

## Chalcogen Bonding

## The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions: A First Experimental Structure from the Gas Phase

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Dedicated to Professor Thomas M. Klapötke on the occasion of his 60th birthday

**Abstract:**  $(C_6F_5)_2Te(CH_2)_3NMe_2$  (**1**), a perfluorophenyltellurium derivative capable of forming intramolecular  $N\cdots Te$  interactions, was prepared and characterized. The donor-free reference substance  $(C_6F_5)_2TeMe$  (**2**) and the unsupported adduct  $(C_6F_5)_2(Me)Te\cdot NMe_2Et$  (**2b**) were studied in parallel. Molecular structures of **1**, **2** and **2b** were determined by single-crystal X-ray diffraction and for **1** and **2** by gas-phase electron diffraction. The structure of **1** shows  $N\cdots Te$  distances of 2.639(1) Å (solid) and 2.92(3) Å (gas). *Ab initio* plus NBO and QTAIM calculations show significant charge transfer effects within the  $N\cdots Te$  interactions and indicate  $\sigma$ -hole interactions.

Dispersion interactions have recently received an increasing amount of attention.<sup>[1]</sup> They can add the decisive component in stabilizing otherwise weak interactions, for example, halogen bonding (XB) systems.<sup>[2]</sup> Hitherto, XB interactions were mainly studied by experiments in the solid or in solution phase.<sup>[3]</sup> However, under these conditions it is difficult to distinguish contributions to the strength of this interaction from intermolecular dispersion or electrostatic forces often summarized nonspecifically as “packing” or “solvent” effects.<sup>[4]</sup> The determination of quantitative energies and a qualitative interpretation of inter- and intramolecular interactions still remain challenging tasks.<sup>[1]</sup> There is also still a distinct paucity in corresponding gas-phase structure data because gas-phase experiments and data analyses are generally much more challenging and labor-intensive than those for the solid state.<sup>[5,6]</sup> The investigation of free molecules is, however, restricted in size, volatility and thermal stability of the compounds, and in particular difficult if weak interactions are involved due to soft-potential motions.

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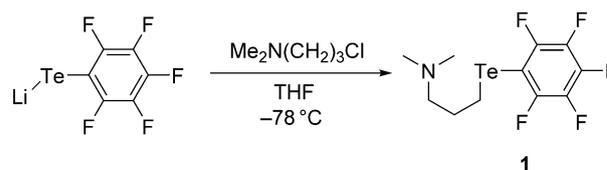
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In 1990 Singh et al. reported the existence of special  $N\cdots Te$  interactions in tellurium(IV) derivatives with benzylamine ligands in the solid phase.<sup>[7]</sup> The stabilizing effect was demonstrated by Hammerl et al. for the same benzylamine derivatives<sup>[8]</sup> and Rakesh et al. crystallized a system containing  $N\cdots Te-Cl$  units with a stronger interaction between nitrogen and tellurium atoms (2.355(3) Å in  $ClTe(o-C_6H_4)-CH_2NMe_2$ ).<sup>[9]</sup> In fact, the investigated systems describe donating interactions between the heavy atom tellurium and the nitrogen atom, but a substantial proof in the gas phase is still missing to exclude pure solid-state effects.

For this purpose we now prepared (*N,N*-dimethylamino-propyl)(pentafluorophenyl)telluride (**1**) (Scheme 1). Its  $^{125}Te\{^1H\}$  NMR spectrum shows a triplet ( $^3J_{Te,F} = 64$  Hz) at 353 ppm. The fact that the  $^{125}Te\{^1H\}$  NMR resonance of  $Te(C_6F_5)_2$  is a quintet at 305 ppm<sup>[10]</sup> allows to conclude the tellurium atom in **1** to be weakly coordinated in solution— intra- or intermolecularly—by an electronegative element such as nitrogen.

Suitable crystals for X-ray diffraction (XRD) of **1** were obtained by sublimation. Its molecular structure in the solid state (Figure 1) shows a  $N\cdots Te$  distance of 2.639(1) Å. The distance from Te1 to the *ipso*-carbon atom C1 of the perfluorophenyl unit is 2.189(1) Å; this is rather long compared to bis(pentafluorophenyl)diteLLuride at 2.124(1) Å<sup>[11]</sup> and bis(pentafluorophenyl)telluride<sup>[10]</sup> (2.101(6) Å) and is explicable by population of the antibonding  $Te1-C1$  orbital by the donating nitrogen function in the NBO picture. As expected, the angle  $C1-Te1-C7$  at 91.3(1)° is close to 90°. The angle  $C1-Te1\cdots N1$  at 166.4(1)° deviates slightly from the expected 180° for chalcogen bonding, likely due to ring restrictions.

The measured  $N\cdots Te$  distance is more than one Å shorter than the sum of the van der Waals radii ( $\Sigma r_{(vdW)} = 3.65$  Å).<sup>[12]</sup> The normalized contact distance, that is, the measured distance divided by the  $\Sigma r_{(vdW)}$ , at 0.72 describes the interaction more properly.

Scheme 1. Synthesis of compound **1**.