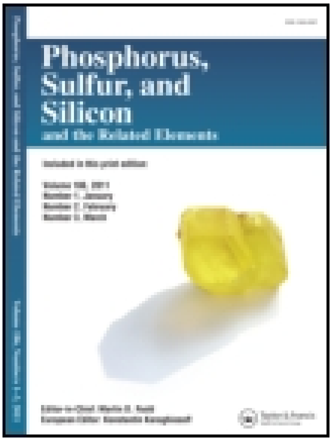

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Diaryl Tellurium Dihalides: From Te-Tetracoordinated Compounds to Te-Tricoordinated Molecular Complexes

Peter H. Laur [a] , Seyedeh M. Saberi-Niaki [a] , Michael Scheiter [a] , Chunhua Hu [a] , Ulli Englert [a] , Yuekui Wang [b] & Jörg Fleischhauer [b]

[a] Institute of Inorganic Chemistry, RWTH Aachen University of Technology , Aachen, Germany

[b] Institute of Organic Chemistry (Theoretical Chem. Section), RWTH Aachen University of Technology , Aachen, Germany

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Diaryl Tellurium Dihalides: From *Te*-Tetracoordinated Compounds to *Te*-Tricoordinated Molecular Complexes

Peter H. Laur
Seyedeh M. Saberi-Niaki
Michael Scheiter
Chunhua Hu
Ulli Englert
Institute of Inorganic Chemistry, RWTH Aachen University of Technology, Aachen, Germany

Yuekui Wang
Jörg Fleischhauer
Institute of Organic Chemistry (Theoretical Chem. Section), RWTH Aachen University of Technology, Aachen, Germany

*X-ray structural studies demonstrate that diaryl tellurium diiodides can be constrained by steric factors (*ortho*-alkyl substituents) to adopt a trigonal pyramidal structure in preference to the expected bisphenoidal structure. DFT calculations are shown to reproduce successfully structural details of the title compounds; they allow one to predict which coordination number should be energetically favored. All compounds are chiral, but the barrier to stereomutation by intra- and intermolecular pathways (60–85 kJmol^{-1}) is rather low.*

Keywords DFT calculations; diaryl chalcogen dihalides; enantiomerization; molecular complexes; stereochemistry; X-ray structural data

INTRODUCTION

The steric disposition of the compounds RR'EHal$_2$ (E = S, Se, Te) in the solid state is known to be either bisphenoidal (ψ-trigonal bipyramidal,

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Dedicated to Professor Kurt Mislow, Princeton University, Princeton, N.J., on account of his 80th birthday.

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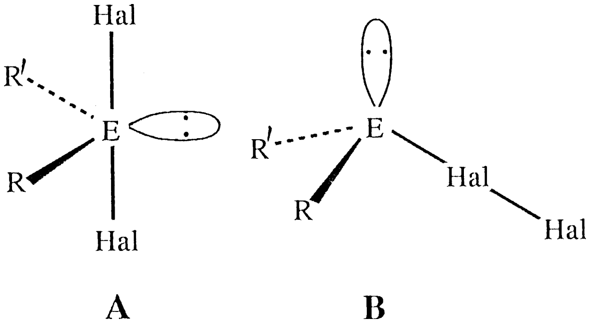
Address correspondence to Peter H. Laur, Institute of Inorganic Chemistry, Ruth Aachen University of Technology, Aachen, Templer-Graben 52056, Germany. E-mail: peter.laur@ac.ruth-aachen.de

