N-Triphenylboryl- and *N*,*N*′-bis(triphenylboryl)benzo-2,1,3-telluradiazole†

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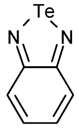
Being isoelectronic and isostructural analogues of *N*-alkyl-substituted telluradiazolyl cations, the adducts of triphenylborane with benzo-2,1,3-telluradiazole provide an electrically neutral point of reference with which the properties of the heterocyclic ions can be compared.

Mono- and di-cations derived by formal *N*-alkylation of 1,2,5-chalcogenadiazolyl heterocycles are receiving increasing attention due to their intriguing structural and chemical properties. The dialkylated systems are regarded as a family of structural analogues of the *N*-heterocyclic carbene (NHC) imidazol-2-ylidene;[1,2] of which the Se member has been described as a "chalcogen dication sequestered by a chelating diimine".[2] In spite of coulombic repulsion, the monoalkylated selenium[3] and tellurium[4] rings can form the dimers that are characteristic of the crystal structures of the parent heterocycles[5] with even shorter secondary-bonding distances. The existence of such aggregates in solution has been proposed as an explanation for the singular redox behaviour of the *N*-methyl benzotelluradiazolylium cation, as compared to its lighter congeners, which prevented the observation of the corresponding neutral free radical by EPR.[4]

Compared to the parent neutral heterocycles, the study of the cations is probably complicated by electrostatic interactions, counterion binding and an enhanced sensitivity to water and nucleophiles in general. Therefore we chose to prepare neutral isoelectronic analogues by reacting benzo-2,1,3-telluradiazole (**1**) with Lewis acids. Both the 2 : 1 (**2**) and 1 : 1 (**3**) triphenylborane adducts were isolated when using the appropriate stoichiometry of reactants in toluene. The products were isolated in micro-crystalline form and fully characterized.† X-Ray diffraction quality crystals of **2** were grown from a 1 : 1 mixture of bromobenzene and acetonitrile while crystals of **3** were grown from toluene.‡



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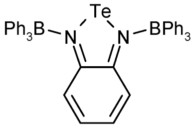

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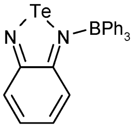

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The crystal structure of **2** (Fig. 1) demonstrated attachment of the triphenylborane moiety to each nitrogen atom of the benzo-2,1,3-telluradiazole molecule. The structure approximates a C_2 symmetry, although it sits in a general position. Two of the phenyl rings hinder access to the chalcogen, preventing association to any Lewis bases. This would be the first example of a $C_2N_2Te^{II}$ ring that does not appear to be associated to another heterocycle molecule, solvent, anion or donor atom in the solid state. However, the role of the aromatic ring might not be innocent. The N–B–C bond angle is significantly smaller for the rings next to the tellurium atom. These rings exhibit short distances from their centroids to Te (3.1188(2) and 3.1311(2) Å). Similar Te–aryl interactions have been examined by Zukerman-Schpector and Haiduc,[6] but in **2** the distances from Te to the centroids of the rings are significantly below the value reported for the shortest contact of this type (3.482 Å).[7] On closer inspection, the chalcogen is in contact (2.801(2) Å) with an atom of one ring while for the other ring the shortest distance (2.7925(2) Å) is to the centroid of a C–C bond. All these distances are shorter than the sum of Te and C van der Waals' radii (3.76 Å).

The Te–N bond lengths of **2** are comparable to those observed in the ribbon polymer of **1** (2.003(7) Å)[8] and dimers of 4,7-dibromobenzo-2,1,3-telluradiazole (1.988(8) unsolvated, 2.001(5) Å DMSO-solvated).[8] The DFT optimized geometry of **2** reproduces all the major structural features.

The crystal structure of **3** (Fig. 2), modelled with 1.4% twinning resulting from 180° rotation about *c*, confirmed the binding of one borane molecule to each heterocycle. Because

