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

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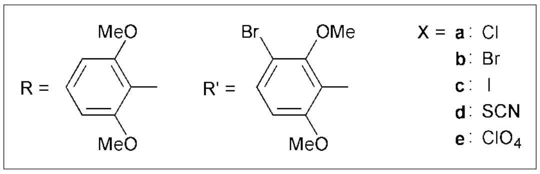
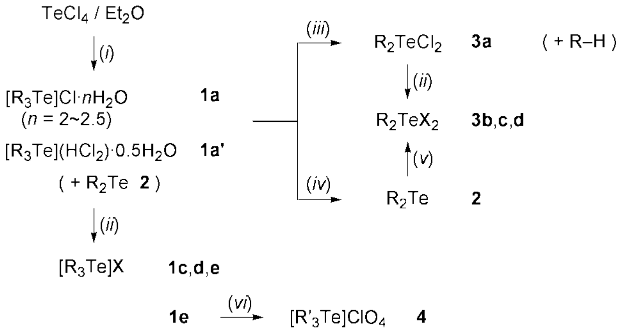
Tris(2,6-dimethoxyphenyl)telluronium chloride hydrate, $[R_3Te]Cl\cdot nH_2O$ **1a** [R = 2,6-$(MeO)_2C_6H_3$, n = 2–2.5] was prepared by the reaction of RLi and $TeCl_4$. It decomposed in hot 0.1 M hydrochloric acid to give R_2TeCl_2 **3a**, exclusively, from which R_2TeX_2 (X = Br **3b**, I **3c** 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 bypyramidal 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 · · · 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)°] than those reported. The X–Te–X bond angles are very close to 180°. The Te · · · 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 $\Delta G^‡$ decreased in the order **3a** (90 kJ mol^{-1} in DMSO-d_6) > **3b** (80 kJ mol^{-1} in DMSO-d_6) > **3d** (≥65 kJ mol^{-1} in $CDCl_3$) > **3c** (60 kJ mol^{-1} in $CDCl_3$) ≥ **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.





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

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 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**.

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Table 1 ^{1}H NMR spectral data for 2,6-dimethoxyphenyltellurium derivatives[a]

Compound	Solvent	T/°C	4-H[b]	3,5-H[c]	O-Me[d]
1a [R_3Te]Cl·$n$$H_2O$	$CDCl_3$	25	7.51	6.68	3.67
1a′ [R_3Te][HCl_2]·0.5H_2O	$CDCl_3$	25	7.51	6.68	3.68
1c [R_3Te]I	$CDCl_3$	25	7.51	6.68	3.68
1d [R_3Te]SCN·H_2O	$CDCl_3$	25	7.51	6.68	3.68
1e [R_3Te]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
	DMSO-d_6	30	7.52	6.87, 6.84	3.94, 3.58
	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
	DMSO-d_6	30	7.53	6.84[e]	3.95, 3.60
	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 $R_2Te(SCN)_2$	$CDCl_3$	25	7.49	6.74, 6.64[e]	4.14, 3.58[e]
	DMSO-d_6	25	7.55	6.86	3.76
4 [R'_3Te]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}C[b]	^{125}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-CH_3; 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 [R'_3Te]ClO_4 **4**.

The ^{1}H, ^{13}C, and ^{125}Te NMR spectral data are summarized in Tables 1 (^{1}H) 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, [R_3Te]X.[6] Structures of second series compounds have been reported for Ph_2TeX_2 (X = F, Cl, Br or I),[7–10] Ph(4-BrC_6H_4)$TeCl_2$,[11] (4-ROC_6H_4)$_2$$TeCl_2$ (R = Me or Ph),[12,13] (4-ClC_6H_4)$_2$$TeI_2$,[14] (4-HO-3-$MeC_6H_3$)$_2$Te-$Cl_2$,[15] (2-$C_{10}H_7$)$_2$$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 Te···X interactions. The structures of $Ph_2Te(NO_2)_2$,[18] (4-$MeOC_6H_4$)$_2$Te(OAc)$_2$,[19] and $Ph_2Te(S_2CNR_2)_2$[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 $ArPhTeX_2$ (Ar = 2-$Me_2NCH_2C_6H_4$; X = Br or I) were indicative of an ionic structure, [ArPhTeX]X, with the 2-Me_2NCH_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 Te···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.

