

New Insights into the Structures of Diorganotellurium Oxides. The First Polymeric Diorganotelluroxane [(*p*-MeOC₆H₄)₂TeO]_{*n*}

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The characterization of the previously reported diorganotellurium oxides R₂TeO (R = Ph (**1**) and *p*-MeOC₆H₄ (**2**)) was revisited by osmometric molecular weight determinations, ¹²⁵Te NMR spectroscopy, and electrospray spectrometry (ESMS) in solution and by ¹²⁵Te MAS NMR spectroscopy in the solid state. The single-crystal X-ray structure of **2** revealed a polymeric arrangement that features a zigzag configured Te–O backbone without any secondary Te···O interactions. In solution **1** and **2** exist predominantly as monomers but appear to be in equilibrium with higher oligomers to a minor extent.

Introduction

Diorganotellurium oxides R₂TeO (R = alkyl, aryl) have been known since the pioneering works of Lederer more than 90 years ago¹ and have been frequently utilized as mild oxygen transfer reagents in organic² and organometallic³ syntheses. Surprisingly little information is available about the solid-state structures of diorganotellurium oxides. Until very recently, only the X-ray structure of Ph₂TeO (**1**) had been reported by Alcock and Harrison; it revealed two crystallographically independent monomers (average Te–O 1.89(1) Å) linked by short secondary Te···O bonds (average Te–O 2.55(1) Å), giving rise to asymmetrical dimers, which are further associated by longer secondary Te···O interactions (average Te–O 3.77(1) Å), as illustrated in Figure 1.⁴

During the course of this study the crystal structure of (C₆F₅)₂TeO (**1a**) was independently published by Naumann et al. (as toluene solvate)^{5a} and Klapötke et al. (as CH₂Cl₂ and benzene solvates),^{5b} it also consists

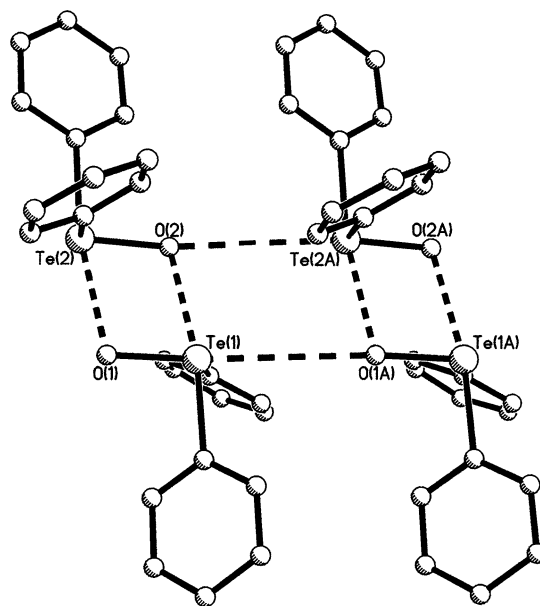


Figure 1. Perspective view (SHELXTL) of the crystal structure of **1**;⁴ coordinates were taken from the CCDC database.

of monomers (Te–O 1.865(10) Å) incorporated into a centrosymmetric dimer by short secondary Te–O bonds (Te–O 2.200(10) Å), but in this case secondary Te···O interactions were no longer observed.^{5a}

Recently, the synthesis of oligomeric diorganotelluroxanes X[(R₂TeO)_{*n*}TeR₂]X (*n* = 2: R = Ph, X = ONC(CN)C(O)NH₂;⁶ R = *p*-MeC₆H₄, X = O₃SCF₃)⁷ was reported, which were regarded by the authors as short

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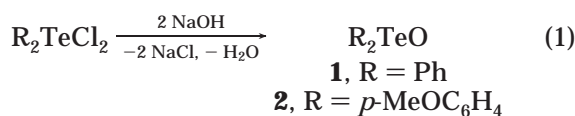
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segments of hitherto unknown polymeric diorganotelluroxanes, $(R_2TeO)_n$.

