

Observations on the synthesis and chemistry of a complete series of phenylazophenyl(C, N') tellurium(II) halides (fluoride, chloride, bromide and iodide)

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Abstract

The formation of the complete series of phenylazophenyl(C, N') tellurium(II) halides (fluoride, chloride, bromide and iodide) is described in this paper. The monoiodide arose from the reaction of the monobromide and diiodine. The new monoclinic modification of phenylazophenyl(C, N') tellurium(II) chloride (RTeCl) contains only one independent molecule in the unit cell, whereas a previously reported modification contains two molecules per unit cell, and is triclinic. The bond lengths Te–N(2) were in the range that were expected for a secondary bonding interaction, i.e., 2.210(7)–2.252(8) Å. On comparison of the Te–N(2) bond length for the series of compounds, it was noted that as a more electronegative atom was attached to the Te atom, the stronger the secondary interaction became. The monofluoride, synthesised by two independent methods, is an orange liquid which is characterised by ¹²⁵Te and ¹⁹F NMR. © 1997 Elsevier Science S.A.

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1. Introduction

Phenylazophenyl(C, N') tellurium(II) chloride was the first compound containing a tellurium–nitrogen *intra*-molecular bond to be structurally characterised [1], although now, many more examples are known [2]. It is perhaps surprising that few complete series of *intra*-molecularly stabilised tellurenyl halides is known, i.e., RTeX, where X = F, Cl, Br, I. The problem is generally the lack of fluoro-derivatives, which is surprising given that the co-existence of the spin 1/2 species ¹⁹F and ¹²⁵Te make such compounds attractive for NMR studies. Emeleus and Heal [3] were the pioneers of the field of organotellurium fluorides reporting for example MeTeF₃ and Me₂TeF₂. Berry et al. [4] prepared Ph₂TeF₂ which was the subject of crystallographic analysis by Berry and Edwards [5]. Pentafluorophenyl-derivatives have been reported, including structural investigations of (C₆F₅)₂TeF₂ [6] and of (C₂F₅)₂TeF₃ [7]. In the case of the difluoride structures, weak *inter*-molecular (Te–

F) contacts were noted. One example of an organytellurium fluoride stabilised by *intra*-molecular co-ordination is known: [2-(*p*-tolyliminomethyl)phenyl]tellurium(II) fluoride [8], but no crystals suitable for crystallographic analysis were obtained. In this paper the synthesis of the complete series of 2-phenylazophenyl(C, N') tellurium(II) crystallographic modification of the chloride, together with those of the bromide and iodide are presented but the fluoride, a liquid, resisted X-ray crystallographic structural characterisation.

2. Experimental and results

2-Phenylazophenyl-(C, N') tellurium(IV) trichloride [1] and 'triiodide' [2] were prepared using literature methods.

2.1. Synthesis of (2-phenylazophenyl-C, N') tellurium(II) chloride (new crystal modification)

(2-Phenylazophenyl-C, N') tellurium(IV) trichloride (3.5 g, 8.5 mmol) was dissolved in methanol (50 cm³)

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and heated under reflux. A solution of hydrazine hydrate (0.5 g, 1.5 mmol) in methanol (50 cm³) was added slowly to the refluxing solution. The solution was filtered and cooled to afford brown crystals. Yield 80%, m.p. 82–83°C (lit. m.p. of triclinic form, 80°C).

2.2. Synthesis of (2-phenylazophenyl-C,N')tellurium(IV) tribromide

(2-Phenylazophenyl-C,N')mercury(II) chloride (2.4 g 5.74 mmol) and tellurium tetrabromide (2.56 g 5.74 mmol) were refluxed in sodium dried 1,4-dioxane (20 cm³) for 6 h under dry nitrogen. On cooling the 2:1 addition compound of dioxane and mercury(II) chloride, it was separated as white plates which were removed by filtration. The filtrate was concentrated on the rotatory evaporator and nitromethane (20 cm³) was added. Evaporation was carried out to dryness and the residue was recrystallised from nitromethane to give reddish-brown crystals. Yield 93%, m.p. 171–174°C. The reaction product was chromatographed on silica gel and eluted with petroleum ether and ethylacetate to give two fractions, the analysis of which gave no clear indication as to its identity.

