

Reply to a Comment on “The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions”

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electron diffraction · quantum chemical calculations ·
solid–gas differences · temperature effects ·
weakly bonded systems

Abstract: We reply to the comment by J.-M. Mewes, A. Hansen and S. Grimme (MHG), who challenged the accuracy of our r_e value for the N··Te distance in $(C_6F_5)Te(CH_2)_3NMe_2$ determined by gas electron diffraction (GED). We conclusively demonstrate that MHG's quoted reference calculations are less accurate than they claim for solid state and gas phase. We show by higher level calculations, that we did not miss substantial contributions from open-chain conformers. Refinements on simulated scattering data show that such contributions would have had only an almost negligible effect on $r_e(N··Te)$. MHG suggested the use of a H0-tuned GFN method for calculating vibrational corrections $r_a - r_e$, but this did not change these values substantially. Alternative amplitude calculations using higher level analytic harmonic and numeric cubic force fields (PBE0-D3BJ/def2-TZVP) yield a GED value for $r_e(N··Te) = 2.852(25)$ Å that is well within the experimental error of our original value $2.918(31)$ Å but far from the $2.67(8)$ Å predicted by MHG. A now improved error estimation accounts for inaccuracies in the calculated auxiliary values. The gas/solid difference of the weak N··Te interaction is in a realistic range compared to other systems involving weak chemical interactions.

The recent comment by Mewes, Hansen and Grimme^[1] (further on abbreviated MHG) on our recent structural work on the weak intramolecular N··Te interaction in $(C_6F_5)Te(CH_2)_3NMe_2$ (**1**)^[2] (Figure 1) has raised some interesting aspects of weak chemical interactions (WCIs), or non-covalent interactions (NCIs) and about the performance of experimental and theoretical methods to capture them

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/anie.202104899>.

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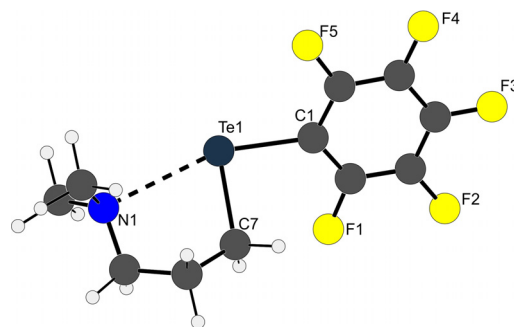


Figure 1. Gas-phase structure of **1** as determined by gas electron diffraction.

structurally. We prefer the term WCI, because ionic or metallic bonding type interactions are also non-covalent, but clearly not, what is under discussion here.

In essence, MHG criticise that our gas phase value for the N··Te distance determined by gas electron diffraction (GED) would be too large in the light of their new and more sophisticated quantum-chemical results on a single molecule. In turn, they claim to exactly reproduce our solid-state values and use this as an argument for the validity of their procedure. They offer to provide an explanation for why our procedure of analysing GED data would inherently lead to too large values due to two issues: a) inadequately corrected large amplitude vibration of the Te–N mode (they suggest H0-tuned GFN1-xTB and GFN2-xTB methods to solve this) and b) overlooking the presence of further conformers contributing to the measured electron diffraction scattering intensities. Both points are dependent on the temperature of experiment, which required 444 K to evaporate **1** at a rate suitable to produce sufficiently fast electron scattering.

We will analyse these issues point by point and will show that our methods are robust to the above effects and that the published gas-phase values are reliable within experimental error.

Intramolecular donor–acceptor bonds in different phases

The subject of debate is a molecule consisting of a ring system involving a donor-acceptor-type of bond. The NMe₂ donor and the Te(C₆F₅) acceptor groups are linked by a 1,3-

propandiyl unit. One of the aims of our contribution was to establish gas-phase and solid-state structural data for comparison. It is well known that weak chemical interactions are sensitive to the environment of the molecule,^[3] and this is in particular true for adducts involving dative bonds, since the formation of dative bonds is usually accompanied by the build-up of (strong) dipole moments. $(\text{C}_6\text{F}_5)_3\text{Te}(\text{CH}_2)_3\text{NMe}_2$ (**1**) can be regarded as a molecule with an intramolecular donor-acceptor bond (dative bond), which can alternatively be described as a chalcogen bond.

