ [101.1–94.2°],^{7–17} reflecting the steric requirements of two R-groups (Fig. 1).

We have been interested in the roles of 2,6-methoxy groups in R-derivatives of a variety of elements. The crystal structures of R₃PS·H₂O and R₃PSe·H₂O showed that the P···O interatomic distances [2.794–3.190 Å] were shorter than the sum of the van der Waals radii [3.32 Å], implying a direct electron-donative interaction from the methoxy oxygen to the phosphorus atom.³⁹ This concept has been proposed by Wood *et al.* for the crystal structure of benzyl(2-methoxyphenyl)-diphenylphosphonium bromide, and was supported by energy minimization calculations.⁴⁰ The oxygen–tellurium distances of **3a–3d** [2.880–3.323 Å] are much longer than a covalent Te–O bond observed for (Ph₂TeN₃)₂O [1.972(3) Å],⁴¹ for 2,5-diphenyl-1,6-dioxo-6a-tellurapentalene [2.142(4) and 2.130(4) Å],⁴² and for its dibromide [2.135(9) and 2.171(9) Å],⁴² but they are significantly shorter than the sum of van der Waals radii [3.60 Å] of O and Te.⁴³ Accordingly, it is expected that there is a weak co-ordinative interaction between the tellurium atom and 2,6-methoxy oxygens. We believe the interaction is attractive since the Te–C bond distances in **3a–3d** are somewhat shorter than those reported for phenyl derivatives.^{7–17} If so, the geometry of **3a–3d** with such Te···O secondary intramolecular co-ordination is pentagonal bipyramidal. This may also explain why no Te···X intermolecular secondary bonds are observed.

¹H, ¹³C, and ¹²⁵Te NMR spectra

The ¹H NMR spectra of R₂E, REER, R₂EO, [MeR₂E]⁺, and [R₂EO]⁺ (E = S, Se or Te) show a triplet due to the 4-proton, a doublet due to the 3,5-protons, and a very sharp singlet due to 2,6-dimethoxy protons on the R group, respectively,¹ as observed for compound **1a** (Table 1). Identical spectra were observed for **1a'** and **1c–1e** in accord with the ionic character of these compounds.

In contrast, the ¹H NMR spectrum of compound **3a** in CDCl₃ showed two singlets due to the 2,6-methoxy protons as well as two doublets due to the 3,5-protons at 25 °C (Table 1). The result is consistent with the structure of **3a** in the solid state, in which each R group is non-symmetrical. It further indicates that the rotation of R–Te bonds is restricted in solution. The rotational barrier must occur between the R group and chlorine atoms rather than between two R groups, since the spectrum of **3b** showed two broad singlets due to 2,6-dimethoxy protons and that of **3c** a normal sharp singlet at 25 °C. The spectrum of **3c** showed two signals at –50 °C as shown in Fig. 2 (c) (coalescence temperature, –29 °C). Analogous spectra were obtained for DMSO-*d*₆ solutions of both **3a** and **3b** at 30 °C, and were also temperature-dependent (Fig. 2 (a) and (b)) (coalescence temperatures, 87 and 51 °C, respectively). Interestingly, the spectrum of **3a** in D₂O showed only one singlet due to the 2,6-methoxy groups even at 25 °C. It is expected that the chloride ions in **3a** dissociate partially in D₂O. The spectrum of **3d** measured in CDCl₃ or CD₃CN showed two methoxy proton resonances, while that in

DMSO-*d*₆ showed only one resonance possibly due to partial dissociation of thiocyanate ions. The coalescence temperature (*T*_c) of **3d** could not be observed in DMSO-*d*₆, but was observed in CDCl₃ (Fig. 2) and in CD₃CN.

The activation energies, Δ*G*[‡], for free rotation were calculated from these temperature-dependent ¹H NMR spectra, and decreased in the order of **3a** (90 kJ mol^{–1} in DMSO-*d*₆) > **3b** (80 kJ mol^{–1} in DMSO-*d*₆) > **3d** (≥65 kJ mol^{–1} in CDCl₃) > **3c** (60 kJ mol^{–1} in CDCl₃) ≥ **3d** (59 kJ mol^{–1} in CD₃CN). It is of interest that the activation energy decreased as the halogen became heavier. This finding is understood by assuming that the bond distance increased with increasing radius of the halogen atom, resulting in a smaller rotation barrier. Another possibility is that there is a co-ordinative interaction between the methoxy oxygen and Te^{IV}, upon which the positive character of Te^{IV} must decrease in the order of electronegativity of the halogen atom, Cl > Br > I, giving a smaller rotational barrier for the R-group. Consistent with the bond length order of Te–X (Table 3), Δ*G*[‡] of **3d** was smaller than those of **3a** and **3b**. It is noted that the *T*_c of **3d** varies with the solvent polarity: CDCl₃ (≥60 °C) > CD₃CN (26 °C) > DMSO-*d*₆ (not observed). Although we could not measure Δ*G*[‡] for **3a** and **3b** in CDCl₃ because of the low boiling point of the solvent, they must be larger in CDCl₃ than in DMSO-*d*₆. These solvent and halogen effects can best be understood by the dissociation of the halide ions.

