Facile Access to Organotellurium Heterocycles by Nitration of Bis(3,5-Dimethylphenyl) Ditelluride

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Efficient access to bis(nitrophenyl) ditellurides was developed and their utility for the preparation of novel nitrogen-containing organotellurium heterocycles demonstrated. The nitration of diphenyl ditellurides resulted in their oxidation to benzenetellurinic acids, followed by nitration in *ortho* or *meta* positions relative to tellurium. Nitration of bis(3,5-dimethylphenyl) ditelluride furnished bis(3,5-dimethyl-2-nitrophenyl) ditelluride, which was elaborated into 2,4,6-trimethylbenzotellurazole and (*Z*)-2-methoxycarbonylmethylene-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine, the first reported 3,4-dihydro-2*H*-benzo-1,4-tellurazine. This compound, as well as 2,4,6-trimethyltellurazolium (4-dicyanomethylene-cyclohexa-2,5-dienylidene)cyanoacetate were characterized by x–ray crystallography.

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Introduction.

In analogy bis-(2-nitrophenyl) diselenides, bis(2-nitroaryl) ditellurides are expected to offer convenient access to various nitrogen-containing organotellurium heterocycles [1]. Bis(2-nitroaryl) ditellurides and their derivatives are of interest as potential precursors to substituted tellurazoles [2-4], polymethine dyes [5], and as organotellurium ligands [6]. Only one example of this class of compounds has been reported, however. Bis(2-nitrophenyl) ditelluride was prepared in two steps, starting with 2-lithionitrobenzene and benzyltellurocyanate [7]. Benzyltellurocyanate is light sensitive and 2-lithionitrobenzene is unstable above -100 °C, giving this approach a somewhat limited scope. More recently, the authors reported the synthesis of bis(2-nitrophenyl) ditelluride from 2-nitrophenylboronic acid [8]. Bis(2-nitrophenyl) ditellurides cannot be accessed by reacting 2-nitrohalobenzenes with the ditelluride anion, due to the strongly reducing properties of tellurium-containing anions of types RTe^-, Te_2^{2-} and Te^{2-} in general [9]. Instead, other synthetic strategies are required for the preparation of organotellurium heterocycles such as tellurazoles and tellurazines. These include their synthesis from organomercury precursors [2], by reduction of oxatellurazolium salts [3], by reduction of 2-azophenyltellurium halides [10], by photostimulated telluromethylation [11], and access *via* 2-nitrophenylboronic acids [8]. All of these have limited scope or utilize relatively inaccessible precursors. Other Te-N heterocycles such as 1,4-benzotellurazines also should be accessible *via* bis(2-nitroaryl) ditellurides, but remain largely unknown to date.

Treatment of diaryl ditellurides with nitric acid invariably leads to oxidation of the ditelluride moiety before ring substitution [12]. Further nitration of the resulting aryltellurinic acids, however, has not been investigated in much detail. Evidence exists for the feasibility of *ortho* nitration with respect to the tellurinic acid moiety despite its electron-withdrawing properties. Thus, nitration of bis-(3,4-dimethoxyphenyl) ditelluride followed by partial reduction in the presence of chloride has been reported to generate 1-chloro-5,6-dimethoxybenzo[2,1,3]oxatellurazole-*N*-oxide, shown in Figure 1 [10].

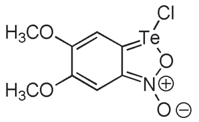


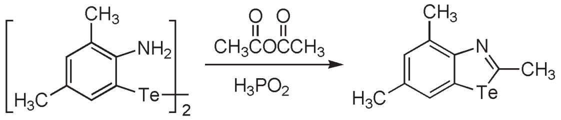
Figure 1. 1-Chloro-5,6-dimethoxybenzo[2,1,3]oxatellurazole-*N*-oxide

This indicates that the regioselectivity of nitration of aryltellurinic acids may not be as predictable as that of the corresponding sulfonic acids due to the formation of products with Te-O coordination. 1-Chloro-5,6-dimethoxybenzo[2,1,3]oxatellurazole-*N*-oxide formally can be regarded as 4,5-dimethoxy-2-nitrophenyl-tellurium chloride; in fact, 2-nitroaryltellurinic acids and their derivatives tend to be heterocyclic in nature [13]. It seemed plausible that 2-nitroaryltellurinic acids can be prepared from appropriately substituted diphenyl ditellurides by a one-pot oxidation-nitration procedure, thereby offering improved access to organotellurium heterocycles.