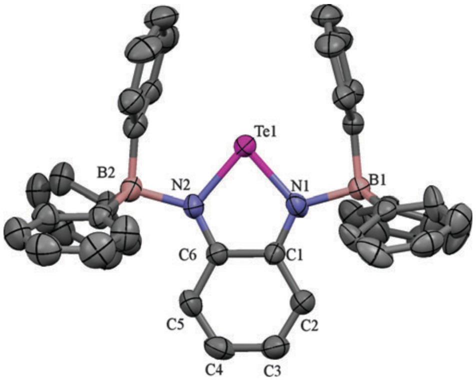

Fig. 1 ORTEP (50% probability) of the asymmetric unit in the crystal of **2**. Hydrogen atoms and disordered atoms are omitted. Selected distances (Å) and angles (°): Te1–N1 1.996(2), Te1–N2 2.006(2), N1–B1 1.629(3), N2–B2 1.646(3); N1–Te1–N2 81.79(7), Te1–N1–B1 116.0(1), Te1–N2–B2 115.1(1), N1–B1–C11 100.2(2), N1–B1–C21 108.8(2), N1–B1–C31 108.0(2), N2–B2–C41 101.2(2), N2–B2–C51 108.6(2), N2–B2–C61 108.8(2).

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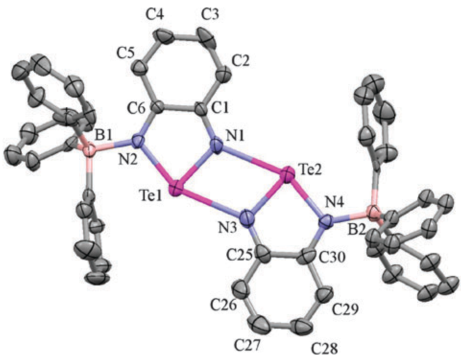

Fig. 2 ORTEP (50% probability) of the asymmetric unit in the crystal of **3**$_2$. Hydrogen atoms are omitted. Selected distances(Å) and angles (°): Te1–N1 1.977(8), Te1–N2 2.056(7), Te2–N3 1.998(9), Te2–N4 2.048(8), N2–B1 1.65(1), N4–B2 1.62(1); N1–Te1–N2 82.3(3), N3–Te2–N4 82.5(3), Te1–N2–B1 118.1(6), Te2–N4–B2 119.2(6), N2–B1–C7 108.6(8), N2–B1–C13 107.9(7), N2–B1–C19 102.1(7), N4–B2–C31 108.7(8), N4–B2–C37 107.8(8), N4–B2–C43 102.8(8).

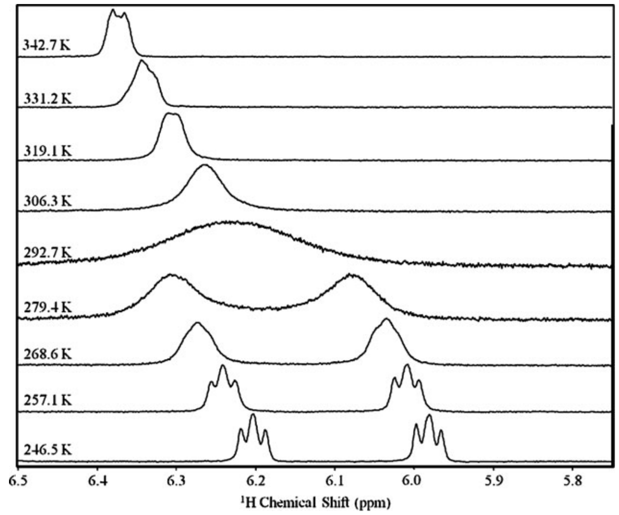

Fig. 3 Resonances of the *ortho* (4,7) protons in the benzo moiety of **3**$_2$ in d_8-toluene solution at different temperatures.

in this 1 : 1 adduct one of the nitrogen atoms and the chalcogen atom are capable of secondary bonding, the [Te–N]$_2$ supramolecular synthon renders a dimeric structure. Although **3**$_2$ is centrosymmetric, its placement in a general position duplicates the metrical parameters. In this case the Te–N supramolecular contacts (2.591(9) and 2.580(8) Å) are *ca.* 0.1 Å shorter than those in the 4,7-dibromobenzo-2,1,3-telluradiazole dimer[8] (2.697(8) Å) but almost 0.2 Å longer than in the analogous structure of the *N*-methylbenzotelluradiazolylium cation (2.471(3) Å).[4] As in those cases, within each heterocycle, the Te–N bond opposite to the secondary interaction is significantly longer than the other. The structure of **3**$_2$ also displays short distances from the heavy atoms to the aromatic rings ($d_{\text{Te–centroid(C–C)}}$ = 2.9157(7), 2.9487(7) Å; $d_{\text{Te–centroid(Ph)}}$ = 3.4108(7), 3.4179(8) Å) and the N–B–C angles are smaller for the phenyl ring that associates with the Te atom. The DFT optimized geometry of **3**$_2$ reproduces all the major structural features.