The ¹³C NMR spectra of compounds **1a, 1c, 1d, 1e** showed five resonances attributable to R-group carbons (Table 2). While **3c** showed analogous resonances, **3a, 3b, 3d** showed six resonances for the phenyl carbons and two for the methoxy carbons. The chemical shifts of **1a, 1c, 1d, 1e** are almost identical reflecting the cationic character of these compounds, while considerable influences of the anionic groups are observed among **3a–3d** reflecting the covalent character. These results are consistent with the ¹H NMR spectra as mentioned above.

The ¹²⁵Te NMR spectra of some [R₃Te]X compounds have been reported.⁴⁴ Although a considerable effect of the counter ions on the chemical shift has been observed for [(alkyl)₃Te]X,⁴⁴ **1a, 1c, 1d, 1e** showed almost identical chemical shifts at δ 553 ± 1 (Table 2). The chemical shifts of **2** and **3a** were observed at δ 236 and 789, respectively, which may be compared with those of Ph₂Te (δ 680) and Ph₂TeCl₂ (δ 917).²⁸ The upfield shifts of those phenyl derivatives are consistent with the electron-donating character (or co-ordination) of *ortho*-methoxy groups in R group. The chemical shifts of **3a, 3b, 3d** fall in the range of δ 713–789. We could not observe any resonance of **3c** due to the poor solubility.

Experimental

General

¹H NMR spectra were recorded for solutions using a JEOL model JNM-GX270 spectrometer. ¹H chemical shifts were referenced to internal TMS (δ 0.00) in CDCl₃ or DMSO-*d*₆ (δ 2.49) or DMSO (δ 2.71) in D₂O. ¹³C and ¹²⁵Te NMR spectra were recorded for solutions in CDCl₃ using a JEOL model JNM-ECP500 spectrometer. ¹³C NMR chemical shifts were referenced to internal TMS (δ 0.00), ¹²⁵Te to external diphenyl ditelluride (δ 450). IR spectra were recorded for Nujol mulls using a Shimadzu FTIR-8300 spectrophotometer. The preparations of R₂Te, R₂TeO·(0.67)H₂O, and RTeTeR have been reported elsewhere.¹

Preparations

Tris(2,6-dimethoxyphenyl)telluronium chloride hydrate 1a. A suspension of RLi was prepared from 1,3-dimethoxybenzene (6.0 cm³, 46 mmol), a 15% hexane solution of *n*-butyllithium (26 cm³, 42 mmol), and a catalytic amount of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.15 cm³) under argon.¹ To this was added dropwise a solution of TeCl₄ (2.70 g,