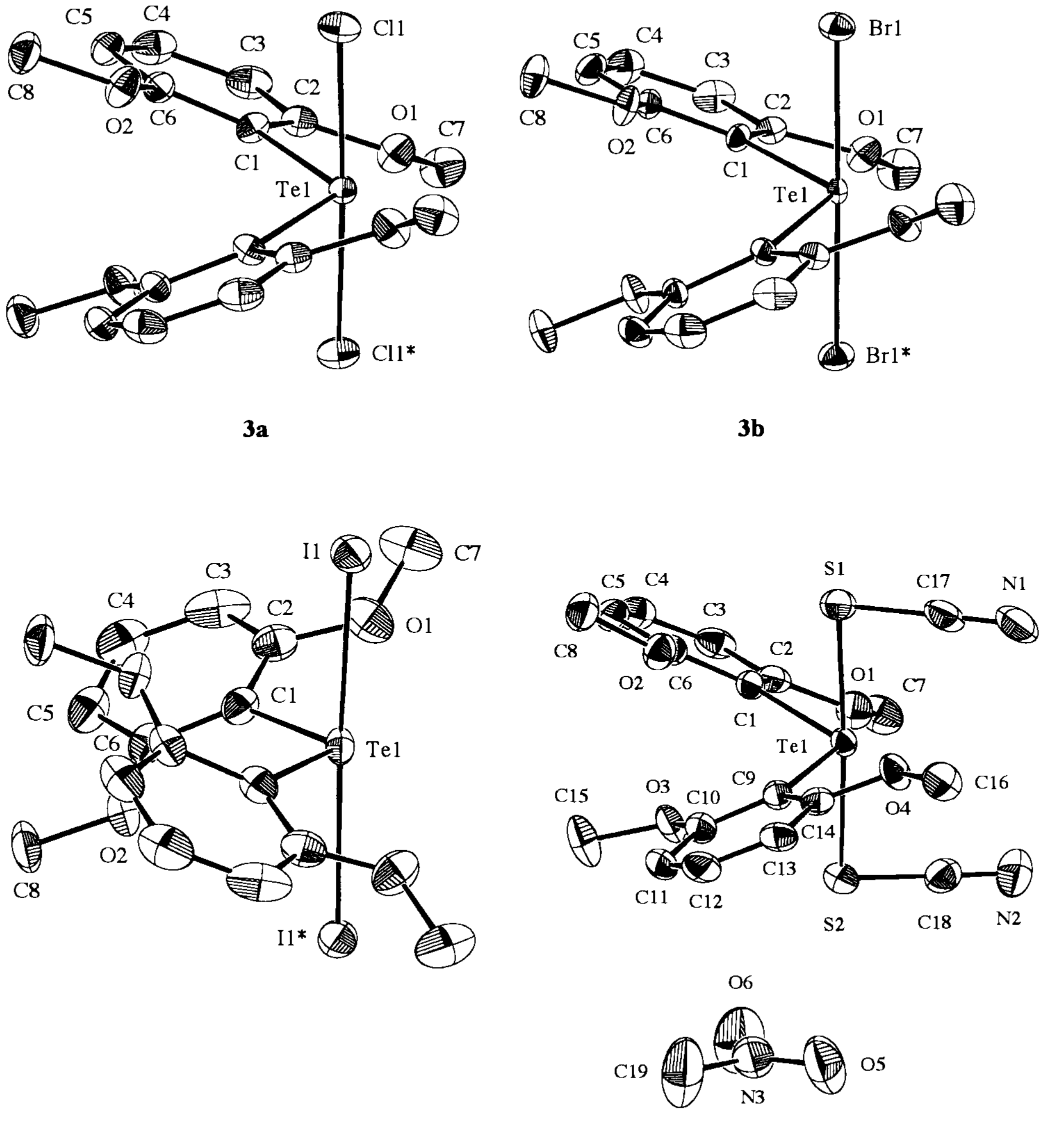
The structures of compounds **3a**–**3d** are shown in Fig. 1. Selected interatomic distances and angles are given in Table 3. The structures of **3a**–**3c** in the solid state show a twofold rotation axis. The co-ordination around the tellurium atom can also be considered as essentially pseudo-trigonal 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 Te···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 Te···X distances are 5.886(1)[**3a**, Te···Cl], 5.9789(4)[**3b**, Te···Br], 5.7380(5)[**3c**, Te···I], and 5.598(3) Å [**3d**, Te···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**	**3e**	**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 $Ar_2Te(SCN)_2$. 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 $Ph_2Te(S_2CNR_2)_2$ [2.588 and 2.649 Å, the shortest Te–S for each ligand],[20] $Ph_2Te[S_2P(OMe)_2]_2$ [2.619 and 2.625 Å],[27] and $Ph_2Te(S_2COEt)_2$ [2.607 and 2.629 Å].[28] Some others include