In the present work we revisit the characterization of the previously described diorganotellurium oxides Ph_2TeO (**1**) and $(p\text{-MeOC}_6\text{H}_4)_2TeO$ (**2**) by solution and solid-state ^{125}Te NMR spectroscopy, electrospray mass spectrometry (ESMS), and molecular weight determinations. We also report the X-ray structure of **2** that exists as a polymer in the solid state and lacks any secondary $Te\cdots O$ interactions. In general, the preparation of inorganic polymer systems remains challenging especially for polymers with well-defined architectures.⁸

Discussion

The diorganotellurium oxides Ph_2TeO (**1**) and $(p\text{-MeOC}_6\text{H}_4)_2TeO$ (**2**) were prepared by hydrolysis of the corresponding diorganotellurium dichlorides in aqueous NaOH solution that contained a small amount of ethanol to improve the solubility (eq 1). This procedure resembles that reported by Alcock et al.⁴ and provided crystalline products having satisfactory elemental analysis. IR spectroscopy confirmed the absence of hydroxy groups or water.



The structure of $(p\text{-MeOC}_6\text{H}_4)_2TeO$ (**2**) was determined by X-ray crystallography and is shown in Figures 2–4; selected bond lengths and angles are collected in the caption of Figure 2. The structure comprises a polymeric arrangement with an alternating sequence of crystallographically related $Te-O$ bonds incorporated into a backbone featuring a zigzag conformation (symmetry operation: $x + 0.5, y, 0.5 - z$). Bearing in mind the steric demand of the lone pair, $Te(1)$ adopts a distorted trigonal bipyramidal geometry, in which two oxygen atoms, $O(1)$ and $O(1a)$, and two carbon atoms, $C(1)$ and $C(1b)$, occupy the axial and equatorial positions, respectively. The slightly different $Te-O$ bond lengths of 2.025(2) and 2.100(2) Å are somewhat longer than values reported for the $Te-O-Te$ linkages of oligomeric diorganotelluroxanes $X[(R_2TeO)_nTeR_2]X$ ($n = 1$: R = Ph, X = SCN (1.985(4) Å);⁹ R = Ph, X = NO₃ (1.971(3)/1.983(2) Å);¹⁰ R = Ph, X = N₃ (1.972(3) Å)¹¹ and R = *p*-MeC₆H₄, X = O₃SCF₃ (1.937(6)/1.957(6) Å)¹²). The distortion is also documented in the slightly bent $O(1)-Te(1)-O(1a)$ angle of 169.61(4)°. The $Te(1)-O(1a)-Te(1a)$ bond angle amounts to 126.0(1)° and is slightly larger than related angles found in oligomeric diorganotelluroxanes $X[(R_2TeO)_nTeR_2]X$ ($n = 1$: R = Ph, X = SCN (121.7(4)°);⁹ R = Ph, X = NO₃ (125.5(1)°);¹⁰ R = Ph, X = N₃ (126.2(4)°)¹¹ and R = *p*-MeC₆H₄, X =