Experimental structures for different phases

There is an overwhelming body of structures of crystalline systems involving WCI (Lewis acid base adducts, halogen- and chalcogen bonded systems and so on). There is also a number of adduct-type systems or those with other WCI that have been studied in the gas phase.^[4]

However, the intersecting set of systems studied experimentally in both phases, gas and solid, is extremely limited, and this holds in particular for systems involving heavy-elements beyond the 3rd row of the PSE. The reasons for this are obvious: it is comparatively easy to determine a structure for solid compounds given they form suitable crystalline material. More sophisticated experiments are necessary for typically volatile compounds, which are often liquids or gases at ambient temperatures. Then in situ crystallization on a diffractometer is the technique of choice, although there are only a few labs with expertise in such experiments.

For gas phase experiments, there are two major methods: rotational (or rotationally resolved) spectroscopy, usually microwave spectroscopy (MW) and gas electron diffraction (GED). Both are confronted with the fact that they produce only a limited amount of information and this leads often to underdetermined cases for structure determination. An important issue in this context is that of molecular vibration. In the analysis of GED data, one fits a model to the experimental scattering data by least squares refinements—similar to the procedure in X-ray crystallography. Parameters in such a GED refinement are geometrical parameters that define a model producing all atom-atom distances contributing to the pair (or triple) correlation functions involved in the scattering theory underlying the analysis programs. In addition, one has to handle molecular vibration. Small amplitude vibrations are straightforward to handle and there exist several protocols of how to work with such problems. However, when weak chemical interactions (WCI) associated with large amplitude motions are involved, the problem becomes much trickier. Under such conditions the models for describing small amplitude vibrations are no longer good approximations. Therefore, in the original work, we used molecular dynamics simulations to extract estimates for the vibrational effect on refined structural parameters and “correct” them to a common physical basis, the “distance between equilibrium nuclear positions” abbreviated r_e . The reader should note that this is a hypothetical value of a vibration-less molecule that does not exist in reality, not even at 0 K. These corrections are done to make data from

different methods with different physical meaning comparable. The question remains whether the choice of a hypothetical state that can never be reached in reality is ideal.

Reliability of theoretical approximations

In their comment, MHG provide a series of results of quantum-chemical methods applied to the structural problem of $(\text{C}_6\text{F}_5)_3\text{Te}(\text{CH}_2)_3\text{NMe}_2$ (**1**). There are large variations in numbers depending on the methods applied, showing that producing a correct result by quantum-chemical methods is by no means a trivial task—nor is it trivial for experiments!

Optimized values for $r_e(\text{N}\cdots\text{Te})$ from DFT hybrid functionals are 2.750 (PBE0-D3), 2.754 (PBE-D4), 2.80 (B3LYP-D4), 2.816 Å (M06-L) and said by MHG to be too large. In contrast, MP2 and in particular GFN1/GFN2 predict much too strong interactions, i. e. too short r_e and a wrong shape of the potential energy surface (PES, for GFN1); the non-modified GFN methods provide GFN2 2.594 and GFN1 2.464 Å. In their extensive calculations MHG finally choose to trust a relaxed scan with their very recently presented $r^2\text{SCAN-3c}$ method followed by single-point calculations with a high-level local coupled-cluster (DLPNO-CCSD(T1)/CBS) method to produce a potential solely for the $\text{N}\cdots\text{Te}$ interaction. From this, they estimate an optimum value for $r_e(\text{N}\cdots\text{Te})$ for the free molecule: 2.67 Å. Of course this procedure works reliably only if all other degrees of freedom also represent minima at this level of theory, which is at least to some degree uncertain.

For testing the performance of their underlying $r^2\text{SCAN-3c}$ approximation MHG performed periodic DFT optimizations for the solid state of **1** and compared their results with our molecular structure in the crystal determined by XRD. They assumed that their data obtained in r_e space are comparable to the values of the crystal structure obtained at 100 K ($r_{\text{exp}} \approx r_e$). Crystal structure distances do not represent r_e values, but the distance between the average nuclear positions at thermal equilibrium, also denoted r_{h1} .