$Te(SPh)_2$ [2.406(2) Å],[29] $Te(SCPh_3)_2$ [2.379(2) Å],[30] $Me_2Te(S_2CNR_2)_2$, $Me_2TeX(S_2CNR_2)$, $Me_2TeX[S_2P(OR)_2]$, and $Me_2Te(S_2COMe)_2$ (X = Cl, Br or I) [2.484–2.649 Å, the shortest Te–S for each ligand],[31–33] $Ph\{2,6\text{-}(PhS)_2C_6H_3\}TeX_2$,[34] and $[Cu(S_6)_2(TeS_3)_2]^{6-}$, $[Mn(TeS_3)_2]^{2-}$, $[Cu(TeS_3)]^-$, $[Ag(TeS_3)]^-$, and $[Au(TeS_3)_2]^{2-}$ [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 Ar_2TeX_2. 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 Ar_2TeX_2 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 Ar_2TeX_2 [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 $R_3PS\cdot H_2O$ and $R_3PSe\cdot H_2O$ showed that all 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 $(Ph_2TeN_3)_2O$ [1.972(3) Å],[41] for 2,5-diphenyl-1,6-dioxa-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, ^{13}C, and ^{125}Te NMR spectra

The ^1H NMR spectra of R_2E, REER, R_2EO, $[MeR_2E]^+$, and $[R_2EOR'']^+$ (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 $CDCl_3$ 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 D_2O 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 D_2O. The spectrum of **3d** measured in $CDCl_3$ or CD_3CN 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 $CDCl_3$ (Fig. 2) and in CD_3CN.

The activation energies, $\Delta G^\ddagger$, 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 $CDCl_3$) > **3c** (60 kJ mol^{-1} in $CDCl_3$) ≥ **3d** (59 kJ mol^{-1} in CD_3CN). 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), $\Delta G^\ddagger$ of **3d** was smaller than those of **3a** and **3b**. It is noted that the T_c of **3d** varies with the solvent polarity: $CDCl_3$ (≥60 °C) > CD_3CN (26 °C) > DMSO-d_6 (not observed). Although we could not measure $\Delta G^\ddagger$ for **3a** and **3b** in $CDCl_3$ because of the low boiling point of the solvent, they must be larger in $CDCl_3$ than in DMSO-d_6. These solvent and halogen effects can best be understood by the dissociation of the halide ions.

The ^{13}C 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 ^{125}Te NMR spectra of some $[R_3Te]X$ 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 Ph_2Te (δ 680) and Ph_2TeCl_2 (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.