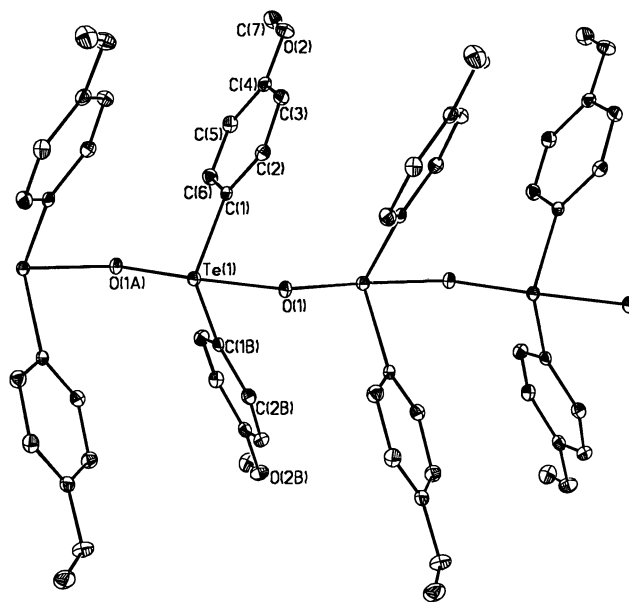


Figure 2. General view (SHELXTL) of the polymeric chain of **2** showing 30% probability displacement ellipsoids and the atom-numbering scheme. Selected bond lengths [Å] and angles [deg]: $Te(1)-O(1)$ 2.100(2), $Te(1)-O(1a)$ 2.025(2), $Te(1)-C(1)$ 2.126(2), $Te(1)-C(1b)$ 2.126(2), $O(1)-Te(1)-O(1a)$ 169.61(4), $C(1)-Te(1)-O(1)$ 86.70(6), $C(1)-Te(1)-O(1a)$ 86.89(6), $C(1)-Te(1)-C(1b)$ 103.6(1), $Te(1)-O(1)-Te(1a)$ 126.0(1) (symmetry operation used to generate equivalent atoms: $a = 0.5 + x, y, 0.5 - z, b = x, 0.5 - y, z$).

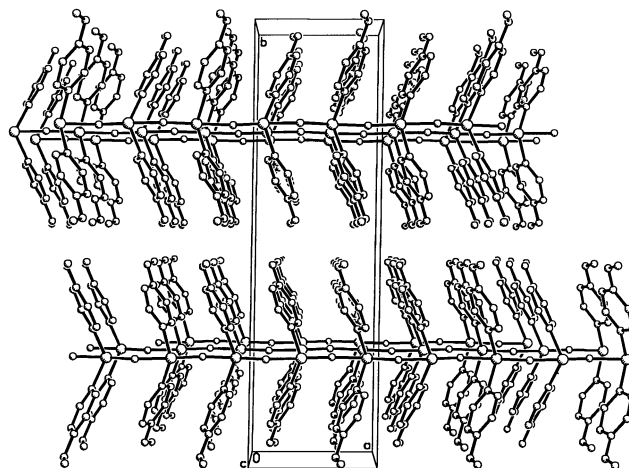


Figure 3. Perspective view (SHELXTL) along the crystallographic *c*-axis showing two layers of parallel polymer chains running through the crystal lattice of **2**.

O₃SCF₃ (123.8(3)°);¹² $n = 2$: R = Ph, X = ONC(CN)-C(O)NH₂ (124.2(2)/124.2(2)°);⁶ R = *p*-MeC₆H₄, X = O₃SCF₃ (122.0(4)/125.3(4)°)⁷). Compared with the structures of Ph_2TeO (**1**) and $(C_6F_5)_2TeO$ (**1a**) the most marked feature of $(p\text{-MeOC}_6\text{H}_4)_2TeO$ (**2**) is the absence of any secondary $Te\cdots O$ interactions. While for the structures of diorganotellurium dichlorides R_2TeCl_2 (R = alkyl, aryl) there appears to be a straightforward relationship between the steric demand of the organic substituents and the presence (e.g., R = Me, Ph, *p*-MeC₆H₄, *p*-MeOC₆H₄)¹³ or absence (e.g., R = α -C₁₀H₇)¹⁴ of secondary $Te\cdots Cl$ interactions, for the diorganotellurium oxides **1**, **1a**, and **2**, there seems to be no obvious relationship. In the crystal lattice of **2** the polymer chains

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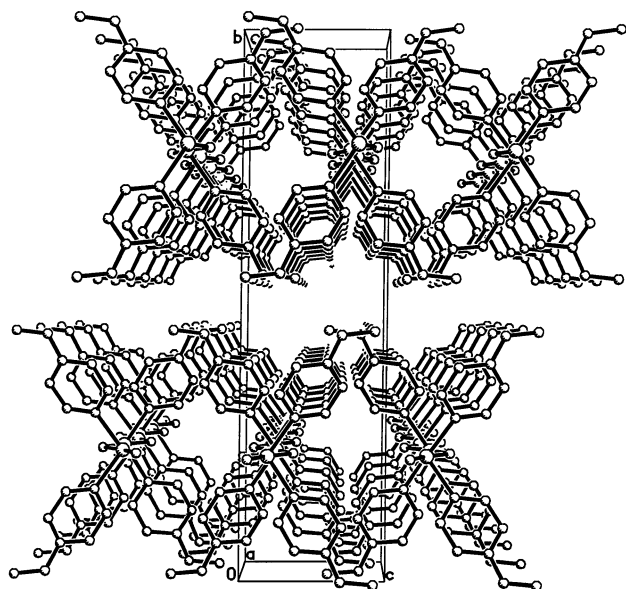