We have now performed a more accurate description of the solid state (XRD) values and calculated corrections for vibrational effects in the solid state, see Table 1. The corrections $r_{\text{h1}} - r_e$ from an r_{h1} type of experimental structure and quantum-chemically computed r_e were calculated using perturbation theory^[5] for an isolated molecule at 100 K using harmonic and cubic force fields at the PBE0-D3BJ/def2-TZVP level. Apparently the $r(\text{N}\cdots\text{Te})$ distance in the crystal

Table 1: Experimental, corrected experimental and calculated geometrical parameters of **1** in the solid state.

Solid 1	$r(\text{N}\cdots\text{Te})$	$r(\text{C1-Te})$	$r(\text{C7-Te})$
XRD measured, r_{h1}	2.639(1)	2.189(1)	2.159(1)
$r_{\text{h1}} - r_e$, estimated for $T = 100$ K	0.024	0.004	0.009
XRD corrected, r_e	2.615	2.185	2.150
$r^2\text{SCAN-3c}$ (MHG), r_e	2.636	2.216	2.184
PBE-D4 (MHG), r_e	2.624	2.223	2.187
M06-L (MHG), r_e	2.730	2.220	2.178

phase is not reproduced so well by the new r^2 SCAN-3c method as reported by MHG. Taking other much less vibration-affected molecular distances also into account it appears that all DFT values are scattered around experimental data with the expected typical accuracy of about several hundreds of an Ångström.

Solely the other two bonds at the tellurium atom deviate by 0.031 ($r(\text{C1-Te})$) and 0.034 Å and ($r(\text{C7-Te})$) (Table 1). We would not have expected a distance for a WCI to be more reliably predicted by DFT than those for the other covalent bonds.

As mentioned above, the equilibrium $r_e(\text{N}\cdots\text{Te})$ distance has not been obtained by full optimization of the complete structure at the DLPNO-CCSD(T1) level of theory, apparently due to too high computational demands. But even if this could be done, to our best knowledge, the accuracy of this theoretical level has not been as thoroughly benchmarked for structures involving heavy elements, as was reported for molecules involving 2nd and 3rd period elements.^[6] One reason for this is the surprisingly limited number of highly accurate experimental structural parameters for isolated molecules, in particular involving such heavy elements. Alone the DLPNO-CCSD(T1)/CBS approximation does not give convergent results. There are still effects of quadrupole, 5-tupole and further excitations, core correlation, relativistic scalar and spin-orbit effects. Each of the effects in turn requires an investigation of basis set convergence. Thus, we believe that the theoretical approximations used by MHG should not be used as reference for the equilibrium N \cdots Te distance.

Finite-temperature effects

From molecular dynamics (MD) simulations MHG concluded that up to 10% of **1** can exist in open-chain forms (no N \cdots Te interaction) in the gas phase at 445 K. They predicted that not accounting for this amount of open-chain forms with very large N \cdots Te distances might lead to an increase in the refined $r_e(\text{N}\cdots\text{Te})$ value for the most stable conformer when it is refined as the sole component during GED analysis. Here we test this hypothesis.

First, we attempted to reproduce MHG's value of 10% open-chain form by explicitly identifying as many stable