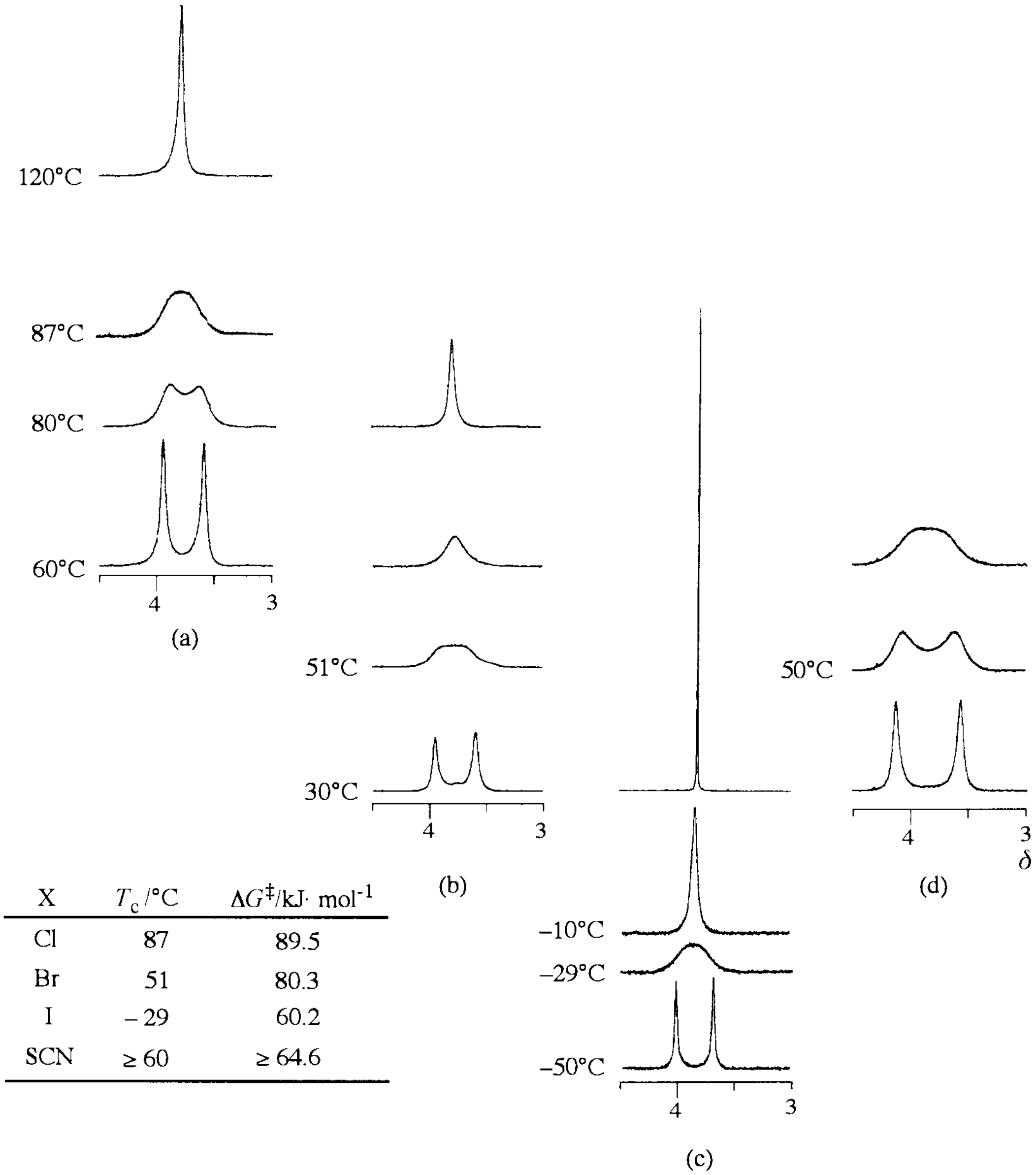
Experimental

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 $CDCl_3$ or DMSO-d_6 (δ 2.49) or DMSO (δ 2.71) in D_2O. ^{13}C and ^{125}Te NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-ECP500 spectrometer. ^{13}C NMR chemical shifts were referenced to internal TMS (δ 0.00), ^{125}Te to external diphenyl ditelluride (δ 450). IR spectra were recorded for Nujol mulls using a Shimadzu FTIR-8300 spectrophotometer. The preparations of R_2Te, $R_2TeO\cdot(0.67)H_2O$, 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 cm^3, 46 mmol), a 15% hexane solution of *n*-butyllithium (26 cm^3, 42 mmol), and a catalytic amount of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.15 cm^3) under argon.[1] To this was added dropwise a solution of $TeCl_4$ (2.70 g,



X	T_c/°C	$\Delta G^{\ddagger}$/kJ· mol^{-1}
Cl	87	89.5
Br	51	80.3
I	- 29	60.2
SCN	≥ 60	≥ 64.6