2.3. Synthesis of (2-phenylazophenyl-C,N')tellurium(II) bromide

(2-Phenylazophenyl-C,N')tellurium(IV) tribromide (the above material, prior to chromatography) (1.76 g, 3.21 mmol) was dissolved in methanol (35 cm³) and heated under reflux. A solution of hydrazine hydrate (0.16 g, 3.21 mmol) in methanol (25 cm³) was added slowly to the refluxing solution. The solution was filtered and cooled to afford red crystals. Yield 40%, m.p. 116–118°C.

2.4. Synthesis of (2-phenylazophenyl-C,N')tellurium(II) iodide

Diiodine (0.13 g, 5.14 mmol) in chloroform (15 cm³) was added dropwise to a solution of (2-Phenylazophenyl-C,N')tellurium(II) bromide (0.2 g, 5.14 mmol) in chloroform (15 cm³). The solution changed colour from red to a very dark red/black and was stirred for 3 h. Then the solvent, together with excess diiodine, was removed on the rotatory evaporator. The product remaining was red in colour and was recrystallised from nitrobenzene to m.p. 149–151°C.

2.5. Synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride

A solution of (2-phenylazophenyl-C,N')tellurium(II) iodide (1 g, 2.3 mmol) in sodium dried toluene (50 cm³), was added slowly to a refluxing solution of silver

Table 1
Analytical data for compounds considered

Compound	Colour	Found (%)			Calculated (%)		
		C	H	N	C	H	N
RTeF	Orange oil	43.8	2.85	8.61	44.0	2.77	8.55
RTeCl	Brown	41.7	2.72	7.97	41.8	2.63	8.14
RTeBr	Red	36.9	2.41	7.35	37.1	2.33	7.20
RTeI	Red	32.8	2.14	6.51	33.1	2.08	6.43

fluoride (2 g, 15 mmol) in sodium dried toluene (50 cm³) under dry dinitrogen. When all the (2-phenylazophenyl-C,N')tellurium(II) iodide had been added, the mixture was left to reflux for a further 2 h, after which the reaction mixture was filtered. The solvent was removed on a rotatory evaporator, giving an orange oil.

2.6. An alternative synthesis of (2-phenylazophenyl-C,N')tellurium(II) fluoride

A solution of (2-phenylazophenyl-C,N')tellurium(IV) triiodide [2] (1 g, 1.5 mmol) in sodium dried toluene (50 cm³), was added slowly to a refluxing solution of silver fluoride (0.63 g, 5 mmol) in sodium dried toluene (50 cm³) under dry dinitrogen. When all (2-phenylazophenyl-C,N')tellurium(IV) triiodide was added, the mixture was left to reflux for a further 2 h, after which the reaction mixture was filtered. The solvent was removed on a rotatory evaporator, producing an orange oil. Analytical data are in Table 1 and some mass spectroscopic data for '(2-phenylazophenyl-C,N')tellurium tribromide' are in Table 2.

2.7. Physical measurements

Infrared spectra were obtained for KBr discs with a BIO-Rad, FTS-40A FTIR spectrometer. Proton (300.133), ¹³C (75.469), ¹²⁵Te (78.580) MHz NMR spectra were obtained with a Bruker AC 300 spectrometer at the indicated frequencies; references used were TMS (¹H, ¹³C) and Me₂Te (¹²⁵Te). Proton and ¹³C

Table 2
Mass spectral data for a crude sample of 'RTeBr₃'

Fragment	(EI) <i>m/z</i>	(FAB) <i>m/z</i>
C ₆ H ₅ ⁺	77	
(C ₆ H ₅) ₂ ⁺	152	152
(C ₆ H ₅) ₂ N ⁺		165
C ₆ H ₅ Te ⁺	206	
(C ₆ H ₅) ₂ Te ⁺	282	
C ₁₂ H ₉ N ₂ Te ⁺	311	311
C ₁₂ H ₉ N ₂ TeBr ⁺	390	391
C ₁₂ H ₉ N ₂ TeBrCl ⁺	425	
C ₁₂ H ₉ N ₂ TeBr ₂ ⁺	469	
C ₁₂ H ₉ N ₂ TeBr ₃ ⁺		549