Because the shorter secondary bonding distances suggest that the supramolecular interactions might be stronger in the borane adducts than in the parent heterocycles, the association energies were estimated from the DFT total bonding energies by considering the reaction enthalpies for eqn (1)–(5); the numbers include contributions from structural relaxation but not BSSE or ZPE, which are very small in closely related systems.[8] The average B–N bond energy from eqn (1) to (2) (126.2 kJ mol^{-1}) is within the range of *ab initio* calculated binding energies for a number of simple Lewis base-borane adducts (59.8–230.8 kJ mol^{-1}).[9,10] The enthalpies of reactions (4) and (5) indicate that the secondary bonding interactions are indeed stronger in the borane adduct. This enhancement of binding energy was analyzed considering three contributions: the Pauli (steric) repulsive contribution that arises from the interaction of completely occupied orbitals, the electrostatic contribution that results from the local dipole moments, and the interaction of empty and occupied orbitals. The Pauli repulsion and the electrostatic interaction became more stabilizing by 57.6 and 25.4 kJ mol^{-1}, respectively, while the orbital interaction became less stabilizing by 74.5 kJ mol^{-1}. The net stabilization of the Te–N intermolecular interactions in **3**$_2$ is therefore primarily the result of the charge redistribution.

$$\mathbf{1} + \mathrm{BPh_3} \rightarrow \mathbf{3};\ \Delta H = -125.1\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

$$\mathbf{3} + \mathrm{BPh_3} \rightarrow \mathbf{2};\ \Delta H = -123.5\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$\mathbf{1}_2 + 2\ \mathrm{BPh_3} \rightarrow \mathbf{3}_2;\ \Delta H = -259.8\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

$$\mathbf{1} + \mathbf{1} \rightarrow \mathbf{1}_2;\ \Delta H = -67.5\ \mathrm{kJ\ mol^{-1}} \tag{4}$$

$$\mathbf{3} + \mathbf{3} \rightarrow \mathbf{3}_2;\ \Delta H = -75.9\ \mathrm{kJ\ mol^{-1}} \tag{5}$$

At room temperature, the ^{1}H NMR spectrum of **2** in solution displayed two resonances for the protons of the benzotelluradiazole moiety, as expected. The corresponding bands in the spectrum of **3**$_2$ appeared as very broad peaks in $CD_3C_6D_5$, C_6D_6 and CD_2Cl_2; the presence of a dynamic exchange process was confirmed by VT experiments in d_8-toluene (Fig. 3).† While two resonances were clearly defined above 340 K, three bands were resolved below 250 K, the fourth was obscured by other aromatic resonances. Line shape analysis for the exchange of the protons in positions 4 and 7 of benzo-2,1,3-telluradiazole gave a concentration independent activation energy of 83 ± 9 kJ mol^{-1}. Although the magnitude of this activation barrier is comparable to the supramolecular association energy calculated for **3**, the high-temperature ^{1}H NMR spectrum implies that the dynamic process includes fast shift of the BPh_3 moiety between the two nitrogen atoms. Such behaviour is observed in the 1 : 1 adduct of pyrazine and BPh_3, for which VT experiments gave an activation barrier of 78 ± 8 kJ mol^{-1} and DFT calculations estimated an association energy of 102.1 kJ mol^{-1}. These observations suggest that the VT ^{1}H NMR spectrum of **3**$_2$ does not reflect the simple dissociation of the dimer and that dissociation of the B–N bond is the most important, if not the only, contribution to the activation barrier.