The synthesis of six-membered Te-N heterocycles is challenging and has been limited to that of phenotellurazines [14,15]. Thus, the preparation of benzo[1,4]thiazines by condensation of α-halocarbonyl compounds with 2-aminobenzenethiols cannot be adapted to generate the corresponding benzotellurazines due to reductive dehalogenation of the α-halocabonyl compound by tellurolate anions [16]. Consequently, the condensation of 2-aminobenzenetellurols with dimethylacetylenedicarboxylate was investigated as a possible entry point to six-membered

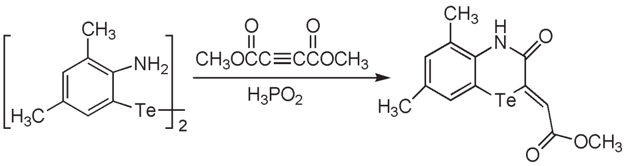
Te-N heterocycles, in analogy to that reported for 2-aminobenzenethiol [17]. The conversion of bis(3,5-dimethyl-2-nitrophenyl) ditelluride to derivatives of benzotellurazole and (*Z*)-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine as shown in Schemes 1 and 2 did indeed proceed smoothly.

Scheme 1



Synthesis of 2,4,6-trimethylbenzotellurazole **6**

Scheme 2



Synthesis of (*Z*)-2-methoxycarbonylmethylene-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine **7**

EXPERIMENTAL

Hydrochloric acid, nitric acid, sulfuric acid and sodium metabisulfite were obtained from Fisher Scientific. Dimethyl acetylenedicarboxylate was purchased from Acros. All other reagents were purchased from Aldrich Chemical Company and used as received. Melting points were recorded using an electrothermal EM-6 apparatus, and are not corrected. Nuclear magnetic resonance spectra were recorded on a Jeol Eclipse 300 MHz spectrometer. Mass spectrometry was performed on a Finnigan Mat GCQ mass spectrometer under 70 eV electron impact conditions with direct probe inlet. Infrared spectra were recorded with the multiple internal reflectance (MIR) technique on a Perkin Elmer Paragon FTIR spectrometer. Elemental analyses were performed by Gailbraith Laboratories and in-house on an Exeter Analytical CE-440 Elemental Analyzer.

Bis(3,5-dimethylphenyl) ditelluride (**1**).

A 250 mL round bottom flask equipped with a magnetic stirrer and reflux condenser was charged with 1-bromo-3,5-dimethylbenzene (10.0 g, 62 mmol), magnesium turnings (1.8 g, 74 mmol) and anhydrous tetrahydrofuran (80 mL). The mixture was heated until no more magnesium dissolved (approx. 1 h) and then chilled to 0 °C in an ice bath. Tellurium powder (200 mesh, 7.92 g, 75 mmol) was added, the mixture removed from the ice bath and stirred vigorously. Most tellurium powder went into solution within 30 min. The mixture was then exposed to air by removing the reflux condenser and leaving the neck of the flask uncovered. Stirring was continued overnight to assure complete oxidation of the intermediate tellurolate. The mixture was then diluted with ice water (100 mL), acidified with 36% hydrochloric acid (10 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The solvent was removed and the residue crystallized by addition of ethanol (15 mL) and chilling in an ice bath. Recrystallization from ethanol furnished 8.82 g (73%) of red needles; mp 50-52 °C; ir: 2915, 1597, 1563, 1458, 1036, 987, 837, 786, 602 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.13 (s, 3H, -CH_3), 2.15 (s, 3H, -CH_3), 6.85 (s, 1H, phenyl), 7.38 (s, 2H, phenyl); ^{13}C nmr ($CDCl_3$): δ 21.14, 130.22, 135.64, 138.77; ^{125}Te ($CDCl_3$): δ 415.1; ms: *m/z* 571 (11), 468 (39), 338 (20), 212 (100). This compound underwent slow oxidation while in solution.

