

# A polyfluoroaromatic tellurium–nitrogen compound: synthesis and properties of 4,5,6,7-tetrafluoro-2λ<sup>4</sup>δ<sup>2</sup>,1,3-benzotelluradiazole†

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4,5,6,7-Tetrafluoro-2λ<sup>4</sup>δ<sup>2</sup>,1,3-benzotelluradiazole compound **2** (and a <sup>15</sup>N-enriched sample) is synthesized by treating TeCl<sub>4</sub> with the corresponding diamine **4** in the absence of HCl acceptors. Some of its properties, e.g. high volatility, facile hydrolysis and vibrational frequencies, are experimentally determined.

2,1,3-Telluradiazole **1** and its derivatives have a crystalline ribbon polymeric structure which accounts for their chalcogenadiazole nontypical properties such as high melting points, nonvolatility and poor solubility in common solvents.<sup>1–4</sup> These properties complicate the investigation of the reactivity of **1** and related compounds so we therefore synthesised and studied compound **2**, which, unlike **1**, has high volatility and strong affinity for double bonds.

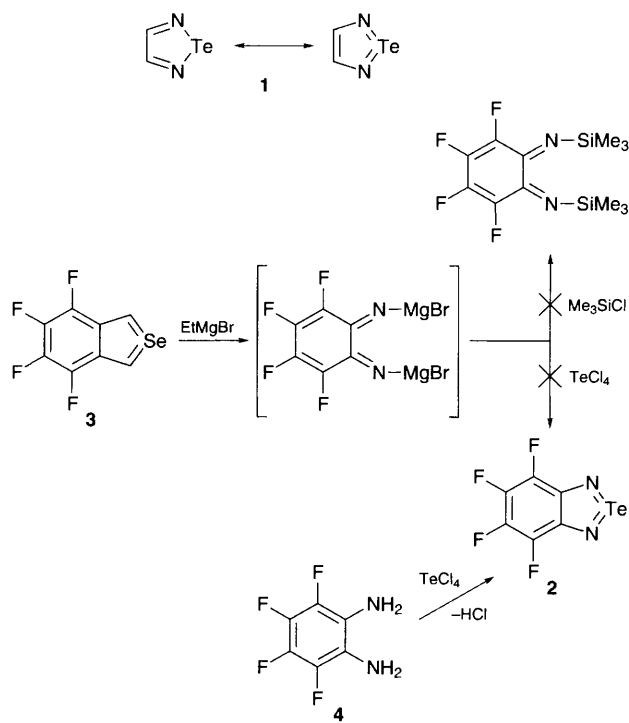
Compound **2** cannot be prepared in a similar way to **1**<sup>1,4</sup> by the treatment of corresponding selenadiazole **3** with EtMgBr and then TeCl<sub>4</sub>. Attempts to trap the postulated<sup>1</sup> key intermediate (Scheme 1) in the form of the *N,N'*-bis(trimethylsilyl) derivative were also unsuccessful. Thus, the suggested<sup>1,4</sup> synthetic pathway to the 2,1,3-telluradiazole system is very limited in the case of fused polyfluoroaromatic derivatives. It has been shown, however, that **2** (including a <sup>15</sup>N-enriched sample) can be synthesized by the treatment of TeCl<sub>4</sub> with the corresponding diamine **4**.‡ It is important not to use HCl

acceptors in this case, unlike the reported syntheses of the sulfur, selenium and hydrocarbon analogues of **4** from chalcogen tetrahalides and the corresponding 1,2-diaminobenzenes.<sup>5</sup> In the presence of common HCl acceptors such as Et<sub>3</sub>N, the formation of unreactive complexes, probably of the type HCl·Et<sub>3</sub>N·TeCl<sub>4</sub>,<sup>6</sup> takes place. The starting diamine **4** does not protonate in the presence of HCl in the reaction conditions because of low basicity typical for polyfluoroarylamines.