Fig. 2 Temperature dependent ^{1}H NMR spectra of (a) compound **3a** in DMSO-d_6, (b) **3b** in 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 R_2Te **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, $[R_3Te]Cl\cdot nH_2O$ (**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%. $C_{24}H_{27}ClO_6Te\cdot 2H_2O$ requires C, 46.99; H, 4.84%). Found: C, 46.59; H, 5.31%. $C_{24}H_{27}ClO_6Te\cdot 2.5H_2O$ 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 $[R_3Te]HCl_2\cdot 0.5H_2O$ **1a′**, in 65% yield, mp 138–139 °C (decomp.), IR 3454 and 3400 cm^{-1} (H_2O) (Found: C, 46.71; H, 4.78%. $C_{24}H_{28}Cl_2O_6Te\cdot 0.5H_2O$ 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 tetahydrofuran (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 $[R_3Te]I$ **1c** in 93–85% yield. The compound could be recrystallized from ethanol; mp 192 °C (decomp.) (Found: C, 42.98; H, 3.99%. $C_{24}H_{27}IO_6Te$ requires C, 43.28; H, 4.09%). In an analogous manner, treatment of **1a** with sodium thiocyanate resulted in yellow crystals of $[R_3Te]SCN\cdot H_2O$ **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%. $C_{25}H_{27}NO_6STe_1\cdot H_2O$ requires C, 48.81; H, 4.75; N, 2.28%). Treatment of **1a** with 60% aqueous perchloric acid resulted in colorless crystals of $[R_3Te]ClO_4$ **1e** in 72% yield; mp not observed below 230 °C; IR 1086 cm^{-1} (ClO_4) (Found: C, 44.71; H, 4.14%. $C_{24}H_{27}ClO_{10}Te$ 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 R_2Te **2**[1] in 87% yield.

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

	3a	**3b**	**3c**	**3d**·$MeNO_2$
Chemical formula	$C_{16}H_{18}Cl_2O_4Te$	$C_{16}H_{18}Br_2O_4Te$	$C_{16}H_{18}I_2O_4Te$	$C_{19}H_{21}N_3O_6S_2Te$
Formula weight	472.82	561.72	655.72	579.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)
a/Å	15.9359(5)	16.3195(9)	17.222(2)	12.0190(4)
b/Å	7.7324(2)	7.7488(3)	7.8424(5)	14.6025(4)
c/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)
U/Å^3	1730.7900	1811.1500	1950.1801	2337.3000
Z	4	4	4	4
μ(Mo-Kα)/cm^{-1}	20.43	60.84	47.08	14.90
No. of reflections	1967	1967	2019	5064
No. of reflections used ($I > 3.00\sigma(I)$)	1772	1746	1771	4656
R	0.040	0.037	0.058	0.041
R_w	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 cm^3) was stirred at 80 °C for 20 h to give white precipitates. The suspension was filtered to give R_2TeCl_2 **3a** in 60% yield; mp not observed below 230 °C (Found: C, 40.58; H, 3.70%. $C_{16}H_{18}Cl_2O_4Te$ 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 R_2TeO·$(0.67)H_2O$[1] 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 cm^3) 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, R_2TeBr_2 **3b**, in 64% yield; mp not observed below 230 °C (Found: C, 34.40; H, 3.14%. $C_{16}H_{18}Br_2O_4Te$ requires C, 34.21; H, 3.23%). The solubility resembled to that of **3a**. Compound **3b** could also be obtained by reaction of R_2Te **2** (1.0 mmol) with bromine (1.2 mmol) in chloroform (10 cm^3) 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, R_2TeI_2 **3c**, in 75% yield; mp 164 °C (decomp.) (Found: C, 29.34; H, 2.69%. $C_{16}H_{18}I_2O_4Te$ 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 R_2Te **2** (1.0 mmol) with iodine (1.2 mmol) in chloroform (10 cm^3) at room temperature to give a precipitate in 70% yield. Treatment of **3a** with sodium thiocyanate gave a pale yellow precipitate of the dithiocyanate, $R_2Te(SCN)_2$ **3d**, in 75% yield; mp 165 °C (decomp.); IR 2116 cm^{-1} (SCN) (Found: C, 41.66; H, 3.45; N, 5.34%. $C_{18}H_{18}N_2O_4S_2Te$ 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 cm^2) was added NBS (1.28 g, 7.2 mmol) and the mixture stirred for 1 h to give a clear solution. Water (120 cm^3) was added to give a white precipitate of $[R'_3Te]ClO_4$ **4** in 78% yield. This compound could be recrystallized from ethanol; mp 212–214 °C; IR 1080 cm^{-1} (ClO_4) (Found: C, 32.86; H, 2.80%. $C_{24}H_{24}Br_3ClO_{10}Te$ 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-Kα ($\lambda = 0.71070$ 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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