Anal. Calcd. for $C_{16}H_{18}Te_2$: C, 41.28; H, 3.90. Found: C, 40.91; H, 4.02.

Bis(3-nitrophenyl) ditelluride (**2**).

A round bottom flask with magnetic stirring was charged with concentrated sulfuric acid (20 mL), submersed in an ice bath, and benzenetellurinic acid nitrate (5.0 g, 17.69 mmol) prepared according to the literature [18] was slowly added in approx. 0.2 g batches. The mixture was stirred at ambient temperature for 12 h and subsequently poured over crushed ice (50 g). Crude 3-nitrobenzenetellurinic acid precipitated and was collected by filtration. Without drying, this was suspended in water (50 mL) and reduced by adding sodium metabisulfite (4.0 g, 21.0 mmol) and stirring for 12 h at ambient temperature. The product was extracted with CH_2Cl_2 (2 x 25 mL). Crystallization from ethanol furnished 2.98 g (68%) dark red crystals. The product was identical to a sample prepared by a previously published procedure [8].

Bis(3,5-dimethyl-2-nitrophenyl) ditelluride (**3**).

A round bottom flask with magnetic stirring was charged with powdered bis(3,5-dimethylphenyl) ditelluride (**1**) (6.0 g, 12.89 mmol). The flask was submersed in an ice bath and 70% nitric acid (12.0 mL, 254 mmol) slowly added using a pipette (**Caution! Copious evolution of nitrous oxides**). Any remaining lumps were broken up with a glass rod. After completed oxidation, concentrated sulfuric acid (16 mL) was slowly added with cooling to keep the temperature of the mixture below 50 °C. The mixture was stirred overnight and then diluted with ice water (100 mL) and ethanol (5 mL). Excess acid was buffered by addition of sodium acetate until pH >4, followed by reduction with sodium metasulfite (8.0 g, 42 mmol). A blood-red precipitate formed (possibly due to formation of an oxatellurazolium salt), which gradually gave way to a brown precipitate upon stirring for 8 h at ambient temperature. Solids were collected on a Büchner funnel, washed with approximately water (50 mL) and dissolved in CH_2Cl_2 (50 mL). Insoluble matter (mostly elemental tellurium) was removed by filtration and the solvent evaporated. Recrystallization from ethyl acetate furnished 5.4 g (75%) of orange crystals; mp 168-170 °C; ir 2928, 1590, 1558, 1505, 1296, 840; ^1H nmr ($CDCl_3$): δ 2.27 (s, 3H, -CH_3), 2.52 (s, 3H, -CH_3), 7.03 (s, 1H, phenyl), 7.80 (s, 1H, phenyl); ^{13}C nmr ($CDCl_3$): δ 21.08, 21.22, 107.98, 133.48, 135.13, 138.72, 143.82, 148.91; ^{125}Te nmr ($CDCl_3$): δ 532.8; ms: *m/z* 556 (20), 430 (24), 359 (59), 264 (100).

Anal. Calcd. for $C_{16}H_{16}N_2O_4Te_2$: C, 34.58; H, 2.88; N, 5.06. Found: C, 34.45; H, 2.90; N, 5.04.

4-*tert*-Butyl-3-nitrophenyl tellurium tribromide (**4**).