Figure 4. Perspective view (SHELXTL) along the crystallographic *a*-axis showing the gear-like arrangement of the methoxy groups in the crystal lattice of **2**.

run parallel to the crystallographic *a*-axis and form layers parallel to the 101 plane. These layers are stacked along the *b*-axis; the closest non-hydrogen contact between two layers is 3.297(3) Å, observed between O(2) and C(7) (symmetry operation: $1.5 - x, 1 - y, z - 0.5$), as illustrated in Figures 3 and 4. The closest intermolecular non-hydrogen contact of two parallel polymer chains is also found between O(2) and C(7) and amounts to 3.457(3) Å (symmetry operation: $x - 0.5, y, 1.5 - z$). Thus, it appears that the methoxy groups of neighboring anisyl groups are arranged like interlocking teeth of gears, as shown in Figure 4. Apparently, this arrangement is energetically favored over an alternative that involves secondary Te \cdots O interactions similar to that found in Ph₂TeO (**1**) and (C₆F₅)₂TeO (**1a**).^{4,5}

The structural differences of **1** and **2** are also reflected by ¹²⁵Te MAS NMR spectroscopy. Consistent with the two crystallographically independent tellurium sites in Ph₂TeO (**1**), the ¹²⁵Te MAS NMR spectrum revealed two signals of equal intensity at δ_{iso} 1133 and 1103, which compare reasonably well with the ¹²⁵Te NMR signal at δ 1082.4 found in solution (*d*₄-MeOH). By contrast, the solution (*d*₄-MeOH) and solid-state ¹²⁵Te NMR chemical shifts of (*p*-MeOC₆H₄)₂TeO (**2**) are δ 1092.7 and δ_{iso} 903, respectively, differing by 189 ppm.¹⁵ The ¹²⁵Te MAS NMR spectra of **1** and **2** exhibit different spinning sideband manifolds indicative of different chemical shielding anisotropies (SA).¹⁶ The three principle tensor components σ_{11} , σ_{22} , and σ_{33} were determined for each compound by tensor analyses according to the method of Herzfeld and Berger¹⁷ and are collected along with

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(15) The ¹²⁵Te NMR chemical shifts of **1** and **2** need to be interpreted with caution, as species such as R₂Te(OH)OMe and R₂Te(OMe)₂ (R = Ph, *p*-MeOC₆H₄) may be formed in *d*₄-MeOH. No reasonable ¹²⁵Te NMR spectra were obtained in CDCl₃.

Table 1. Solution and Solid-State ¹²⁵Te NMR Parameters of **1** and **2**^a

compound	$\delta_{d_4\text{-MeOH}}$	δ_{iso}	ζ	η	σ_{11}	σ_{22}	σ_{33}
Ph ₂ TeO (1)	1082.4	1133	570	0.60	-1589	-1247	-563
		1103	545	0.75	-1580	-1171	-558
(<i>p</i> -MeOC ₆ H ₄) ₂ TeO (2)	1092.7	903	210	0.00	-1008	-1008	-693

^a δ_{iso} (ppm) = $-\sigma_{\text{iso}} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) = $\sigma_{33} - \sigma_{\text{iso}}$ and $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$, where σ_{11} , σ_{22} , and σ_{33} (ppm) are the principal tensor components of the shielding anisotropy (SA), sorted as follows: $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$.

the more convenient parameters, anisotropy ζ and asymmetry η , in Table 1. Comparison of the anisotropies ζ and asymmetries η of **1** and **2** demonstrates that these parameters are even more sensitive to the structural differences than the isotropic chemical shift δ_{iso} . The asymmetry η of 0.00 for compound **2** deserves special comment; usually group theory considerations for this case require that (i) the geometry of the NMR nucleus adopts a 3-fold or higher symmetry axis or, alternatively, that (ii) a rotation process takes place in the crystal lattice that is fast on the NMR time scale.¹⁸ However, in this case there is no 3-fold symmetry axis nor evidence for any dynamic process that involves the rotation of (*p*-MeOC₆H₄)₂Te moieties around their O-Te-O axis. Apparently, in this case the lone pair has about the same shielding effect as the organic substituents.