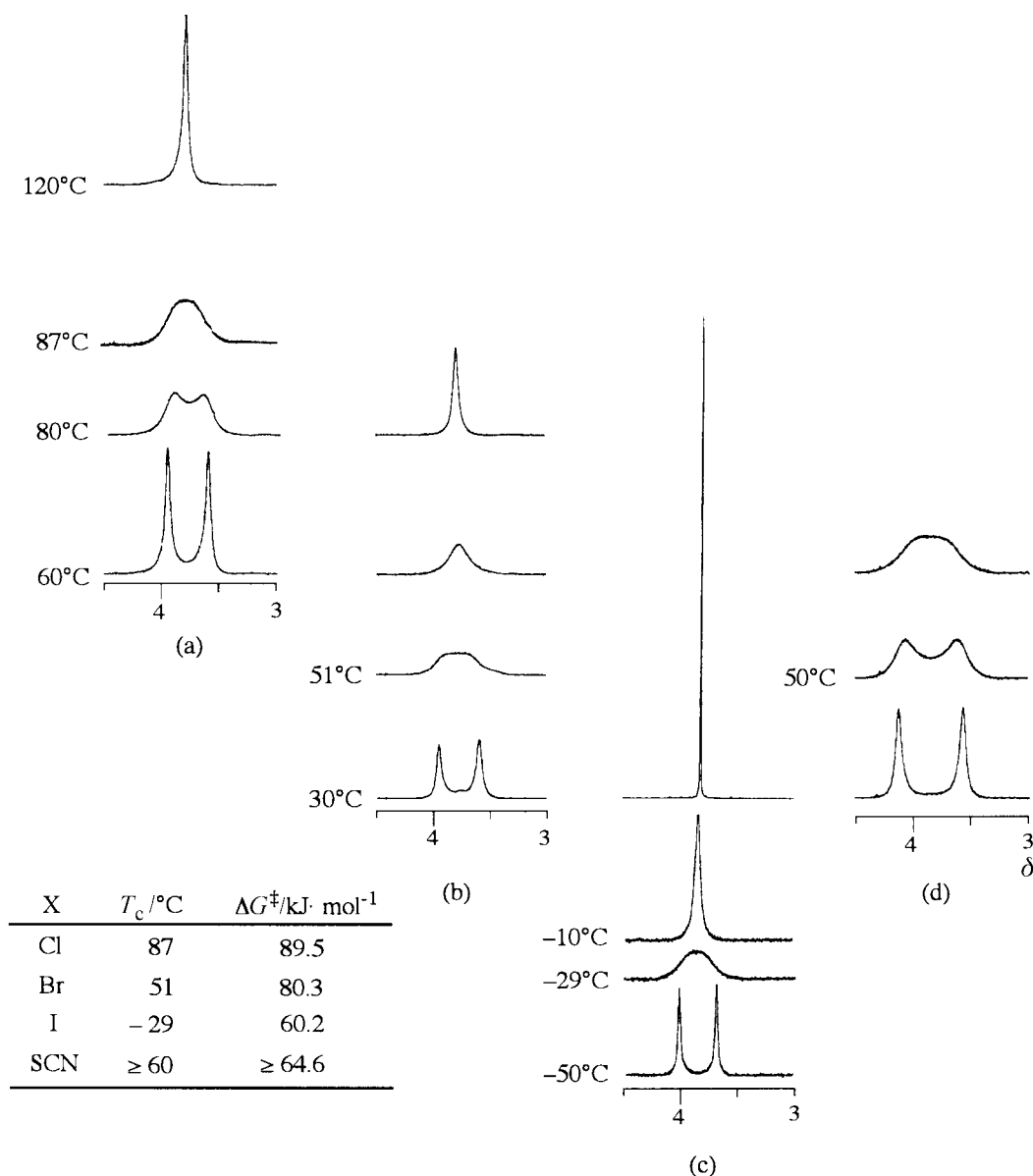


Fig. 2 Temperature dependent ^1H NMR spectra of (a) compound **3a** in $\text{DMSO}-d_6$, (b) **3b** in $\text{DMSO}-d_6$, (c) **3c** in CDCl_3 , and (d) **3d** in CDCl_3 .

10 mmol) dissolved in dry diethyl ether (30 cm^3), and the reaction mixture stirred at room temperature for 5 h to give a yellow suspension. Methanol (2 cm^3) was added with vigorous stirring, and the suspension filtered to give a white solid. The solid was washed with hot water (80 cm^3) to leave a small amount of insoluble material. The insoluble material was recrystallized from 2-butanone to give $\text{R}_2\text{Te } \mathbf{2}^1$ in 15% yield (1.5 mmol). The aqueous filtrate was cooled to 0°C to give colorless crystals of tris(2,6-dimethoxyphenyl)telluronium chloride hydrate, $[\text{R}_3\text{Te}]\text{Cl}\cdot n\text{H}_2\text{O}$ (**1a** $n = 2$ –2.5), in 60–66% yield; mp 140°C (decomp.); IR 3360 cm^{-1} (H_2O) [we performed elemental analyses for two batch samples (Found: C, 46.99; H, 5.21%. $\text{C}_{24}\text{H}_{27}\text{ClO}_6\text{Te}\cdot 2\text{H}_2\text{O}$ requires C, 46.99; H, 4.84%). Found: C, 46.59; H, 5.31%. $\text{C}_{24}\text{H}_{27}\text{ClO}_6\text{Te}\cdot 2.5\text{H}_2\text{O}$ requires C, 46.53; H, 5.21%)]. In another experiment the aqueous filtrate was acidified by adding cold 6 M hydrochloric acid to give a white precipitate of $[\text{R}_3\text{Te}]\text{HCl}_2\cdot 0.5\text{H}_2\text{O}$ **1a'**, in 65% yield, mp 138 – 139°C (decomp.), IR 3454 and 3400 cm^{-1} (H_2O) (Found: C, 46.71; H, 4.78%. $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{O}_6\text{Te}\cdot 0.5\text{H}_2\text{O}$ requires C, 46.49; H, 4.71%).