A round bottom flask with magnetic stirring was charged with of powdered bis(4-*tert*-butylphenyl) ditelluride (2.0 g, 3.83 mmol), prepared according to Haller and Irgolic's procedure [19]. The flask was immersed in an in an ice bath and 70% nitric acid

(4.0 mL 63 mmol) was then slowly added (**Caution! Copious evolution of nitrous oxides**). Any remaining lumps were broken up with a glass rod. The mixture was stirred overnight after which it had turned into an off-white paste. Acetonitrile (10 mL) was added and precipitated crude tellurinic acid nitrate collected by filtration. This crude product was added to an ice-cold mixture of 70% nitric acid (3 mL, 23.5 mmol) and concentrated sulfuric acid (6 mL). The mixture was stirred overnight and then heated to 50 °C for one hour in a water bath. It was diluted with water (150 mL), buffered to pH >4 with sodium acetate, and reduced by adding of sodium metabisulfite (6.0 g, 31.5 mmol) and stirring for 12 h at ambient temperature. The product was extracted with CH_2Cl_2 (2 x 20 mL) and the solvent removed by evaporation. All efforts to crystallize bis(4-*tert*-butyl-3-nitrophenyl) ditelluride failed; consequently, the crude ditelluride was taken up in carbon tetrachloride (10 mL) and converted to 4-*tert*-butyl-3-nitrophenyl tellurium tribromide by adding a 50% solution of bromine in carbon tetrachloride until the color of the solution changed from red to lemon-yellow. The product precipitated as a yellow microcrystalline solid, yield 3.10 g (74%). An analytical sample was obtained by recrystallization from acetic acid; mp 210-212 °C (with partial decomposition); ir: 2962, 2525, 1532, 1365, 1060, 823, 662; ^{1}H nmr (DMSO-d_6): δ 1.37 (s, 9H), 7.80 (d, 1H, phenyl), 8.53 (m, 1H, phenyl), 8.74 (m, 1H, phenyl); ms: *m/z* 466 (26, M^+-Br), 387 (100), 372 (52).

Anal. Calcd. for $C_{10}H_{12}Br_3NO_2Te$: C, 22.02; H, 2.22. Found: C, 22.16; H 2.42.

Bis(2-amino-3,5-dimethylphenyl) ditelluride (**5**).

Bis(3,5-dimethyl-2-nitrophenyl) ditelluride (**3**) (0.50 g, 0.90 mmol) was suspended in absolute ethanol (30 mL) and the mixture was magnetically stirred and heated to 90 °C. Sodium borohydride was slowly added and the mixture warmed until the color of the mixture faded. An additional **3** (4.5 g) was then added in batches of approximately 100 mg, followed each time by as much sodium borohydride as necessary for complete discoloration. No effort was made to control the temperature of the reaction mixture, resulting in boiling and considerable loss of ethanol by evaporation. In total, **3** (5.0 g, 9.0 mmol) was reduced with sodium borohydride (6.02 g, 159.1 mmol). The resulting solution was diluted with water (200 mL) and the mixture stirred for 48 h in an open beaker to assure complete oxidation of the tellurol to the ditelluride. The product was collected by filtration, dissolved in CH_2Cl_2 (50 mL), insoluble matter removed by filtration and the solvent removed by evaporation on a water bath at 60 ºC under an aspirator vacuum. Crystallization from ethanol produced 3.8 g (85%) of product as orange crystals; mp 138-139 °C; ir 3402, 3330, 2921, 2851, 1614, 1470, 1234, 862; ^{1}H nmr ($CDCl_3$): δ 2.12 (s, 3H, $-CH_3$), 2.14 (s, 3H, $-CH_3$), 4.03 (2H, NH), 6.84 (s, 1H, phenyl), 7.39 (s, 1H, phenyl); ^{13}C nmr ($CDCl_3$): δ 18.99, 20,00, 96.11, 121.21, 128.23, 133.70, 141.29, 146.18; ^{125}Te nmr ($CDCl_3$): δ 271.6; ms: *m/z* 496 (15), 375 (28), 240 (100). The compound has a pronounced tendency to undergo decomposition in solution and usually is contaminated with traces of elemental tellurium.

Anal. Calcd. for $C_{16}H_{20}N_2Te_2$: C, 38.74; H, 4.04; N, 5.65. Found: C, 38.50; H, 3.82; N, 5.44.

2,4,6-Trimethylbenzotellurazole (**6**).