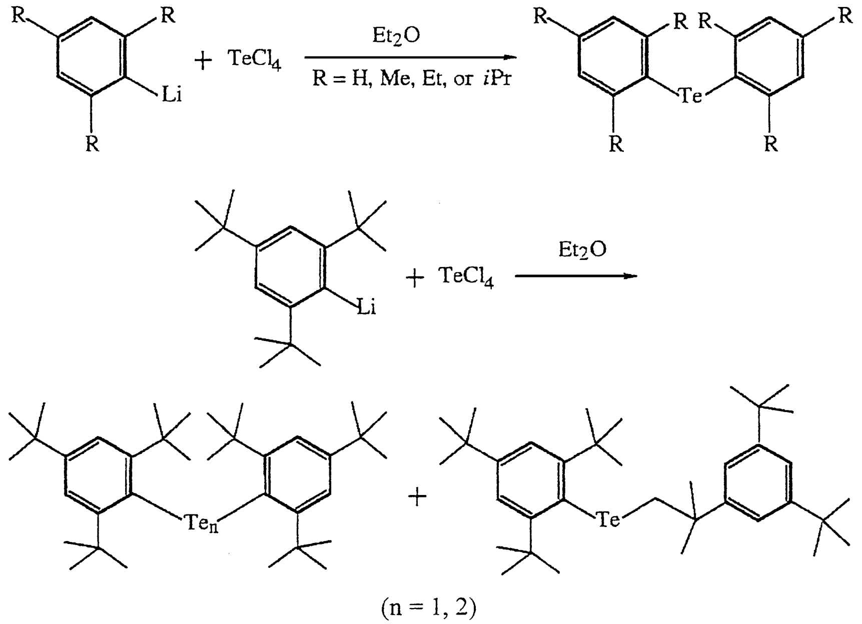


SCHEME 1

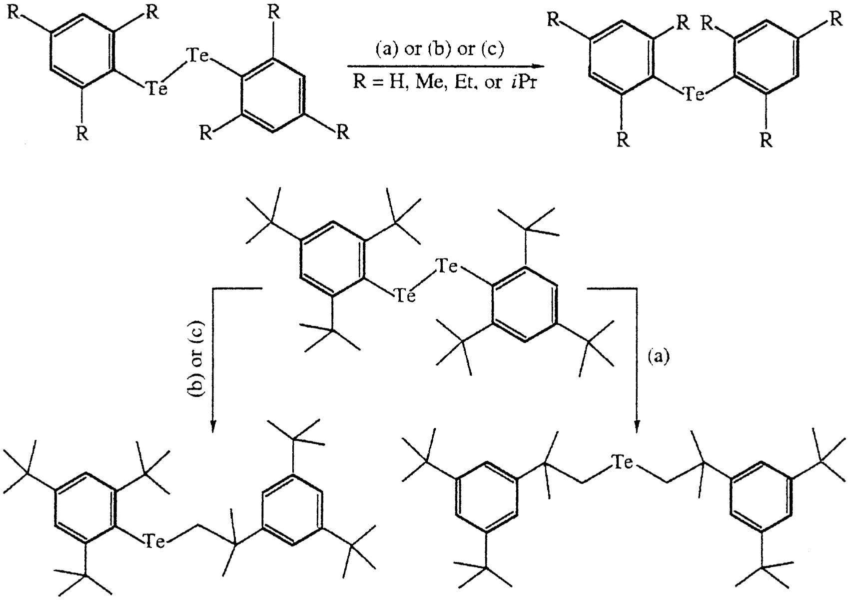
distorted tetrahedral), **A** (cn = 4, coordination number at the chalcogen), or trigonal pyramidal, **B** (cn = 3), (Scheme 1) depending on the relative electronegativity of the chalcogen and the halogen atoms.[1] Whereas class **A** compounds are covalent molecules, **B** constitute molecular complexes RR'E(Hal_2) or ionic species RR'$EHal^+Hal^-$. All diorganyl tellurium dihalides, including, e.g., Ph_2TeI_2, are expected to be of type **A**, which has been amply substantiated by structure determinations.[2] We have observed, however, that the properties of sterically hindered diaryl tellurium diiodides (and also of related diaryl selenium dibromides) differ in typical ways from those of the unhindered molecules, as described below; these compounds show rather a close similarity to diorganylselenium diiodides that are unquestionably of type **B**. We have, therefore, carried out some investigations in order to test whether steric hindrance could cause a change-over from the more space-demanding cn = 4 to cn = 3.