Table 3
Crystal and experimental data

Formula	C ₁₂ H ₉ ClN ₂ Te	C ₁₂ H ₉ BrN ₂ Te	C ₁₂ H ₉ IN ₂ Te
Mr	344.3	388.7	435.7
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>I</i> 2/ <i>a</i>	<i>P</i> – 1	<i>P</i> – 1
<i>a</i> (Å)	20.217(10)	7.897(2)	8.011(2)
<i>b</i> (Å)	4.088(3)	11.022(2)	11.228(2)
<i>c</i> (Å)	28.863(14)	7.537(2)	7.677(2)
α (deg)	90.0	105.08(2)	105.81(3)
β (deg)	102.84(2)	91.94(1)	91.60(2)
γ (deg)	90.0	74.46(2)	73.85(3)
<i>V</i> (Å ³)	2326(2)	609.8(2)	637.4(2)
<i>Z</i>	8	2	2
<i>D</i> _c (g cm ⁻³)	1.966	2.117	2.270
μ (Mo K α)(mm ⁻¹)	2.759	5.688	4.750
Crystal size (mm)	0.2 × 0.15 × 0.15	0.3 × 0.3 × 0.25	0.2 × 0.2 × 0.15
Data range (θ) (deg)	3.2–25.3	2.8–25.2	2.8–25.2
Rflns. measured [<i>I</i> > σ (<i>I</i>)]	3234	3649	7145
Unique reflections	1573	1936	2034
<i>R</i> (int)	0.030	0.038	0.033
Variables	145	145	145
Δ/σ (max)	0.001	0.001	< 0.001
$\Delta\rho$ (max + ve)(eÅ ⁻³)	0.81	0.94	1.05
$\Delta\rho$ (max – ve)(eÅ ⁻³)	–0.91	–1.25	–1.21
<i>R</i>	0.0638	0.0551	0.0592
w <i>R</i> 2 ^a	0.1565	0.1569	0.1110
w(<i>a</i> · <i>b</i>) ^b	0.113, 0	0.089, 2.69	0.014, 6.12

^a w*R*2 = [$\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2$]^{1/2}.

^b w = 1/[$\sigma^2(F_o^2) + (aP)^2 + bP$] where $P = (F_o^2 + 2F_c^2)/3$.

NMR data were used for characterization purposes; the data were unremarkable and are not presented in this paper. The electron impact (Ei) and fast atom bombardment (FAB) mass spectra were obtained via the EPSRC Mass Spectrometry Service, University College, Swansea.

2.8. Crystallographic analysis

Data for all three structures were measured on a Rigaku *R*-axis II area detector diffractometer with Mo K α radiation at 293(2) K. The structures were determined by direct methods [9] and refined [10] by full-ma-

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for Chloride. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Te(1)	2613(1)	577(2)	–1774(1)	47(1)
Cl(1)	3495(1)	–1628(7)	–2193(1)	63(1)
N(1)	2336(4)	2244(18)	–809(2)	50(2)
N(2)	2044(3)	2329(18)	–1251(2)	43(2)
C(1)	3249(4)	–137(21)	–1117(3)	45(2)
C(2)	3887(4)	–1604(24)	–1019(3)	53(2)
C(3)	4241(5)	–1940(30)	–561(3)	64(3)
C(4)	3971(6)	–811(31)	–186(4)	74(4)
C(5)	3350(5)	534(27)	–262(4)	62(3)
C(6)	2983(5)	888(23)	–732(3)	51(2)
C(7)	1368(5)	3696(23)	–1367(3)	47(2)
C(8)	1115(6)	5546(22)	–1040(4)	55(2)
C(9)	465(5)	6742(27)	–1176(4)	61(3)
C(10)	77(5)	6167(27)	–1618(4)	59(3)
C(11)	328(6)	4372(24)	–1936(4)	57(3)
C(12)	983(4)	3134(25)	–1820(3)	52(2)

