

The supramolecular chemistry of 1,2,5-chalcogenadiazoles

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Abstract

1,2,5-Chalcogenadiazoles, in particular the tellurium derivatives, are promising building blocks for the assembly supramolecular structures through the formation of the $[E-N]_2$ ($E = S, Se, Te$) supramolecular synthon. This short account summarizes initial experimental and computational investigations in this area.

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1. Introduction

During the last 30 years there has been astonishing progress in using interactions between molecules to construct supramolecular structures with increasing complexity. Hydrogen bonds and the coordination of metal ions have been the most-commonly used forces to drive the spontaneous organization of small building blocks into large, complex, and sometimes functional structures. While one major endeavor in this area is the construction of bigger and hierarchical structures, another pursues the expansion of the self-assembly paradigm to take advantage of other interactions. The use of π -stacking of aromatic rings and “van der Waals forces” is now well documented.

Other intermolecular forces have not been used mostly because they are less well-understood, as is the case for the inter-atomic contacts made by the heavy p-block elements. The variety of names given to this phenomenon illustrates the problem. *Non-bonded contact* is not appropriate because the inter-atomic distances can be much shorter than the sum of van der Waals radii; *weakly bonding interaction* implies that the interaction energy is known but this is impossible for most cases. The term *secondary*

bonding interaction (abbreviated here as SBI), introduced by Alcock [1] is more appropriate and is gaining increasing acceptance. It is established that in many instances two closed-shell atoms can interact attractively [2] but Alcock recognized that atoms of heavy p-block elements have a remarkable affinity for atoms with lone pairs [3] and proposed a bonding model based on the donation of a lone pair into a σ^* antibonding orbital. This model is consistent with crystallographic data available for a number of compounds containing chalcogens and pnictogens [4].

The potential of SBIs in supramolecular chemistry has been recognized before. Orpen established structural parallels between pnictogen-centered SBIs and hydrogen bonds [5], but SBIs have distinctive features that could be used to control the properties of self-assembled materials. For example, while hydrogen bonds are barriers to electron mobility, SBIs enhance conductivity; in addition, SBIs can stabilize unusual oxidation states.

A single building block can in principle lead to more than one supramolecular arrangement, e.g., chains or rings. This has been observed many times in the case of molecules associated by main-group SBIs. To some extent, this problem has discouraged the use of SBIs in supramolecular chemistry. It has been pointed out that the effective use of these interactions requires the identification of the most efficient supramolecular synthon, [6,7,5] the basic structural units that are assembled by an operation of supramolecular synthesis.

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2. The [E–N]₂ (E = S, Se, Te) supramolecular synthon

The ideal supramolecular synthon should be strong to hold the overall structure together, directional to guide the process of assembly and reversible to allow for error self-correction. By analogy with the case of the most efficient supramolecular synthons assembled with hydrogen bonds, we have proposed the use of building blocks that bind each other through multiple simultaneous points of attachment. The simplest design of such a supramolecular synthon would consist of two SBIs joining two molecules to form a virtual ring, one example of this is the four membered [E–N]₂ ring that is frequently observed [8] in the crystal structures of molecules that contain the 1,2,5-chalcogenadiazole ring (Scheme 1), forming dimers or ribbon polymers when each heterocycle forms the supramolecular synthon twice. Table 1 compares the observed averages of SBI length with the sum of the van der Waals radii, the trend suggests that the SBI becomes stronger as the mass of the chalcogen increases.

3. The nature of the E–N SBI

Divalent chalcogen atoms frequently engage in SBIs with other atoms that contain lone pairs of electrons [10,11], these interactions are the result of a combination of electrostatic, covalent, and dispersion contributions that overcome the strong Pauli repulsion between lone pairs [12–14]. A thorough computational (DFT) study of the

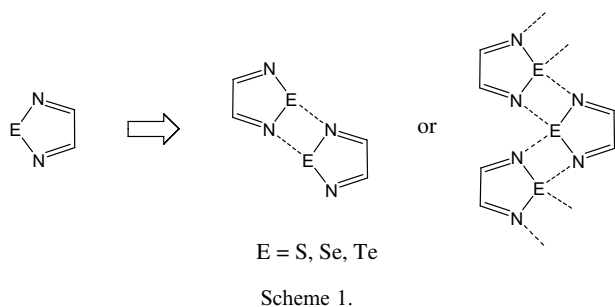


Table 1

Average length of SBI distances (Å) in the crystal structures of 1,2,5-chalcogenadiazoles compared to the sum of van der Waals radii

	E		
	S	Se	Te
$r_{\text{EvdW}} + r_{\text{NvdW}}^{\text{a}}$	3.26	3.36	3.54
$\text{E} \cdots \text{N}_{(\text{Average})}^{\text{b}}$	3.20	2.95	2.77

^a Based on Ref. [9].