A round bottom flask with magnetic stirring and reflux condenser was charged with a solution of bis(2-amino-3,5-dimethylphenyl) ditelluride (**5**) (1.0 g, 2.02 mmol) in THF (10 mL), acetic anhydride (20 mL) and 50% hypophosphorous acid (2.0 mL, 38.5 mmol). The mixture was heated at reflux for 15 min, after which time its color had changed from dark brown to yellow-gray. The mixture was diluted with water (100 mL), neutralized with sodium bicarbonate and solid material collected by filtration. This was dissolved in CH_2Cl_2 (10 mL), byproducts removed by flash chromatography (1.5 × 5 cm column, 200 mesh silica gel, CH_2Cl_2) and the solvent removed by evaporation. Treatment of the remaining orange oil with methanol (2 mL) and chilling in an ice bath induced crystallization. (In some instances, crystallization was achieved with difficulty and seeding or extensive refrigeration became necessary). Recrystallization from methanol at -20° C produced 0.40 g (36%) of product as pale yellow solid; mp 42-44° C; ir 2915, 1599, 1560, 1543, 1429, 1286, 1120, 845, 776, 735, 558; ^{1}H nmr ($CDCl_3$): δ 2.34 (s, 3H, 2-CH_3), 2.74 (s, 3H, phenyl-CH_3), 2.84 (s, 3H, phenyl-CH_3), 7.02 (s, 1H, phenyl), 7.48 (s, 1H, phenyl); ^{13}C nmr ($CDCl_3$): δ 20.92, 21.19, 30.79, 129.22, 129.25, 129.28, 134.74, 135.04, 157.81, 166.84; ^{125}Te nmr ($CDCl_3$): δ 911.1; ms: m/z 275 (75), 234 (21), 103 (95). 77 (100).

Anal. Calcd. for $C_{10}H_{11}NTe$: C, 44.02; H, 4.07; N, 5.12. Found: C, 43.98; H, 4.13; N, 4.95.

(*Z*)-2-Methoxycarbonylmethylene-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine (**7**).

A round bottom flask with stirring and reflux condenser was charged with bis-(2-amino-3,5-dimethylphenyl) ditelluride (**5**) (100 mg, 0.20 mmol), dimethyl acetylenedicarboxylate (85 mg, 0.60 mmol), THF (2 mL) and methanol (3 mL). To this solution was added 50% hypophosphorous acid (50 mg, 0.76 mmol), followed by 37% hydrochloric acid (50 mg, 18.5 mmol). The mixture was stirred and heated to reflux for 10 min, then diluted with water (20 mL). Solids were collected by filtration, taken up in CH_2Cl_2 (10 mL) and chromatographed on a 0.8 × 4 cm column (neutral alumina, CH_2Cl_2 followed by CH_2Cl_2-acetonitrile 10:1 v/v). A small quantity of light yellow material eluted before the main fraction, which was collected as an orange band. Recrystallization from nitromethane furnished 33 mg (24%) of product as pale yellow crystals; mp 226-228 °C (with darkening and partial decomposition); ir: 2924, 2360, 1639, 1546, 1304, 1204; ^{1}H nmr ($CDCl_3$): δ 2.26 (s, 3H, phenyl-CH_3), 2.36 (s, 3H, phenyl-CH_3), 3.87 (s, 3H, $-OCH_3$), 6.90 (a, 1H, =CH), 7.16 (s, 1H, phenyl), 7.93 (1H, NH); 8.23 (1H, phenyl); ^{13}C nmr ($CDCl_3$): δ 13.37, 15.52, 39.89, 79.06, 94.31, 94.80, 98.56, 98.97, 100.69, 101.66, 118.96, 128.64; ^{125}Te nmr ($CDCl_3$): δ 656.0; ms: *m/z* 361 (56), 231 (100), 172 (63).

Anal. Calcd. for $C_{13}H_{13}NO_3Te$: C, 43.51; H, 3.65; N, 3.90. Found: C, 43.73; H, 3.71; N, 3.65.

2,4,6-Trimethyltellurazolium (4-dicyanomethylenecyclohexa-2,5-dienylidene)cyanoacetate (**8**).