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for Bromide. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Te(1)	8281(1)	6335(1)	3261(1)	49(1)
Br(1)	9112(2)	3708(1)	2463(2)	74(1)
N(1)	6567(9)	8755(7)	1941(10)	48(2)
N(2)	7335(9)	8437(8)	3356(10)	48(2)
C(1)	7067(11)	6400(9)	785(11)	45(2)
C(2)	5865(12)	5349(10)	–629(12)	55(2)
C(3)	6022(13)	5578(10)	–2165(14)	61(2)
C(4)	5375(13)	6819(11)	–2372(13)	61(2)
C(5)	5544(12)	7881(11)	–1019(13)	57(2)
C(6)	6407(11)	7682(8)	577(11)	43(2)
C(7)	7585(11)	9475(8)	4828(12)	48(2)
C(8)	7593(13)	10697(9)	4569(13)	57(2)
C(9)	7885(15)	11643(11)	6091(16)	69(3)
C(10)	8184(14)	11395(12)	7769(15)	76(3)
C(11)	8211(15)	10192(10)	8003(14)	65(3)
C(12)	7900(13)	9219(10)	6557(12)	57(2)

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for iodide. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U(\text{eq})$
Te(1)	8209(1)	6405(1)	3218(1)	49(1)
I(1)	9121(1)	3643(1)	2471(1)	71(1)
N(1)	6572(10)	8785(8)	1881(11)	51(2)
N(2)	7277(11)	8503(8)	3282(11)	51(2)
C(1)	7055(12)	6450(9)	781(13)	46(2)
C(2)	6861(13)	5402(10)	-608(14)	54(3)
C(3)	6066(15)	5601(11)	-2141(15)	60(3)
C(4)	5441(14)	6845(12)	-2369(15)	60(3)
C(5)	5619(13)	7890(11)	-1046(14)	56(3)
C(6)	6441(12)	7701(10)	545(13)	48(2)
C(7)	7526(13)	9549(9)	4748(14)	49(2)
C(8)	7600(14)	10718(10)	4474(16)	60(3)
C(9)	7864(17)	11662(12)	5940(19)	74(3)
C(10)	8081(15)	11449(11)	7597(17)	69(3)
C(11)	8053(16)	10285(12)	7863(16)	72(3)
C(12)	7782(15)	9343(11)	6441(14)	60(3)

Table 7

Selected bond lengths (\AA) and angles (deg) with e.s.d.s in parentheses

	X = Cl	X = Br	X = I	X = Cl ^{a,b}
Te–C(1)	2.062(9)	2.078(8)	2.070(10)	2.12(8)
Te...N(2)	2.210(7)	2.219(8)	2.252(8)	2.21(2)
Te–X	2.533(3)	2.698(1)	2.877(1)	2.550(2)
N(1)–N(2)	1.281(9)	1.290(10)	1.276(11)	1.26(2)
N(1)–C(6)	1.392(11)	1.382(11)	1.388(13)	1.39(4)
N(2)–C(7)	1.445(11)	1.423(11)	1.444(13)	1.45(0)
C(1)–Te...N(2)	74.4(3)	74.7(3)	74.3(3)	74.8(20)
C(1)–Te–X	91.5(3)	93.4(3)	94.8(3)	91.9(29)
N(2)...Te–X	165.9(2)	168.1(2)	169.1(2)	166.6(10)
N(1)–N(2)...Te	118.5(5)	118.2(6)	117.8(7)	119(0)
C(7)–N(2)...Te	125.1(5)	125.1(5)	124.6(6)	125.5(15)

^aPrevious work [1].

^bMean values averaged over two independent molecules; standard deviations calculated from $|x_1 - x_2|/2$.

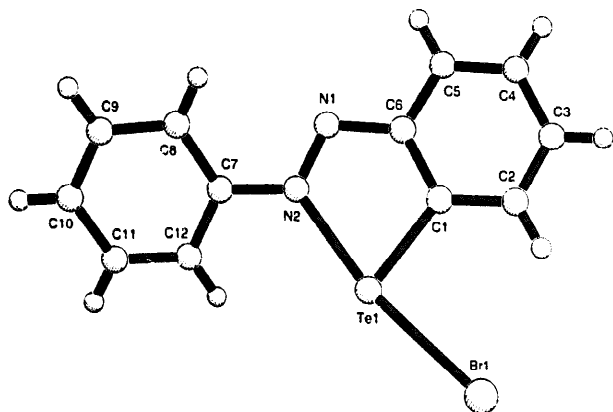


Fig. 1. CHARON plot of one molecule of phenylazophenyl(C,N')tellurium(II) chloride, showing the atom numbering.