The IR spectrum of **1** was already discussed by Alcock and Harrison; the absorptions at 711 and 658 cm⁻¹ were assigned to asymmetric and symmetric Te-O stretching vibrations, respectively.⁴ The IR spectrum (KBr) of **2** reveals no absorptions between 750 and 600 cm⁻¹, but two absorptions at 587 and 424 cm⁻¹, which closely resemble values reported for the asymmetric and symmetric Te-O stretching vibrations of the oligomeric diorganotelluroxanes X(R₂TeO)_{*n*}TeR₂X (*n* = 1: R = Ph, X = NO₃ (607/426 cm⁻¹);¹⁰ *n* = 2: R = Ph, X = ONC(CN)C(O)NH₂ (595/445 cm⁻¹)⁶).

As reported by Lederer, Ph₂TeO (**1**) and (*p*-MeOC₆H₄)₂TeO (**2**) are readily soluble in a variety of solvents. Osmometric molecular weight determinations in CHCl₃ at 30 °C revealed that the degree of association at a concentration of 5 mg g⁻¹ amounts to 1.2 (360 g mol⁻¹) and 1.3 (460 g mol⁻¹) for **1** and **2**, respectively. This observation is consistent with equilibria between monomers, dimers, and possibly low concentrations of higher

(16) It is worth mentioning that **2** exhibits a fairly long ¹²⁵Te T₁ time that amounts to 178 s as determined by a saturation recovery measurement. Attempts to perform ¹H-¹²⁵Te CP MAS experiments to enhance the signal and decrease the recycling delay were very effective for **2**, as spectra with reasonable signal-to-noise ratios could be obtained within 5 min (32 transients, ν_{MAS} 14 kHz, P₉₀ 4 μ s, contact time 10 ms, recycle delay 10 s). Under CP conditions, a ¹²⁵Te NMR static spectrum of **2** could even be obtained within 20 h. Notably, the ¹²⁵Te SA parameters obtained for **2** under CP MAS or CP STAT conditions were identical to those obtained under MAS conditions. By contrast, no ¹²⁵Te CP MAS spectrum could be obtained for **1**. The reason therefore seems to be a very long ¹H T₁ time (estimated at more than a minute), which imposed recycling delays even longer than under MAS conditions.

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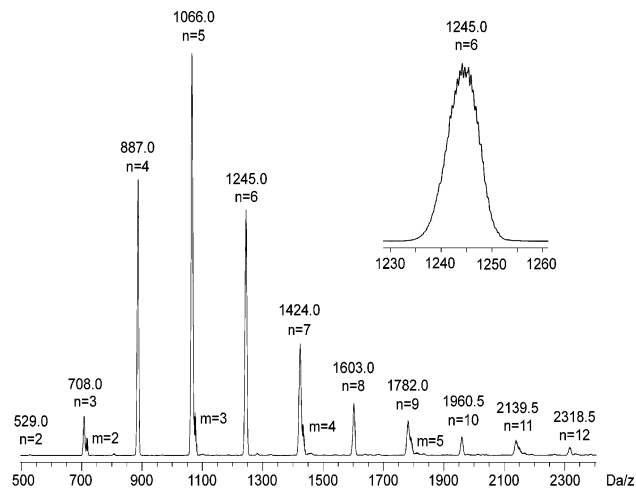


Figure 5. Electrospray mass spectrum (MeCN, positive mode, cone voltage 30 V) revealing mass clusters of the cationic and dicationic oligotelluroxanes $[(R_2TeO)_nH]^+$ ($m = 2-6$) and $[(R_2TeO)_nTeR_2]^{2+}$ ($n = 2-12$), being related to R_2TeO (**2**; $R = p\text{-MeOC}_6\text{H}_4$) by autoionization.