EXPERIMENTAL

We have prepared and studied various, mostly new, multiply *o*-alkyl substituted diaryl tellurium dihalides, including (2,4,6-$R_3C_6H_2)_2TeHal_2$ **1–3** (**1**, R = Me: **Mes**; **2**, Et: **Tep**; **3**, *i*Pr: **Tip**; **a**, Hal = F; **b**, Cl;, **c**, Br; **d**, I), and some derivatives thereof, starting from the corresponding diaryl tellurides. The latter were obtained either (a) by the reaction of aryllithiums with $TeCl_4$, or (b) by detelluration of the ditellurides [thermal or Cu-catalyzed or by use of the reagent [$(Me_2N)_3P$]. In contrast, attempts at similar detellurations of the sterically even more biased bis(supermesityl) ditelluride led only to rearranged or cyclized products, probably by radical reactions. However, the desired (2,4,6-$t$$Bu_3C_6H_2)_2Te$ could be isolated from the complex product mixture of the ArLi/$TeCl_4$ reaction (see Schemes 2 and 3; only main products shown). The dihalides easily were prepared by standard methods (reaction of



SCHEME 2 ArLi/TeCl$_4$—reaction.



SCHEME 3 Detelluration reactions. (a): Δ > 2000°C (melt); (b): Cu, toluene (reflux); (c): $(Me_2N)_3P$, r.t. ($CHCl_3$). (analogous reactions have been observed in the Se series.)

TABLE I (2,4,6-$R_3C_6H_2)_2TeHal_2$; Mes: R = CH_3; Tep: R = C_2H_5; Tip = $(CH_3)_2CH$

	mp [°C]	^{125}Te NMR δ [ppm]	^{125}Te NMR $\Delta_{1/2}$[Hz]
Mes_2Te[3]	128	275	(2)
Tep_2Te	34	209	(10)
Tip_2Te	80	171	(10)
Mes_2TeBr_2[3] (**1c**)	195	744	(6)
Tep_2TeBr_2 (**2c**)	172	722	(10)
Tip_2TeBr_2 (**3c**)	148	823	(20)
Mes_2TeI_2[3] (**1d**)	95	389	(200)
Tep_2TeI_2 (**2d**)	70	234	(200)
Tip_2TeI_2 (**3d**)	153	297	(200)

Ar_2Te with elemental halogen or XeF_2; halogen exchange of Ar_2TeBr_2 with AgF), except for the supermesityl system: Here, halogenation afforded derivatives of the rearranged products exclusively.

The diaryl tellurium difluorides/dichlorides/dibromides are stable compounds, but the diiodides tend to disintegrate, both in solid and in solution, with the liberation of iodine. This instability increases with increasing steric hindrance and is paralleled by broadening of the ^{125}Te NMR signals: $\Delta_{1/2}$ Ph_2TeI_2 40, Mes_2TeI_2 200, (*p*-Tol)MesTeI_2 even 1000 Hz) (see Table I). In solution, free iodine can be monitored by spectroscopy (UV, MCD), and its concentration increases on dilution. The dibromides tend to dissociate only upon high dilution in polar solvents, but rather into $Ar_2TeBr^+ + Br^-$. The corresponding dichlorides and difluorides do not decompose under similar conditions.

RESULTS

In order to ascertain unequivocally, the structures of the halogen adducts we have resorted to single crystal X-ray structure determination. In Tables II and III the results are listed as to the compounds **1c**–**3c** and **1d**–**3d**, respectively.