conformers as possible. By systematic one-dimensional scanning (PBE0-D3BJ/def2-TZVP level) along different torsional coordinates we found and optimized 17 structures (PBE0-D3BJ/def2-QZVPP, some of them are described in Table 2). Calculations of harmonic vibrational frequencies (PBE0-D3BJ/def2-QZVPP) revealed one imaginary frequency for structure **1f**, the other structures were confirmed to be minima on the PES. For the optimized structures in Table 2 single-point energies were computed at the DLPNO-CCSD(T)/def2-QZVPP level. Coupled-cluster energies corrected for harmonic zero-point vibrational energies (ZPVE) from the aforementioned DFT calculations were used to compute the abundancies of the identified conformers in the gas phase at 445 K. The results show the major contribution of conformers **1a** and **1b**, both having ring-structures with relatively close N \cdots Te contacts. These two conformers together with the far less stable **1c** were used during GED data analysis in our original work. Models of **1a** and **1b** fit the GED data equally well and thus cannot be distinguished. The differences between these structures are minimal in concerning the N \cdots Te interaction and thus, as before, we discuss only the most stable **1a**. Conformer **1c** has also been tested against GED, but showed a poor fit and thus was rejected. Inclusion of **1c** as a second conformer was attempted but led consistently to higher *R* factors than the single conformer model we finally chose. The most stable open-chain conformer **1j** has a contribution of about 0.2%. All other conformers not listed in Table 2 have larger energies and contributions below 0.1% (see Supporting Information for the complete list of structures). Considering the chemical structure of **1** we did not expect any other energetically low-lying conformers apart from **1a** and **1b**. The results summarized in Table 2 confirm this. In essence they show that the contribution of open-chain forms is about 0.5%. We also tested the effect of vibrational anharmonicity on the zero-point energies. For the selected conformers **1a** and **1c** we calculated harmonic and anharmonic frequencies and respective ZPVE using VPT2^[7] theory with PBE0-D3BJ/def2-SVP electronic approximation as implemented in Gaussian 16. The change of the difference between ZPVE values for **1a** and **1c** due to the anharmonicity was as small as 0.036 kcal mol⁻¹, which is negligible in comparison to the energy values in Table 2. This result is also supported taking into account the available literature on

Table 2: Optimized structures of conformers of **1** and their zero-point-corrected energies (kcal mol⁻¹) and abundancies *x* at 445 K according to the Boltzmann distribution.

Conf.	N \cdots Te	CCTeC	CTeCC	TeCCC	CCCN	CCNC-1	CCNC-2	$E_{\text{DFT/QZ}}$	$E_{\text{CC/QZ}}$	<i>x</i> , %
1a	2.744	-51.6	-155.3	-56.3	63.0	80.2	-153.4	0.0	0.0	60.0
1b	2.738	-60.8	157.5	54.1	-63.1	154.2	-79.4	0.336	0.369	39.5
1c	5.486	-46.2	-163.3	-178.3	175.1	68.7	-166.6	6.850	6.679	< 0.1
1d	5.485	-50.5	-172.9	-179.7	-174.4	-68.5	166.8	6.969	6.812	< 0.1
1e	5.547	-48.0	-168.3	-178.6	-179.6	65.7	-65.6	7.580	7.795	< 0.1
1f ^[a]	4.958	v53.9	178.2	-179.3	55.0	-169.2	65.4	6.210	6.064	< 0.1
1g	4.955	-47.2	-162.0	178.4	-56.6	-66.7	168.0	6.059	5.915	< 0.1
1h	4.761	-54.9	136.3	-72.7	170.8	67.4	-167.8	7.178	7.213	< 0.1
1i	4.720	-58.1	154.8	59.2	172.9	-169.1	66.0	6.540	6.588	< 0.1
1j	3.486	-45.8	-47.3	-54.0	90.3	76.8	-157.2	5.264	4.827	0.2

[a] Has one imaginary frequency in the DFT calculation.

benchmarks of scaling factors for harmonic frequencies and ZPVE^[8] and investigations of thermodynamic functions for flexible systems at different temperatures.^[9] Note, according to all our DFT calculations both, closed-ring and all open-chain conformers, have low vibrational frequencies in the range 10–20 cm⁻¹. Thus accounting for various vibrational effects does not significantly influence the differences between energies of these two types of conformers.

Although it is still possible that we overlooked some other stable open-chain high-energy conformers, it would hardly be possible that they all exceed in sum 2% abundance according to the used theoretical approximations. In the light of this higher-level treatment we cannot support the finding of MHG regarding the contribution of opened forms of about 10%, at least in the commonly accepted understanding of this term.