oligomers.¹⁹ The assumption of equilibria is further supported by electrospray mass spectrometry (ESMS). This technique generally allows the detection of trace amounts of ionic species being related to their parent compounds by autoionization. The electrospray mass spectra of **1** and **2** (MeCN, cone voltage 30 V) reveal the following singly and doubly charged mass clusters in the positive mode: $[(R_2TeO)_nH]^+$ ($n = 2-13$ for $R = \text{Ph}$, $n = 2-11$ for $R = p\text{-MeOC}_6\text{H}_4$), $[(R_2TeO)_nTeR_2]^{2+}$ ($n = 2-24$ for $R = \text{Ph}$, $n = 2-22$ for $R = p\text{-MeOC}_6\text{H}_4$); and in the negative mode: $[(R_2TeO)_nCl]^-$ ($n = 1-7$ for $R = \text{Ph}$ and $p\text{-MeOC}_6\text{H}_4$); a representative spectrum is shown in Figure 5. The detection of mass clusters with more than 20 heavy organoelement fragments, e.g., R_2Te groups, is unprecedented in organometallic chemistry, and the detection limit of the ESMS spectrometer (4000 Da) is presumably the limitation for the detection of even higher mass clusters of the type $[(R_2TeO)_nTeR_2]^{2+}$. Although ESMS allows no conclusion regarding the absolute concentration of charged species in solution, it may be that these species play an important role in the equilibria proposed on the basis of the molecular weight determinations. It is worth mentioning that oligomeric diorganotelluroxanes $[(R_2TeO)_nTeR_2]-(O_3SCF_3)_2$ ($n = 1-4$; $R = p\text{-MeOC}_6\text{H}_4$) have been reported before by the reaction of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ with triflic acid.^{7,12} The molecular structures of these compounds consist of $[(R_2TeO)_nTeR_2]^{2+}$ dications featuring rather symmetric Te–O–Te linkages similar to those found in the crystal structure of **2**.^{7,12} These observations may hold some consequences for the recently reported racemization of optically active diorganotellurium oxides, $RR'TeO$ ($R \neq R' = \text{Ph}$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$, 2,4,6- $i\text{-Pr}_3\text{C}_6\text{H}_2$, 2,4,6- $t\text{-Bu}_3\text{C}_6\text{H}_2$),²⁰ where it was speculated that the mechanism of the racemizations involves hydrated diorganotellurium oxides in low concentrations.²¹ Since the racemizations occurs also in dry solvents, albeit at

a lower rate, we propose that charged species such as $[(RR'TeO)_nTeRR']^{2+}$ might also be responsible for the loss of optical activity.

Experimental Section

All solvents were freshly distilled prior to use. Ph_2TeCl_2 and $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ were prepared according to literature procedures.²² The solution NMR spectra were measured using a JEOL Eclipse Plus 400 spectrometer (at 399.78 Mz (^1H), 100.54 (^{13}C), and 126.26 (^{125}Te)) and were referenced against SiMe_4 and Me_2Te . The ^{125}Te MAS NMR experiments were performed using a Bruker MSL 300 spectrometer (at 94.65 MHz) equipped with a high-speed locked 4 mm Bruker probe. Crystalline $\text{Te}(\text{OH})_6$ was used as secondary external reference ($\delta_{\text{iso}} 692.2/685.5$) against Me_2Te .²³ Experimental conditions: Pulse duration 1 μs (pulse angle $< 30^\circ$), recycle delay 30 s, 100–2000 transients. Each sample was investigated at two independent spinning frequencies, between 7 and 14 kHz, to unambiguously assign the isotropic chemical shift δ_{iso} . The tensor analyses were performed with Winfit Software²⁴ using the method of Herzfeld and Berger.¹⁷ The definitions of δ_{iso} , ζ , η , σ_{iso} , σ_{11} , σ_{22} , and σ_{33} are given in the footnote of Table 1. The ^{125}Te T_1 time (longitudinal relaxation) was measured by saturation recovery at 13 kHz. One hundred 90° pulses, separated by 1 ms, were used to nullify the magnetization along z . Then ^{125}Te nuclei were allowed to relax for a time τ , and the magnetization was measured through a 90° pulse. This cycle was repeated 200 times for each relaxation delay (τ). Seven values of τ (10, 30, 50, 100, 200, 300, and 400 s) have allowed construction of the curve $M_z(t) = M_z^0[1 - \exp(-t/T_1)]$, from which T_1 was extracted by simulation. The electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 $\mu\text{L min}^{-1}$. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1} , respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically 10 signal averaged spectra were collected. The IR spectra were recorded using a BioRad FTIR spectrometer. Microanalyses were carried out by CMAS, Belmont, Australia. The molecular weight determinations were performed using a Gonotec Osmomat 070 vapor pressure osmometer.