All dibromides, including the most hindered compound studied so far, viz., **3c**, belong to class **A**, as expected. Their structures are strictly similar to one another, including the conformation. However, steric congestion leads to a breakdown of the extensive intermolecular bonding network otherwise typical of Te(IV) centers.[2] No significant intermolecular contacts that involve either tellurium or bromine exist at distances shorter than the sum of the van der Waals-radii. Whereas all bond

TABLE II **Mes$_2$TeBr$_2$, Tep$_2$TeBr$_2$, Tip$_2$TeBr$_2$ (C_2 Structure/type A) (X-ray Data). Rot$_{Ar}$: Rotation of the Aryl Rings from the Plane of the C—Te—C Bonds; Σr_{cov}:[5] Te—C 213, Te—Br 250 pm**

	Te—C	Te—Br	C—Te—C	C—Te—Br	Br—Te—Br	Rot$_{Ar}$
Mes$_2$TeBr$_2$	213.8 (3) pm	269.14 (9)	113.50 (16)°	86.96 (8)°	179.98 (2)°	31.87 (16)°
(**1c**)	213.8 (3)	269.14 (9)		93.03 (8)		31.87 (16)
Tep$_2$TeBr$_2$	213.8 (7)	266.71 (10)	112.3 (3)	89.00 (19)	177.23 (4)	26.8 (4)
(**2c**)	214.3 (7)	270.93 (10)		91.8 (2)		28.8 (4)
				90.27 (19)		
				91.0 (2)		
Tip$_2$TeBr$_2$	217.7 (4)	267.39 (8)	122.63 (17)	87.49 (11)	176.58 (2)	28.1 (2)
(**3c**)	217.7 (4)	267.74 (8)		93.34 (11)		31.9 (2)
				88.09 (11)		
				94.36 (11)		
Ph$_2$TeBr$_2$[4]	214 ± 3	268.2 ± 0.3	96.3 ± 1.2		178.0 ± 0.2	56

distances and most bond and dihedral angles are unexceptional, the molecules obviously alleviate steric strain by opening of the C—Te—C angle from typically 100° (unhindered Ar$_2$TeBr$_2$) to 113° in **1c** and **2c**, and even 123° in **3c**.

On the other hand, the diiodides **1d**–**3d** are novel compounds of class **B**, in contrast to the Ar$_2$TeI$_2$ compounds previously investigated. Also here the molecular packing in the crystal does not indicate any intermolecular association. Clearly, both the Te—I and (less so) the I—I bonds are considerably longer than the sum of the van der Waals-radii, but the iodine molecular unit is still distinctly recognizable, allowing the compounds to be described as molecular complexes. The most conspicuous structural feature results from the fact that the Te—I—I unit, bisects the C—Te—C angle asymmetrically giving rise to two different C—Te—I angles of approximately 100° and 120°. The Te—I—I unit itself is slightly bent at *ca.* 172°, probably also indicating some steric influence.

In order to understand better the observed structural variations, we have performed a series of density functional theory calculations (DFT/TZVP/B3LYP). The results match almost exactly the experimentally obtained structural data, as is apparent from a comparison of the observed and calculated molecular structures of, e.g., **1c** and **1d** as depicted in Figures 1 and 2. This correspondence supports our contention that the molecules discussed are *gas-phase like* also in the crystal. Assuming that the title compounds could in principle adopt both structural types **A** and **B**, we have extended our calculations to include also the

TABLE III Mes$_2$TeI$_2$, Tep$_2$TeI$_2$, Tip$_2$TeI$_2$ (C_1 Structure/type B) (X-ray data). Rot$_{Ar}$: Rotation of the aryl rings from the plane of the C–Te–C bonds; Σr_{cov}:[5] Te—C 213, Te—I 270, I—I 268 pm