Robustness of GED refinements to temperature effects

Nevertheless, we explicitly tested further the possible influence of finite-temperature effects on the refined $r_e(\text{N}\cdots\text{Te})$ value. For this, we generated simulated GED data sets, by calculating (and then analyzing) scattering data of mixtures of **1a** and **1c** from theoretical models. In these simulations the amount of **1c** was set to 2, 5 and 10%. The geometrical parameters for these conformers were taken from PBE0-D3BJ/def2-TZVP optimizations.

These simulated data sets were analyzed in the same way as we analyzed our experimental data set. Vibrational amplitudes and corrections for interatomic pairs were calculated using the same procedure as before (path-integral MD simulations) but with the tuned GFN1(0.9) method as recommended by MHG. The simulated GED data sets were used for the refinement of parameter values for **1a** using a model with only this single conformer, as was done in our original contribution. Indeed, the refined $r_e(\text{N}\cdots\text{Te})$ distances of **1a** were found increased in comparison to the expected values, when neglecting **1c** in the model. However, contrarily to MHG's predictions, the effect was very small: 0.0004, 0.0014 and 0.0026 Å for the data sets containing 2, 5 and 10% of **1c** (along with increasing *R* factors by 0.03, 0.06 and 0.22%)—all well within our quoted experimental error. Thus, our modelling shows no significant influence of finite-temperature effects on the $r_e(\text{N}\cdots\text{Te})$ value of **1**. Taking also into account the theoretical energies of all identified stable forms we can reject this hypothesis of overlooked conformer contributions.

Large-amplitude motion

It is possible that our GED results are affected by theoretical parameters used to supplement the interpretation of the data. Especially vibrational corrections $r_a - r_e$ can directly influence the refinement. In our original work we used path-integral molecular dynamics (PIMD) simulations based on the original GFN1 method as implemented in the CP2K code. Note, that in contrast to PIMD simulations, the

MD cannot be used in GED^[10] due to the inability to cover quantum effects, which is critical for light elements, in particular for hydrogen atoms. In GED it is impossible to investigate an isolated interatomic distance without considering the whole molecule and therefore uniform accuracy is required for calculating corrections for all interatomic distances. Also, we need to note explicitly, that vibrational amplitudes and corrections are defined only for particular conformers.^[11] Thus, in the processing of PIMD trajectories we control that only those structures are taken into account, which belong to the basin of the conformer under consideration. In our practice, we start PIMD simulations from the optimized structures of the respective stable conformers, for which we calculate vibrational parameters. Thus, there is no need to start, for example, from the global minimum and accumulate very long trajectories in the hope of obtaining convergent sampling of a desired high-energy conformer. We also do not average the values of interatomic distances belonging to different conformers. Having said that, we stress that the MD simulations of MHG, with trajectories passing through multiple conformers, are not directly suitable for the interpretation of GED data.

However, we believe that MHG have a better understanding concerning the accuracy of the original GFN methods which Grimme and co-workers have introduced not long ago under the title “A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements (*Z* = 1–86)”.^[12] Despite this title, MHG describe the N \cdots Te interaction in their comment as “exotic” and consequently suggested H0-tuning in order to adapt this method to their higher-level treatment results.

We are grateful that MHG gave us the opportunity to test the tuned GFN1(0.9) method for our purposes in GED analysis. Consequently, we performed a new set of PIMD simulations based on the tuned GFN1(0.9) as suggested by MHG. The length of the PIMD trajectory was 44 ps, which allowed obtaining converged parameters for the single conformer. Note, its lowest vibrational frequency was ca. 20 cm⁻¹ according to DFT. With the improved calculated sets of amplitude starting values and interatomic corrections we refined the structural parameters of **1a** and obtained an $r_e(\text{N}\cdots\text{Te})$ value of 2.916(11) Å, which is only slightly shorter in comparison to the originally refined value of 2.918(10) Å (here: 1σ least-squares standard deviations are in parentheses). Note, that in all refinements, original and new ones, we applied restraints on the geometrical parameters of **1** taken from a calculated structure optimized at the PBE0-D3BJ/def2-TZVP level with $r_e(\text{N}\cdots\text{Te}) = 2.751$ Å. Despite this, the values always refine to a larger value.