trix least squares on F^2 using anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions. Crystal and refinement data are presented in Table 3. Atomic coordinates are given in Tables 4–6. Selected geometrical parameters are listed in Table 7. Hydrogen coordinates, displacement parameters and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Fig. 1 gives a CHARON [11] plot of one molecule of phenylazophenyl(C,N')tellurium(II) chloride, showing the atom numbering. Fig. 1 also represents the bromide and iodide molecules, the only visible differences being an approximately 0.14 \AA longer Te–halogen bond in the bromide, and a 0.34 \AA longer length for that bond in the iodide.

3. Discussion

Reaction of (2-phenylazophenyl-C,N')tellurenyl iodide with silver(I) fluoride following the method of Emeleus and Heal [3] gave an orange oil analysing as the monofluoride; interestingly the same product was obtained from 'RTeI₃,' [2] providing further support for the view that the triiodide is a charge transfer complex of the monoiodide and diiodine.

The analytical data obtained for the oil were found to be in agreement with the calculated values for 2-phenylazophenyl(C,N')tellurium fluoride (Table 1). ¹⁹F NMR of the oil, gave a resonance at -47.5 ppm with respect to aqueous sodium fluoride. Satellites due to ¹²⁵Te coupling were not seen in the spectra either because the samples was not pulsed for long enough, or the NMR solutions scanned were too dilute. ¹⁹F NMR spectroscopy of the oil showed a doublet ($J^{125}\text{Te}-^{19}\text{F} = 1197$ Hz) at 1234 ppm with respect to dimethyltellurium. The chemical shifts of the oils were consistent with formulation as tellurium(II) compounds [12], thereby supporting the identification as the monofluoride. The coupling constant may be compared with that measured for [2-(tolyliminomethyl)phenyl]tellurium(II) fluoride, 1346.5 Hz and it is noted that the Te atom is significantly more deshielded in the latter molecule ($\delta = 1634$ ppm vs. Me_2Te) [8].

Attempts were made to form 2-phenylazophenyl-(C,N')tellurium(IV) tribromide, RTeBr_3 by the reaction of 2-phenylazophenyl(C,N')mercury(II) chloride, RHgCl , with tellurium tetrabromide, but this gave an impure product. The mass spectra (Table 2) of the crude product, gave a parent ion of the tribromide ($\text{C}_{12}\text{H}_9\text{N}_2\text{TeBr}_3^+$, $m/z = 549$), providing evidence of the formation of the tribromide. However, the mass spectra also contained fragments having the correct isotopic patterns for mixed Te–halide species, e.g., $\text{C}_{12}\text{H}_9\text{N}_2\text{TeBrCl}^+$, $m/z = 425$. Mass spectral data were

also collected for the two samples that were separated by chromatography, but analysis of the data showed that the separation was not complete and that the components were mixtures.

The crude impure tribromide was however reduced, using hydrazine hydrate, to give pure monobromide, RTeBr. Synthesis of 2-phenylazophenyl(C,N')tellurium(II) iodide, RTeI occurred when the monobromide reacted with diiodine. It was interesting to note that crystals obtained from this synthesis diffracted well, yet when the same compound (analytically) was synthesised from metathesis of the monochloride with sodium iodide, the crystals failed to diffract [2]. It is interesting that oxidative addition of diiodine to the monobromide failed to afford a tellurium(IV) product. Immediate reductive elimination of BrI is possible, but it is believed that the monoiodide arose via a labile charge-transfer intermediate, a proposal which we believe to be supported by our previous studies of diiodine with tellurenyl compounds stabilised by intra-molecular co-ordination [7]:



Both the monobromide ($\delta = 983.25$ ppm, vs. Me_2Te) and monoiodide ($\delta = 989.9$ ppm, vs. Me_2Te), gave ^{125}Te NMR spectra consistent with expectation for Te(II) compounds.