	Te—C	Te—I	I—I	C—Te—C	C—Te—I	Te—I—I	Rot$_{Ar}$
Mes$_2$TeI$_2$	212.9 (4) pm	304.00 (6) pm	284.44 (6) pm	98.08 (13)°	101.39 (9)°	171.012 (13)°	58.22 (17)°
(**1d**)	213.9 (4)				120.98 (10)		68.09 (17)
Tep$_2$TeI$_2$	213.4 (4)	306.21 (5)	281.65 (6)	100.79 (16)	95.17 (12)	171.276 (19)	51.5 (3)
(2d)	214.7 (4)				121.42 (11)		61.5 (2)
Tip$_2$TeI$_2$	214.0 (4)	305.05 (6)	284.46 (6)	96.41 (17)	98.75 (12)	173.340 (18)	59.2 (2)
(**3d**)	214.6 (5)				121.29 (13)		56.5 (2)

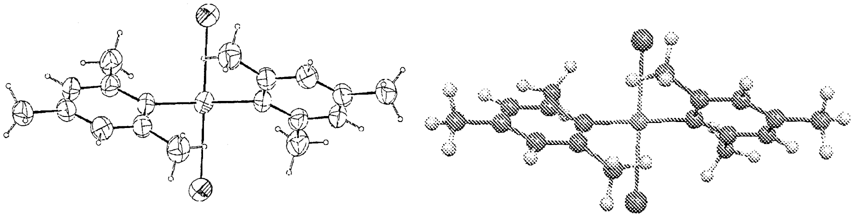


FIGURE 1 Experimental (left) and calculated (right) Solid State Structure of Mes_2TeBr_2 (**1c**).

(so far not realized) alternative isomers, like **1c** of type **B** or **1d** of type **A**. For these hypothetical molecules, reasonable geometric parameters are found that agree well with those observed in the related real compounds. It is striking, however, that the calculated parameters of type **B** molecules lacking steric strain neither exhibit the C—Te—I nor the Te—I—I angle peculiarities denoted above for **1d–3d** (e.g., Ph_2TeI_2 of C_1 structure/type **B**, calc.: C—Te—I 99.5, 101.4°; Te—I—I 179.6°).

The calculations also yield data on the relative ground-state energies of the related isomers of type **A** and **B**; the results are displayed in Table IV.

Clearly, even in sterically burdened Ar_2TeBr_2 molecules the C_2 structure/type **A** should be much preferred, as found by experiment, whereas in Ar_2TeI_2 the preference for C_2 is only slight and can be reversed easily by steric factors (Sterically hindered Ar_2SeBr_2 and Ar_2SCl_2 molecules should also adopt a C_1 rather than the common C_2 structure, as indicated in Table IV). We therefore propose to modify the structure matrix for RR'$EHal_2$,[1] as suggested in Scheme 4, with the molecular complexes

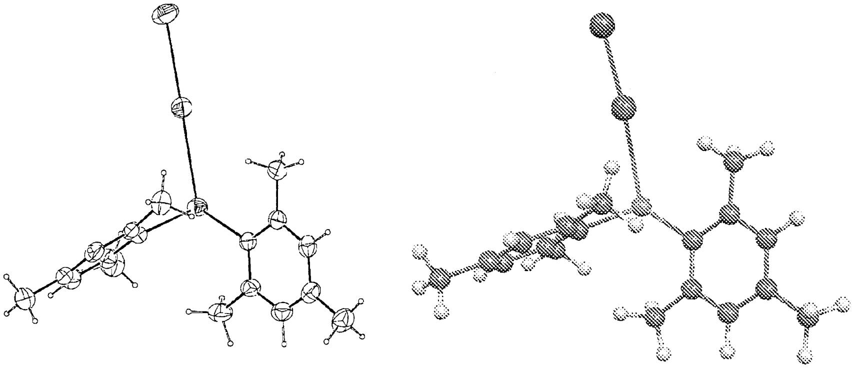


FIGURE 2 Experimental (left) and calculated (right) Solid State Structure of Mes_2TeI_2 (**1d**).