The ^{125}Te resonance shifted to lower frequencies upon attachment of each BPh_3 molecule; from 2401 ppm in **1**§ to 2203 ppm in **3**$_2$, and 2188 ppm in **2**. A similar trend was

Table 1 Hirshfeld and VDD (in parentheses) atomic/group charges (a.u.) for **1**, BPh_3 and their adducts calculated using PW91 with the TZP basis set

	1	$\mathbf{1}_2$	BPh_3	**3**	$\mathbf{3}_2$	**2**
Te	0.37 (0.32)	0.36 (0.30)		0.47 (0.39)	0.47 (0.36)	0.58 (0.63)
N	−0.23 (−0.23)	−0.20 (−0.19)		−0.23 (−0.23)		
N (B)				−0.08 (−0.08)	−0.09 (−0.09)	−0.09 (−0.10)
N (SBI)		−0.24 (−0.24)			−0.19 (−0.19)	
C_6H_4	0.09 (0.13)	0.08 (0.14)		0.19 (0.23)	0.19 (0.27)	0.25 (0.28)
B			0.13 (0.09)	0.01 (−0.05)	0.01 (−0.05)	0.01 (0.03)
Ph_a			−0.04 (−0.03)	−0.08 (0.01)	−0.11 (−0.03)	−0.06 (−0.08)
Ph_b			−0.04 (−0.03)	−0.14 (−0.14)	−0.14 (−0.14)	−0.14 (−0.15)
Ph_c			−0.04 (−0.03)	−0.14 (−0.13)	−0.14 (−0.13)	−0.14 (−0.15)

observed for the resonances of the benzo protons, extrapolated to 306.3 K. Atomic charges were calculated in order to examine the influence of the Lewis acid on the electron density as a possible explanation for this trend. Mulliken and Natural Population (NPA) analyses, Hirschfeld and Atoms-In-Molecules (AIM) charges, and the Voronoi Deformation Densities (VDD) were evaluated under the PW91 GGA and the B3LYP hybrid exchange–correlation functionals with the DZ, DZP, TZP and TZ2P basis sets and the ZORA relativistic correction. As it is often the case,[11,12] the Mulliken, AIM and NPA charges were inconsistent across basis sets and functionals, precluding a meaningful interpretation. Density-based charges (Hirschfeld and VDD) were less dependent on the basis set and functional; Table 1 summarizes these results. While the dimerization of **1** and **3** causes minimal changes to the charges, formation of the B–N bond has a more significant influence. The most significant increases of positive charge are located at the tellurium atom and the benzo moiety. The positive charge on boron decreases and the phenyl rings acquire a more negative charge; this change is less pronounced on the aromatic ring which is in contact with the chalcogen. Consequently, the observed changes of ^1H and ^{125}Te chemical shifts upon borane coordination are probably due to depletion of π electron density on the benzo ring and the anisotropic shielding of tellurium by the phenyl rings.

While these investigations showed that attachment of a Lewis acid to one of the nitrogen atoms of the telluradiazole ring results in stronger secondary bonding interactions (assessed from experimental distances and calculated dimerization energies), there was no direct evidence of the existence of dimers in solution. On the other hand, the structures of **2** and $\mathbf{3}_2$ invite further research into the use of Lewis acid coordination as a means to control the association of chalcogenadiazoles and related heterocycles and to introduce functionality to their supramolecular structures.

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Notes and references

‡ *Crystal data* at 286(2) K for **2**: $C_{42}H_{34}B_2N_2Te_1$, M = 715.03 g mol^{-1}, $P2_1/c$, a = 13.0123(7), b = 15.2679(6), c = 17.828(1) Å, β = 106.256(4)°, V = 3400.3(3) Å^3, Z = 4, D_c = 1.399 g cm^{-3}, μ = 0.908 mm^{-1}; 517 parameters were refined with 250 restraints using 41 888 reflections to give R = 0.0393, R_w = 0.0712 and R_{int} = 0.0000. CCDC 720234. *Crystal data* at 296(2) K for **3**: $C_{24}H_{19}B_1N_2Te_1$, M = 473.82 g mol^{-1}, $P2_1/n$, a = 8.0389(6), b = 32.245(3), c = 15.754(1) Å, β = 90.755(1)°, V = 4083.2(6) Å^3, Z = 8, D_c = 1.542 g cm^{-3}, μ = 1.468 mm^{-1}; 506 parameters were refined with 0 restraints using 8396 unique reflections to give R = 0.0713 and R_w = 0.1508 and R_{int} = 0.1341. CCDC 720235.

§ Because a different ^{125}Te NMR chemical shift was recently published for **1**,[4] the value reported here, and elsewhere,[8] was verified by acquiring the spectrum using various spectral widths and different centre frequencies while locking to d_6-DMSO at 303 K. The resonance was consistently found at 158.1689 MHz (2401 ppm *vs.* an actual standard of neat Me_2Te measured at 157.7900 MHz, *cf.* the literature value of 157.7899 MHz[13]).

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