Compounds **1a** and **1a'** showed analogous solubilities: quite soluble in chloroform, methanol, ethanol, 2-propanol, acetonitrile, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and nitromethane, soluble in water and acetone (recrystallizable), poorly soluble in diethyl ether and tetrahydrofuran (THF), and insoluble in toluene and hexane.

In hot hydrochloric acid these compounds decompose as described below.

Tris(2,6-dimethoxyphenyl)telluronium salts 1c–1e. To a solution of compound **1a** (0.62 g, 1 mmol) in water (25 cm^3) was added ammonium iodide (0.17 g, 1.2 mmol) or potassium iodide (0.25 g, 1.5 mmol), and the resultant suspension stirred vigorously for 1 h to give light yellow crystals of $[\text{R}_3\text{Te}]\text{I}$ **1c** in 93–85% yield. The compound could be recrystallized from ethanol; mp 192°C (decomp.) (Found: C, 42.98; H, 3.99%. $\text{C}_{24}\text{H}_{27}\text{IO}_6\text{Te}$ requires C, 43.28; H, 4.09%). In an analogous manner, treatment of **1a** with sodium thiocyanate resulted in yellow crystals of $[\text{R}_3\text{Te}]\text{SCN}\cdot\text{H}_2\text{O}$ **1d** in 80% yield; mp 187°C (decomp.); IR 3492 and 3406 (H_2O), and 2058 cm^{-1} (SCN), (Found: C, 48.60; H, 4.41; N, 2.23%. $\text{C}_{25}\text{H}_{27}\text{NO}_6\text{STe}\cdot\text{H}_2\text{O}$ requires C, 48.81; H, 4.75; N, 2.28%). Treatment of **1a** with 60% aqueous perchloric acid resulted in colorless crystals of $[\text{R}_3\text{Te}]\text{ClO}_4$ **1e** in 72% yield; mp not observed below 230°C ; IR 1086 cm^{-1} (ClO_4) (Found: C, 44.71; H, 4.14%. $\text{C}_{24}\text{H}_{27}\text{ClO}_{10}\text{Te}$ requires C, 45.14; H, 4.26%).

Reaction of compound 1a with sodium tetrahydroborate. To a solution of compound **1a** (0.62 g, 1 mmol) in water (25 cm^3) was added NaBH_4 (0.77 g; 2.0 mmol), and the resultant suspension stirred vigorously for 1 h to give $\text{R}_2\text{Te } \mathbf{2}^1$ in 87% yield.

Table 4 Crystallographic data for compounds **3a–3d**

	3a	3b	3c	3d·MeNO₂
Chemical formula	C ₁₆ H ₁₈ Cl ₂ O ₄ Te	C ₁₆ H ₁₈ Br ₂ O ₄ Te	C ₁₆ H ₁₈ I ₂ O ₄ Te	C ₁₉ H ₂₁ N ₃ O ₆ S ₂ Te
Formula weight	472.82	561.72	655.72	579.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c (no. 15)	C2/c (no. 15)	C2/c (no. 15)	P2 ₁ /n (no. 14)
<i>a</i> /Å	15.9359(5)	16.3195(9)	17.222(2)	12.0190(4)
<i>b</i> /Å	7.7324(2)	7.7488(3)	7.8424(5)	14.6025(4)
<i>c</i> /Å	16.5329(8)	16.3042(8)	14.510(2)	13.3830(4)
β /°	121.834(2)	118.546(3)	95.665(5)	95.673(2)
<i>U</i> /Å ³	1730.7900	1811.1500	1950.1801	2337.3000
<i>Z</i>	4	4	4	4
μ (Mo-K α)/cm ^{−1}	20.43	60.84	47.08	14.90
No. of reflections	1967	1967	2019	5064
No. of reflections used (<i>I</i> > 3.00 σ (<i>I</i>))	1772	1746	1771	4656
<i>R</i>	0.040	0.037	0.058	0.041
<i>R_w</i>	0.062	0.050	0.086	0.063