TABLE IV DFT/TZVP/B3LYP Calculations of some $Ar_2ChalcHal_2$ (Relative Ground State Energies [kcal/mol])

	$Ar_2Chalc(Hal)(Hal)$ (C_2-Structure/Type **A**	$Ar_2Chalc(Hal_2)$ (C_1-Structure/Type **B**)
Ph_2TeBr_2	0	17.1
Mes_2TeBr_2	0	8.5
Ph_2TeI_2	0	2.8
Mes_2TeI_2	7.6	0
Mes_2SeBr_2	6.8	0
Mes_2SCl_2	8.3	0

B in sterically biased Te/I, Se/Br, and S/Cl systems competing with the otherwise preferred type **A** molecules.

	Cl	Br	I
S	**TBP/MC**	MC	MC
Se	TBP	**TBP/MC**	MC
Te	TBP	TBP	**TBP/MC**

TBP = ψ-Trigonal Bipyramidal, $R_2Chalc(Hal)(Hal)$
MC = Molecular Complex, $R_2Chalc(Hal_2)$

SCHEME 4 Solid state structure matrix of diorganyl chalcogen dihalides.

DISCUSSION

All compounds **A** are chiral as a consequence of the contra-rotation of the aromatic rings; the highest possible symmetry is C_2. If enantiomerization by rotation and/or Berry pseudorotation should be hindered in such *o*-substituted diaryl chalcogen dihalides, anisochrony of various groupings is expected to be evident in the NMR spectra. For example, the Me/Et/*i*Pr substituents in the *o* and *o*′ positions on each aryl ring of **1A–3A** should give rise to different signals, as is in fact always observed at room temperature. Similar effects can also be seen in related compounds with bulky substituents on one ligand only, like $PhMesTeBr_2$, but a differentiation of the two *ortho* or *meta* positions of unsubstituted phenyl rings cannot be discerned. At elevated temperatures coalescence is observed, while the Te/F coupling is maintained in, e.g., **1a–3a**. This latter phenomenon indicates that the coalescence results from an intramolecular process. The general similarity of the physical and chemical character of the dichlorides/dibromides with that of the difluorides suggests an intramolecular reorganization to cause the coalescence also in their respective cases. The barriers to stereomutation deduced from the NMR spectra lie in the range of 60–85 $kJmol^{-1}$ (e.g., **1a**, 69; **1b**, 64; **1c**, 85 $kJmol^{-1}$). Such barriers are too low as to enable the existence of optically stable enantiomers at room temperature. We have, therefore, not tried to resolve the compounds.

The NMR features described should also pertain to the diiodides of type **B**, viz., **1d–3d**. However, none of the anisochrony expected for a pyramidal structure of the sterically biased diiodides can be observed by solution NMR, contrary to the case of the corresponding *Te*-oxides. Although this finding could be rationalized by invoking a low barrier to pyramidal inversion in the diiodides, it is not clear why such a barrier should be much lower than in the oxides. The presence of free iodine in the solution rather suggests a different mechanism, viz., dissociation/association.

Since all the compounds **1–3** discussed are chiral, there in principle could exist the possibility of obtaining optically active samples—albeit of fleeting optical stability—by spontaneous resolution. We have, therefore, checked the space group symmetry of the crystals of the dibromides **1c–3c** and the diiodides **1d–3d**, as well as of some related diaryl tellurium *Te*-oxides like Tep_2TeO: In all cases, the crystals themselves are achiral, *i.e.*, they contain an equal number of *R* and *S* molecules (*true racemates*) and cannot give rise to optical activity on solution.

In this context, earlier reports of optical activity in solutions of, e.g., Ph_2TeBr_2 and $Ph(p\text{-Tol})TeI_2$ should be mentioned.[6] Although the reported experimental details are not convincing and the very small and variable rotations vanished within minutes, and although the stereochemical theory[7] prompting the investigations (predicting D_2 symmetry for R_4Te) is now obsolete, occasional observations of optical activity in solutions of such compounds might well be trustworthy, as both Ph_2TeBr_2[4] and α-Ph_2TeI_2[8] crystallize in chiral crystals consisting of homochiral molecules (*conglomerates*), and should be resolvable by crystal picking.

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