Solutions of 2,4,6-trimethyl-benzotellurazole (**6**) (300 mg, 1.1 mmol) and 7,7,8,8-tetracyanoquinodimethane (225 mg, 1.1 mmol) in acetonitrile (5 mL) each were combined in a glass vial and set aside for slow open-air evaporation over approx. 5 days. The mixture gradually darkened and approximately 40 mg of metallic-blue crystals formed. Several well-formed crystals were manually separated from oily byproducts and collected for x-ray crystallography. Attempts to isolate the product in analytically pure form were unsuccessful.

Tellurium Expulsion from Bis(2-amino-3,5-dimethylphenyl) ditelluride.

A round bottom flask with magnetic stirring and reflux condenser was charged with a solution of bis(2-amino-3,5-dimethylphenyl) ditelluride (**5**) (0.5 g 1.0 mmol) in 37% hydrochloric acid (10 mL) The mixture was heated at reflux for 2 h. The reaction mixture was diluted with water (20 mL) and precipitated solids removed by filtration. The filtrate was neutralized with sodium carbonate solution and extracted with CH_2Cl_2 (2×10 mL). Rotary evaporation produced a pale yellow oil (211 mg), which was analyzed by GC-MS. Comparison with authentic material indicated the formation of 3,5-dimethylaniline as the only major product. No semivolatile organic tellurium compounds were observed.

Results and Discussion.

The nitration of diphenyl ditelluride and bis(4-*tert*-butylphenyl) ditelluride did not produce benzo[2,1,3]oxatellurazole *N*-oxides in analogy to that of bis(3,4-dimethoxyphenyl) ditelluride. Instead, *meta*-nitrated products were isolated exclusively. Clearly, potential Te-O coordination in the product and moderate steric hindrance in *para* position did not impose the desired regioselectivity. While *meta* nitrated diaryl ditellurides are of potential interest for the preparation of macrocyclic organotellurium compounds, they clearly are not suited for the synthesis of tellurazoles and tellurazines. In contrast, blockage of both *meta* positions resulted in *ortho* nitration without evidence for the formation of a *para* isomer. Temperatures in excess of 50 °C during nitration were found to result in increased tellurium-carbon bond fission. No satisfactory conditions could be found for the reduction of bis(3,5-dimethyl-2-nitrophenyl) ditelluride (**3**) directly to bis(2-amino-3,5-dimethylphenyl) ditelluride (**5**). Instead, the complete reduction of **3** to 2-amino-3,5-dimethylbenzenetellurol was followed by air oxidation to **5**. The use of hypophosphorous acid in excess to counteract atmospheric re-oxidation was found to be more convenient than work under inert atmosphere. The acid sensitivity of **5** is noteworthy in light of acidic conditions used in subsequent cyclizations. Clearly, exposure of this compound to acids has to be kept as brief as possible. Indeed, tellurium expulsion appears to be a major side reaction inherently limiting the yields of **6** and **7** under acidic conditions.

Spectroscopy.

In accordance with those of other benzotellurazoles [2], the mass spectrum of **6** featured a strong molecular ion cluster. Other intense ions correspond to the loss of acetonitrile and to tellurium elimination. The ^{125}Te shift of **6** indicates significant deshielding of tellurium and is very similar to those measured for other benzotellurazoles [2]. Deshielding is less pronounced for **7**, the ^{125}Te shift of which is typical of that expected for organotellurium(II) compounds [20].