Error estimation including calculation errors

In our original work the uncertainties for both, XRD and GED structures, were standard deviations from least-squares method. This is usual practice in structural studies, although in some GED cases scale errors are also included. However, the

contributions from other sources to the uncertainties of the refined parameters can be also calculated. Here we investigate how the inaccuracy in the theoretical vibrational amplitudes and corrections could possibly influence the uncertainty of the refined value of $r_e(\text{N}\cdots\text{Te})$. For this the direct Monte-Carlo method (MC)^[13] has been used. Scale factors for amplitudes and values of r_a-r_e corrections have been sampled in ranges $\pm 50\%$ and $\pm 100\%$ around the calculated values with uniform distributions. The value for 1σ for the parameter $r_e(\text{N}\cdots\text{Te})$ calculated in this simulation was 0.025 \AA . This does now include contributions from experimental data and the calculated vibrational parameters.

Alternative ways for amplitude calculations

Further, we tested an alternative way for the calculation of vibrational amplitudes and corrections at the DFT level, without using any semi-empirical methods at all. Using the PBE0-D3BJ/def2-TZVP approximation (according to MHG, the PBE0-D3 approximation predicts reliably the form of the potential energy curve for $r(\text{N}\cdots\text{Te})$), analytical harmonic and numerical cubic force fields were computed. Note that at this DFT level, the $\text{N}\cdots\text{Te}$ stretching is mainly localized to three vibrational modes with frequencies of $81\text{--}105\text{ cm}^{-1}$. Therefore, no dynamic GED model is required to describe the $r(\text{N}\cdots\text{Te})$ distance. The force fields were further processed to calculate the required vibration parameters using perturbation theory.^[5] Subsequent structural refinement of **1a** based on the experimental GED scattering intensities with these parameters gave $r_e(\text{N}\cdots\text{Te}) = 2.852(25)\text{ \AA}$ (the uncertainty is 1σ from MC as described above). This value is smaller than the previously refined one, so the level of theory and the method of vibrational calculations have the greatest influence on the refined $\text{N}\cdots\text{Te}$ distance. However, both values we obtained, 2.852 and 2.916 \AA are well within the $\pm 2\sigma = 0.05\text{ \AA}$ determined, but still far from the value $2.67 \pm 0.08\text{ \AA}$ calculated by MHG.

The closer chemical context: data of similar compounds

The question of what is a reasonable range for dative-type $\text{N}\cdots\text{Te}$ distances can be answered using the following literature data. The closest related compound to **1** is probably $(\text{C}_6\text{F}_5)_3\text{TeMe}\cdots\text{NMe}_2\text{Et}$, which we discussed in our original article for comparison. This compound has the same surrounding for the directly interacting partners of Te and N atoms and is formally derived from **1** by cleavage of a C–C bond and saturation of the ends with hydrogen. Only a crystal structure exists for this compound, showing an $\text{N}\cdots\text{Te}$ distance of $2.854(1)\text{ \AA}$, that is, 0.218 \AA larger than in **1**. This demonstrates the great flexibility of this parameter, which is also seen in several *o*-phenylenemethyl-bridged intramolecular $\text{N}\cdots\text{Te}$ interactions: in $\text{ClTe}(o\text{-C}_6\text{H}_4)\text{CH}_2\text{NMe}_2$ ($2.355(3)\text{ \AA}$ if monoclinic $P2_1/n$ ^[14] and $2.362(3)\text{ \AA}$ if orthorhombic $P2_12_12_1$ ^[15]), in $\text{PhTe}(o\text{-C}_6\text{H}_4)\text{-CH}_2\text{NMe}_2$ ($2.8079(16)\text{ \AA}$)^[16] in the three structures of the $[2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{TeSP}(\text{S})\text{R}_2$

derivatives [$\text{R} = \text{Me}$ ($2.48(2)\text{ \AA}$), $\text{R} = \text{Ph}$ ($2.439(2)\text{ \AA}$), $\text{R} = \text{OiPr}$ ($2.467(3)\text{ \AA}$)^[17] ($2\text{-NMe}_2\text{CH}_2\text{C}_6\text{H}_4$) TeR , where $\text{R} = 2,6\text{-MeC}_6\text{H}_3$ ($2.786(4)\text{ \AA}$) and $\text{R} = 2,6\text{-iPrC}_6\text{H}_3$ ($2.844(2)\text{ \AA}$)^[18]]. The gas phase values are expected to be larger than the solid state values (see below), and therefore these values indicate that our reported values for solid state and gas phase of **1** are well within a reasonable chemical range for this type of compounds.