As expected, **2** is quite volatile‡ as compared with known telluradiazoles<sup>1,4</sup> so their is potential to study its reactivity. Among the chemical properties of **2** a moderate sensitivity to air moisture should be noted first of all. Hydrolysis in aqueous Me<sub>2</sub>SO occurs readily to give **4** and TeO<sub>2</sub>. This is different from the properties of both **3** (which is stable towards H<sub>2</sub>O) and **1** (which easily decomposes by acidic water to give the corresponding 1,2-dicarbonyl compound besides H<sub>2</sub>TeO<sub>3</sub>, elemental Te and ammonium salts<sup>1</sup>).§

The IR spectrum of **2** is very similar to that of **3**<sup>7</sup> except in the 850–500 cm<sup>-1</sup> region where vibrations with large XN bonds (X = Se, Te) predominate. The corresponding frequencies (identified by means of <sup>15</sup>N isotopic band shifts) are 696, 660 and 548 cm<sup>-1</sup> for **2**‡ as compared with 829, 757 and 689 cm<sup>-1</sup> for **3**.<sup>7</sup> According to normal calculations,<sup>3</sup> analogous values for **1** are equal to 660, 480 and 378 cm<sup>-1</sup>.

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Scheme 1

## Footnotes

† According to the results of a search of the CA database of STN international, the parent 2,1,3-benzotelluradiazole is unknown.

‡ A typical procedure is as follows. A stirred mixture of **4** (0.45 g), TeCl<sub>4</sub> (0.67 g) and *ortho*-dichlorobenzene (40 cm<sup>3</sup>) was boiled for 1.5 h in an argon atmosphere. The mixture was cooled to 20 °C, the dark precipitate was filtered off, sublimed in 10<sup>-2</sup> Torr vacuum at 180 °C and then recrystallized from DMF to give **2**, 0.16 g (20%) shiny orange–brown flakes, mp > 265 °C. A sample of **2** labelled with <sup>15</sup>N (ca. 80% enrichment) at the 1-position was prepared in the same way. *Physical and spectroscopic data* for **2**. <sup>19</sup>F NMR (Bruker AM-400, 376.4 MHz) δ<sub>F</sub> (internal C<sub>6</sub>F<sub>6</sub>; [2H<sub>6</sub>]Me<sub>2</sub>SO): 13.09 (2 F) and 0.36 (2 F). UV–VIS (Specord M40) λ<sub>max</sub>/nm (KBr): 395. IR (Bruker IFS 66) ν(Δν <sup>15</sup>N)/cm<sup>-1</sup> (KBr): 1680 s, 1599 m, 1526 (2) s, 1466 (2) vs, 1371 vs, 1339 vs, 1059 (2) m, 1036 (2) vs, 1015 vs, 696 (11) m, 660 (6) m, 548 (4) s, 451 (2) m and 436 m (weak bands have been omitted). M<sup>+</sup> (Finnigan MAT MS-8200, EI, 70 eV), *m/z*, measured (calculated): 305.9059 (305.9065, <sup>130</sup>Te); <sup>15</sup>N-enriched sample: 306.9025 (306.9035; <sup>15</sup>N, <sup>130</sup>Te).

§ The <sup>19</sup>F NMR spectrum shows that in water containing Me<sub>2</sub>SO, **2** turns quickly to **4** (δ<sub>19F</sub>: -1.27 and -15.11; δ<sub>H</sub>: 4.92). A white precipitate of TeO<sub>2</sub> appears at the same time. It follows from PM3 calculations with geometry optimization that in the case of **2** nucleophilic attack on Te is aided by complete localization of the LUMO on the positively charged Te atom (q<sub>Te</sub> 0.48). Unlike **3**<sup>6</sup> which has Te-frontier MOs, in **2** these MOs (–ε, eV: HOMO 9.88, LUMO 2.32) are Te-localized σ (HOMO can be described as n<sub>Te</sub>).

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