3.1. Crystallographic investigations

Apart from the tellurium-halogen bond length, there is a close correspondence between the three structures, the bromide and iodide being, in fact, isomorphous. The nine-atom moiety, Te, N(1), N(2), C(1)–C(6), is essentially planar, r.m.s. atomic deviations 0.020 Å in the chloride, 0.010 Å in the bromide, and 0.015 Å in the iodide. The C(7)–C(12) phenyl ring is planar, r.m.s. deviations < 0.010 Å and is rotated about the N(2)–C(7) bond, relative to the nine-atom plane, by 16.7(4), 22.1(3) and 23.0(3)°, respectively, for the three structures.

The tellurium atom is formally bonded to a halogen atom and to an aromatic carbon atom, with an additional link to nitrogen atom N(2) *trans* to the halogen. The Te–Cl distance (Table 7) is near the upper end of the range 2.34–2.60 Å given in their compilation by Allen et al. [13] for this bond and is in good agreement with the mean value of 2.520(7) Å, but is slightly shorter than the lengths of 2.568 Å measured [14] in 1-chloro-1-hydro-*N-p*-tolyl-1-telluraisoindole and 2.606(11) Å in 2-(2'-pyridyl)phenyltellurium(II) chloride [2]. The Te–Br distance is in good agreement with the 2.707(11) Å found [15] in 2-(2'-pyridyl)phenyltellurium(II) bromide and is also within the range of distances, 2.632–2.758 Å, in the Te(IV) complex [2-(dimethylaminomethyl)-phenyl]tellurium tribromide [16]. Longer Te–Br distances, 2.835(1) Å and 2.969(1) Å, in

two crystal modifications of (ethylenethiourea)phenyltellurium(II) bromide [17] are associated with the stronger *trans*-influence of a sulfur atom, as compared with nitrogen, and the occurrence of N–H...Br hydrogen bonding. The flexibility of Te–halogen bonds is also demonstrated by the Te–Cl lengths in the hexachlorotellurate dianion in the bis(*NN'*-dimethylformamide)disulphide salt [18]. Here, there are three short Te–Cl bonds of 2.42–2.47 Å and three longer bonds of 2.60–2.74 Å, the long bonds each being involved in N–H...Cl hydrogen bonding [18].

The Te–I bond is slightly shorter than that given by Allen et al. [13] of 2.926(9) Å. It is also slightly shorter than measured [2] in 2-(2'-pyridyl)phenyltellurium(II) iodide, 2.917(1) Å and in 1-iodo-2-*p*-tolyl-1-tellura-2-azaindene [19], 2.936(1) Å, but falls well within the rather broad range of lengths which have been found previously for such bonds [20].

The Te–C bonds do not show any trend and are all close to 2.07 Å. This is somewhat shorter than generally found previously for tellurium bonded to an aromatic carbon atom, e.g., 2.116(2) Å, Allen et al. [13] and 2.077–2.112 Å in 2-(2'-pyridyl)phenyltellurium(II) halides [2,15].

The Te–N interaction (N donating an electron pair to Te) completes a trigonal bipyramidal type of coordination about the central tellurium atom, two lone pairs and the carbon atom C(1) equatorial, and the more electronegative nitrogen and halogen atoms, axial, in accord with VSEPR theory. The Te–N distances are similar to those observed [2,15] in the 2-(2'-pyridyl)-phenyl tellurium halides and follow the trend noted [2], that there is a slight increase in this distance as the atomic number of the *trans* halogen increases.

In each crystal structure there is one relatively short Te...halogen intermolecular contact, approximately *trans* to the bonded carbon atom. The relevant distances are 3.680(3) Å (chloride), 3.769(1) Å (bromide) and 3.895(1) Å (iodide), and the C(1)–Te...X angles are, respectively, 145.7(3), 173.9(3) and 173.0(3)°. These Te...X contacts fall within the category of secondary interactions [21].

Structural parameters obtained previously [1] for a triclinic modification of phenylazophenyl(C,N')tellurium(II) chloride are also listed in Table 7. This modification contains two independent molecules. The mean values listed in Table 7 are generally in good agreement with the values obtained in the present study.

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