Bis(2,6-dimethoxyphenyl)tellurium dichloride 3a. A solution of compound **1a** (0.620 g, 1.0 mmol) in hot 0.1 M hydrochloric acid (100 cm³) was stirred at 80 °C for 20 h to give white precipitates. The suspension was filtered to give R₂TeCl₂ **3a** in 60% yield; mp not observed below 230 °C (Found: C, 40.58; H, 3.70%. C₁₆H₁₈Cl₂O₄Te requires C, 40.64; H, 3.84%). Compound **3a** is soluble in hot chloroform, hot DMSO, and hot acetonitrile, poorly soluble in acetone, THF, and DMF, and insoluble in methanol, 2-propanol, diethyl ether, toluene, and hexane. It is also soluble in water but precipitates on addition of concentrated hydrochloric acid. It could also be obtained by heating R₂TeO·(0.67)H₂O¹ in 0.1 M hydrochloric acid.

Bis(2,6-dimethoxyphenyl)tellurium dibromide 3b, diiodide 3c, and dithiocyanate 3d. To a solution of compound **3a** (0.48 g, 1.0 mmol) in water (80 cm³) was added sodium bromide (0.52 g, 5.0 mmol) and the mixture stirred vigorously for 1 h to give a yellow precipitate of bis(2,6-dimethoxyphenyl)tellurium dibromide, R₂TeBr₂ **3b**, in 64% yield; mp not observed below 230 °C (Found: C, 34.40; H, 3.14%. C₁₆H₁₈Br₂O₄Te requires C, 34.21; H, 3.23%). The solubility resembled to that of **3a**. Compound **3b** could also be obtained by reaction of R₂Te **2** (1.0 mmol) with bromine (1.2 mmol) in chloroform (10 cm³) at room temperature to give a precipitate in 60% yield.

Essentially in an analogous manner, a treatment of **3a** with potassium iodide gave an orange precipitate of the diiodide, R₂TeI₂ **3c**, in 75% yield; mp 164 °C (decomp.) (Found: C, 29.34; H, 2.69%. C₁₆H₁₈I₂O₄Te requires C, 29.31; H, 2.77%). Compound **3c** is soluble in hot chloroform and hot DMSO, poorly soluble in acetone, acetonitrile, and toluene, but insoluble in methanol. It could also be obtained by reaction of R₂Te **2** (1.0 mmol) with iodine (1.2 mmol) in chloroform (10 cm³) at room temperature to give a precipitate in 70% yield. Treatment of **3a** with sodium thiocyanate gave a pale yellow precipitate of the dithiocyanate, R₂Te(SCN)₂ **3d**, in 75% yield; mp 165 °C (decomp.); IR 2116 cm^{−1} (SCN) (Found: C, 41.66; H, 3.45; N, 5.34%. C₁₈H₁₈N₂O₄S₂Te requires C, 41.73; H, 3.50; N, 5.41%).

Compounds **3a–3d** could be recrystallized from nitromethane to give single crystals. The crystals of **3d**, thus obtained, are solvated by nitromethane when fresh and become turbid on standing in air probably due to desolvation.

Reaction of tris(2,6-dimethoxyphenyl)telluronium perchlorate 1e with NBS. To a solution of compound **1e** (2.0 mmol) in acetone (40 cm²) was added NBS (1.28 g, 7.2 mmol) and the mixture stirred for 1 h to give a clear solution. Water (120 cm³) was added to give a white precipitate of [R'₃Te]ClO₄ **4** in 78% yield. This compound could be recrystallized from ethanol; mp 212–214 °C; IR 1080 cm^{−1} (ClO₄) (Found: C, 32.86; H, 2.80%. C₂₄H₂₄Br₃ClO₁₀Te requires C, 32.94; H, 2.76%).

X-Ray crystallography

Single crystals of compounds **3a–d** suitable for structure analysis were obtained by recrystallization from nitromethane. The intensity data were collected at 173 K on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo-K α (λ = 0.71070 Å) radiation from a rotating-anode generator operating at 50 kV and 100 mA. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structures of **3a–3c** were solved by heavy-atom Patterson methods (PATTY)⁴⁵ and expanded using Fourier techniques (DIRDIF 94).⁴⁶ The structure of **3d** was solved by direct methods (SIR 92)⁴⁷ and expanded using Fourier techniques (DIRDIF 94).⁴⁶ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions but not refined. All calculations were performed using the TEXSAN package.⁴⁸ Crystal data and experimental details are listed in Table 4.

CCDC reference number 186/2172.

See <http://www.rsc.org/suppdata/dt/b0/b005273f/> for crystallographic files in .cif format.

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