Molecular Structure of the 2,4,6-Trimethylbenzotellurazolium Cation

Several attempts to obtain crystals of **6** suitable for X-ray crystallography were unsuccessful, due to the pronounced tendency of this compound to form disordered crystals of poor quality. Consequently, the preparation of a 1:1 adduct of **6** with 7,7,8,8-tetracyanoquinodimethane (TCNQ) was attempted, with unexpected results. The formation of several well-formed crystals of **8** appears to have resulted from partial hydrolysis of TCNQ under open-air conditions [21]. No attempt was made to optimize the preparation of **8** as its sole purpose was the characterization of the benzotellurazole structure by X-ray crystallography. The structure of **8** can be compared to that of 2-phenylbenzotellurazole **9** (Figure 2), the only benzotellurazole derivative for which structural parameters have been reported [22]. Table 1 summarizes selected properties for both compounds. The Te-C1 and Te-C3 bond lengths are within the normal ranges of those typically observed for sp^3 and sp^2 carbon-tellurium bonds, respectively. The angles C1-Te-C8 are similar to that of 80.3° previously reported for tellurophene [23]. The 2,4,6-benzotellurazolium cation was found to be essentially planar, with a mean standard deviation from planarity for all non-hydrogen atoms of 0.017 Å.

Compound	**8**	**9**
Te–C1 bond length, Å	2.06(2)	2.12
Te–C3 bond length, Å	2.08(2)	2.08
C1–N bond length, Å	1.30(3)	1.29
C1-Te-C3 bond angle	80.1(5)	78.6

Table 1. Selected structural parameters for the 2,4,6-benzotellurazolium cation in **8** as compared to those published for 2-phenylbenzotellurazole **9**. Indexing follows that in Figure 2

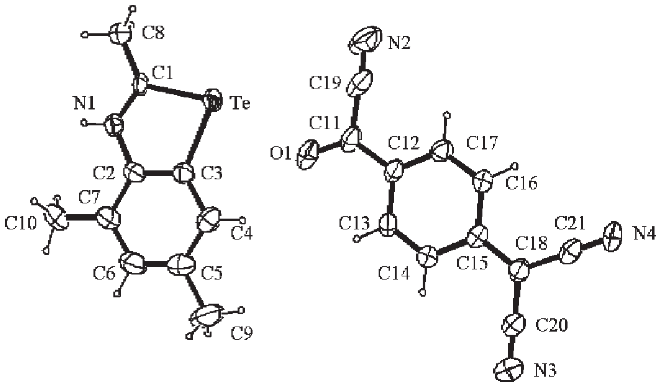


Figure 2. ORTEP plot of 2,4,6-trimethyltellurazolium cyano-(4-dicyanomethylene-cyclohexa-2,5-dienylidene)-acetate **8**.

Molecular Structure of (*Z*)-2-Methoxycarbonylmethylene-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine (**7**).

Well-formed crystals of **7** were obtained by slow evaporation of a solution in DCM. Each unit cell contains two molecules of nearly identical geometry, one of which is shown in Figure 3. Bond lenghts of 1.413(2) Å for the C2-N1 bond and 2.0954(2) Å for the C1-Te distance resemble the molecular geometry of phenotellurazine, for which average lengths of 1.40 Å and 2.10 Å were reported for the C-N and C-Te bonds, respectively [14]. In contrast to benzotellurazine, however, **7** was found to be planar with a mean standard deviation from palanrity of 0.072 Å for all non-hydrogen atoms. The angle C1-Te-C4 of 93.38(6)° is significantly larger that those found in benzotellurazoles.

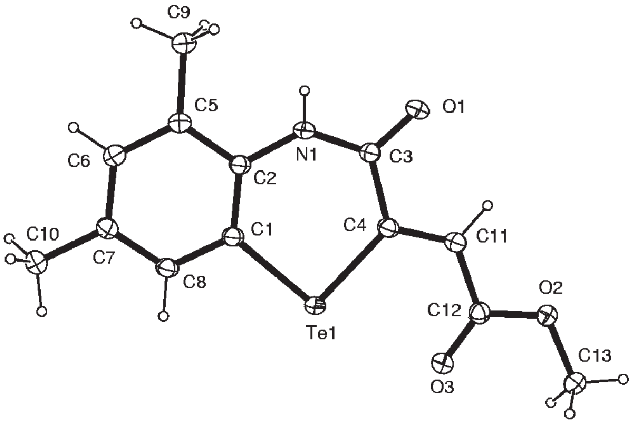


Figure 3. ORTEP plot of (*Z*)-2-methoxycarbonylmethylene-3,4-dihydro-3-oxo-2*H*-benzo-1,4-tellurazine **7**.

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