Synthesis of the Diorganotellurium Oxides $R_2\text{TeO}$ ($R = \text{Ph}$ (1**), $p\text{-MeOC}_6\text{H}_4$ (**2**)).** Ph_2TeCl_2 (10.6 g, 30.0 mmol) or $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ (12.4 g, 30.0 mmol) was suspended in 2 M NaOH solution (50 mL) and stirred vigorously at reflux for 3 h. Then, a few drops of EtOH were added until the product had entirely dissolved. The clear solution was slowly cooled to room temperature and allowed to stand overnight to give a colorless crystalline solid that was filtered and dried in air for 12 h.

Ph_2TeO (1**):** 8.31 g, 27.9 mmol; 93%; mp 182–186 $^\circ\text{C}$ (dec); lit. 192–193 $^\circ\text{C}$ (dec);^{1a} IR (KBr) ν 3055m, 3044m, 2993w, 1572w, 1474m, 1433s, 1058.5m, 1018w, 994w, 731vs, 719vs, 462s, 439s cm^{-1} ; ^1H NMR ($d_4\text{-MeOH}$) δ 7.5–8.0 (10H); ^{13}C NMR ($d_4\text{-MeOH}$) δ 130.7, 132.3, 133.6, 135.9. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{OTe}$ (297.84): C, 48.39; H, 3.38. Found: C, 48.22; H, 3.21.

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(19) The molecular weight measurement was performed under noninert conditions, and the involvement of water in the equilibria may be taken into consideration.

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(*p*-MeOC₆H₄)₂TeO (2**):** 9.56 g, 26.7 mmol; 89%, mp 185–188 °C (dec); lit. 180–182 °C (dec);^{1b} IR (KBr) ν 3083w, 3062w, 3047w, 3014m, 2979m, 2940m, 2896w, 2839m, 1582s, 1489s, 1462m, 1440sh, 1291s, 1256vs, 1175s, 1063m, 1026m, 827s, 811sh, 786m, 587w, 473sh, 424s cm⁻¹; ¹H NMR (*d*₄-MeOH) δ 3.72 (6H), 6.90 (4H), ³*J*(¹H–¹H) 9.2 Hz, 7.85 (4H), ³*J*(¹H–¹H) 9.0 Hz; ¹³C NMR (*d*₄-MeOH) δ 55.9, 116.2, 126.1, 135.0, 163.4. Anal. Calcd for C₁₄H₁₄O₃Te (357.89): C, 46.98; H, 3.94. Found: C, 46.67; H, 3.86.

Crystallography. Crystal data and structure solution of [(*p*-MeOC₆H₄)₂TeO]_{*n*}: C₁₄H₁₄O₃Te, *M*_r = 357.85, orthorhombic, *Pnma*, *a* = 7.3277(1) Å, *b* = 25.5681(6) Å, *c* = 6.8723(1) Å, *V* = 1287.56(4) Å³, *Z* = 4, *D*_x = 1.846 Mg/m³, *F*(000) = 696, λ (Mo K α) = 0.71073 Å, μ = 2.307 mm⁻¹, *T* = 173(1) K. The data were collected to a maximum θ = 27.46° with three sets at different κ -angles and 221 frames via ω -rotation (Δ/ω = 1°) at 2 times 10 s per frame on a Nonius Kappa CCD diffractometer with a completeness of 96.9% (θ_{\max}). The structure was solved by direct methods SHELXS-97²⁵ and refined by full-matrix least-squares calculations using all measured *F*² data and

SHELXL-97.²⁶ All non-H atoms were refined anisotropically. The H atoms were placed in geometrically calculated positions using a riding model (including free rotation about C–C) with *U*_{iso} constrained at 1.2 for aryl and 1.5 for methyl group times *U*_{eq} of the carrier C atom. *R*₁ = 0.0200 for 1290 [*I* > 2 σ (*I*)] and *wR*₂ = 0.0401 for 1455 independent reflections. The max. and min. residual electron densities were 0.573 and –0.599 e Å⁻³.

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Supporting Information Available: Figures of the ¹²⁵Te MAS NMR spectra of **1** and **2**. Figures of selected ESMS mass clusters of **2**. Tables of all coordinates, anisotropic displacement parameters, and geometric data for compound **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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