^b From Ref. [8].

association of 1,2,5-chalcogenadiazoles showed that the covalent interactions represent the largest contribution to the stabilization of the (E–N)₂ supramolecular synthon. The covalent character of the E–N SBI can be appreciated from a CSOV analysis and from maps of change of electron density upon dimerization (Fig. 1), in all three cases the electron density increases in the internuclear region between the atoms involved in the SBI. Formation of the E–N SBI can be interpreted using Alcock's model [3], as a donor acceptor interaction in which a lone pair of N donates electron density into a $\sigma_{\text{E–N}}^*$ orbital. The calculated energy of interaction between two heterocycles parallels the observed trend in SBI distances (E = S: –2.82 kJ/mol, Se: –15.54 kJ/mol and Te: –53.85 kJ/mol). The complete characterization of the potential energy surface for supramolecular association indicated that the virtual four-membered ring is fairly rigid and yet the dissociation of the SBIs should proceed with no activation barrier. This analysis concluded that [Te–N]₂ supramolecular synthon is as strong as some hydrogen bonds, the double antiparallel Te–N SBI confers directionality and the formation of this unit should be in principle reversible [4].

4. Synthesis

Considering the relative stabilities of the [E–N]₂ supramolecular synthons, the tellurium heterocycles have the greatest potential as supramolecular building blocks. However, they are also more sensitive to hydrolysis and their synthetic chemistry is not as well studied as that of the

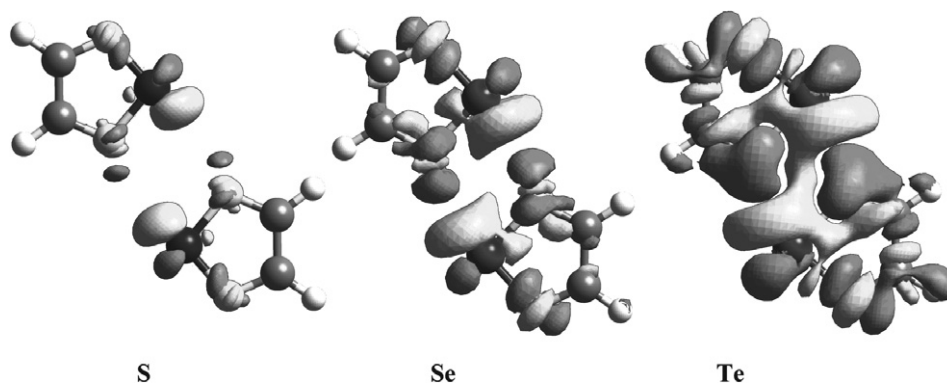


Fig. 1. Redistribution of electron density upon dimerization of 1,2,5-chalcogenadiazoles. The dark gray zones correspond to increase of density, light gray areas correspond to depletion of electron density (isosurfaces plotted at 0.05).

lighter analogues. 1,2,5-Telluradiazoles have been prepared by very different synthetic routes (Scheme 2). The parent telluradiazole and other derivatives has been obtained from the corresponding thia- and selenadiazoles by reaction with Grignard reagents, followed by TeCl_4 [15]. Unexpectedly, an attempt to prepare a tellurium diimide by reaction II resulted in the formation of a benzotelluradiazole. The simplest method, III, is the reaction of an aromatic vicinal diamine with TeCl_4 [16]. In an early report [17] the attempted preparation of benzo-2,1,3-telluradiazole from *o*-phenylenediamine afforded a thermally unstable product; our own experiments identified this material as the result of incomplete deprotonation, $\text{C}_6\text{H}_4(\text{NH})_2(\text{TeCl}_2)$, which was transformed by addition of an ancillary base into the desired compound in high yield. This method is applicable to the preparation of substituted benzotelluradiazoles. These compounds are in general tolerant to exposure to the atmosphere for brief periods of time and can be purified by sublimation [18].

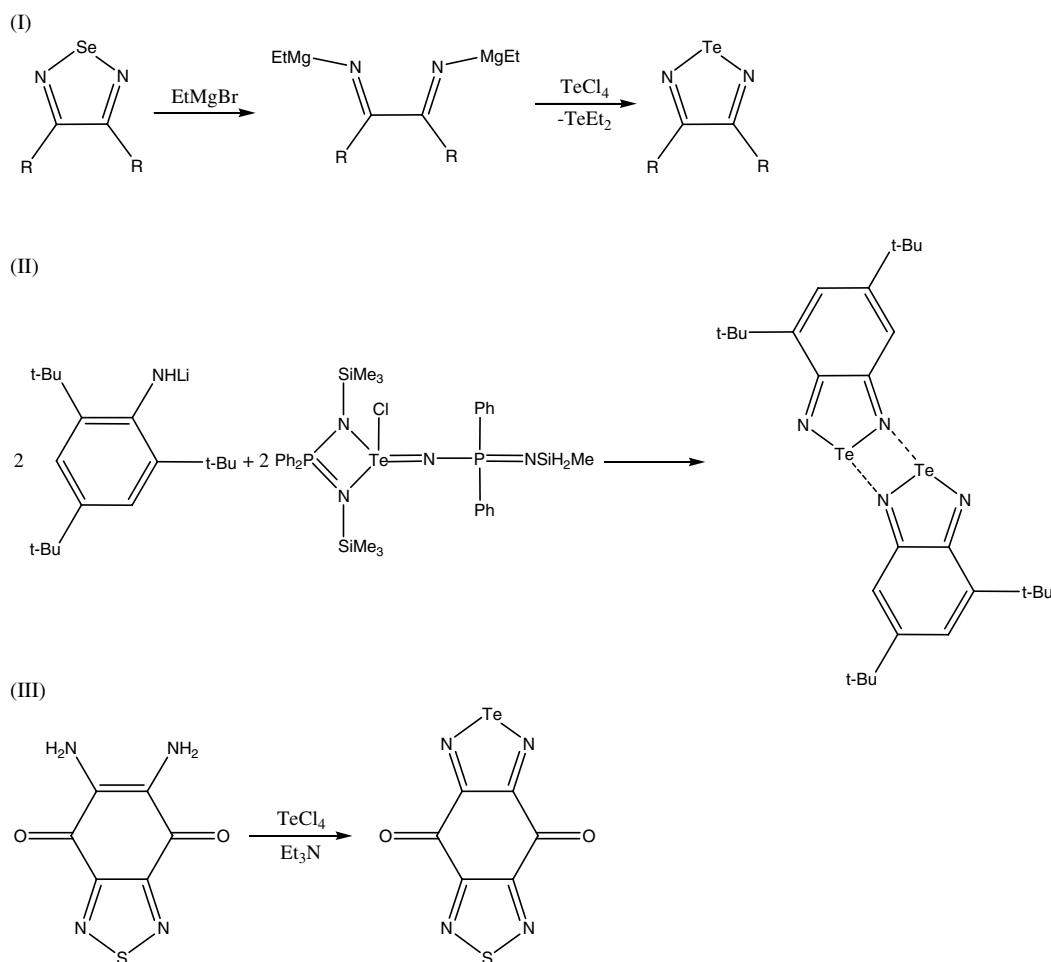
5. Structures

The structure of 2,1,3-benzotelluradiazole was of particular interest because the sulfur and selenium analogues do

not form the $[\text{E}-\text{N}]_2$ supramolecular synthon. DFT calculations had estimated that the steric repulsion between the hydrogen atoms of the aromatic ring would be intense enough to prevent the formation of ribbon polymers in the case of the lighter chalcogens, but not in the case of tellurium. The crystallographic determination confirmed that 2,1,3-benzotelluradiazole forms a ribbon polymer (Fig. 2). In contrast, the bis-*o*-bromo substituted benzotelluradiazole is only able to form dimers (Fig. 3), which was also predicted by DFT calculations. Although the functional employed is unable to account for the contribution of dispersion forces, the computational method is not only able to predict the degree of association of the molecules in the solid state but also reproduces with great accuracy molecular dimensions (Table 2), including bond distances and angles pertaining the $[\text{Te}-\text{N}]_2$ supramolecular synthon, and the elongation of the SBI that takes pace when the dimer is solvated by DMSO (Fig. 4) [18].

6. Outlook

The initial investigations outlined here have identified the $[\text{Te}-\text{N}]_2$ supramolecular synthon as a promising structural unit for the construction of supramolecular



Scheme 2.

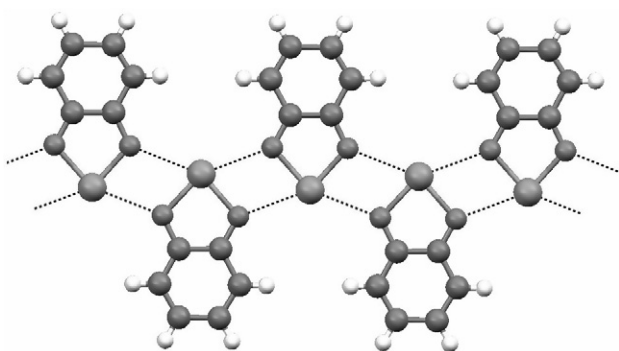


Fig. 2. Arrangement of molecules in a ribbon chain within the crystal structure of 2,1,3-benzotelluradiazole, $C_6H_4N_2Te$.

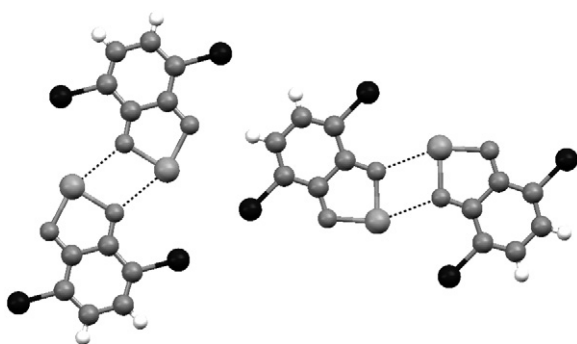


Fig. 3. Arrangement of molecular dimers in the crystal structure of 4,7-dibromo-2,1,3-benzotelluradiazole, $C_6H_2Br_2N_2Te$.

Table 2
Comparison of Te–N SBI distances determined by X-ray diffraction and calculated using DFT (ADF, TZP, VWN, PW91, ZORA)

Compound	Te–N SBI distance (Å)	
	Experimental	Calculated (DFT)
$C_6H_4N_2Te$	2.682(7)–2.720(7)	2.690
$C_6H_2Br_2N_2Te$	2.697(8)	2.620
$C_6H_2Br_2N_2Te \cdot (CH_3)_2SO$	2.744(4)	2.728

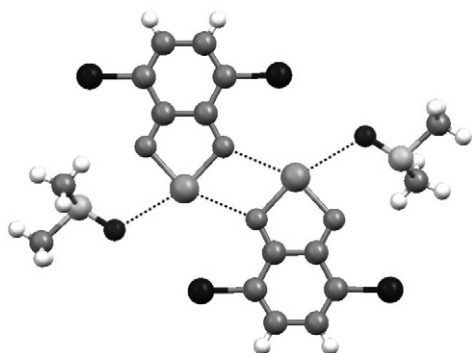


Fig. 4. The DMSO-solvated dimer observed in the crystal structure of 4,7-dibromo-2,1,3-benzotelluradiazole, $C_6H_2Br_2N_2Te \cdot (CH_3)_2SO$.

structures. Current efforts are centered on the identification of spectroscopic signatures characteristic of chalcogen-centered secondary bonding interactions and on the design of new supramolecular structures. Electronic spectroscopies, PES and UV–Vis absorption, should provide evidence to confirm the composition of the electronic structures calculated with DFT. Vibrational methods, infrared and specially Raman, would be able to probe the strength of the interactions through the force constants. Although there is evidence of the existence of intramolecular chalcogen–nitrogen SBIs in solution, the intermolecular interactions have only been observed in the solid state; given the magnitude of interaction energy obtained in the computational study, it should be possible to detect this interactions in liquid and gas phase. Although DFT has been very successful in accurately reproducing the structures of the heterocycles and their supramolecular dimers and polymers, modeling large supramolecular structures will require of a more efficient method such as molecular mechanics.

Acknowledgements

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