The broader chemical context: comparing solid and gas phase data for the same compound

As shown in Table 3, there are not many, but at least some compounds for which experimental data are available from both the solid state and the gas phase. The case of “partial bonds” was addressed by Leopold, Canagaratna and Phillips in their article “Partially bonded molecules from the solid state to the stratosphere”.^[3] This and the information from the now larger body of examples in Table 3 show a relatively clear picture for systems that are adducts in the sense of dative bonds (including related electrostatically controlled interactions such as halogen or chalcogen bonds). A prerequisite for a reliable comparison of solid state and gas phase values for molecular compounds is that the same coordination numbers and no more complex structural motifs of aggregation are present in the solid state.

Regarding the structural features concerning the dative bond, it can be summarized that a) the values in the gas-phase are always longer than the values in the solid state and b) the difference between solid and gas phase is larger the weaker the dative bonding for the free molecule.

There are only few data for dissociation enthalpies. Only the examples in Table 3 with the strongest dative bonds ($> 18\text{ kcal mol}^{-1}$), $\text{H}_3\text{B}\cdots\text{NMe}_3$, $\text{F}_3\text{B}\cdots\text{NMe}_3$, $\text{F}_3\text{B}\cdots\text{NH}_3$, $\text{Me}_3\text{Al}\cdots\text{OMe}_2$, $\text{Me}_3\text{Al}\cdots\text{SMe}_2$ and $\text{O}_3\text{S}\cdots\text{NH}_3$, consistently show rather small differences between solid and gas phase values for the lengths of the dative bonds ($0.021(11)$ to $0.094(11)\text{ \AA}$) the only exception being $\text{O}_3\text{S}\cdots\text{NH}_3$ with a larger difference of $0.186(23)\text{ \AA}$. All other adducts with weaker dative bonds $\text{F}_3\text{B}\cdots\text{NCCH}_3$, $\text{O}_2\text{S}\cdots\text{NHMe}_2$, $\text{O}_2\text{S}\cdots\text{NMe}_3$ show significantly larger values ($0.214(30)\text{--}0.381(8)\text{ \AA}$). If one extrapolates to related situations, one can classify the other systems as well: all strongly bound adducts have smaller solid–gas differences, all more weakly bound have larger differences, and only the very strongest adducts are in the range of 0.082 \AA , as was predicted by MHG for the weakly bound **1**.

However, if we consider bond strength value of about 8 kcal mol^{-1} predicted by MHG for **1**, it becomes difficult to fit this into the general landscape outlined in Table 3, i. e., a difference of only $0.034(80)\text{ \AA}$ seems rather unreasonable. It could be argued that most of the values compiled in Table 3 involve elements from the second and third rows of the periodic table and only a few values for gallium compound are from the fourth row, and therefore this cannot be representative. Rather, it shows that our knowledge of such behaviour for the heavier elements is meagre. However, this concerns experimental facts as well as validated theoretical methods.

Table 3: Compilation of the results of experimental structure determinations of weakly bound adduct systems for which values exist in both, the crystalline and the gas phase (the column r provides information on the structure type of the gas phase value,^[a] Δr is the difference $r(\text{gas}) - r(\text{solid})$, BDE is the experimental bond dissociation enthalpy in kcal mol⁻¹, where available).

Compound	$r(\text{solid})$	$r(\text{gas})$	r	Δr	BDE
<i>intermolecular</i>					
H ₃ B...NH ₃	1.56(5) ^[19]	1.6453(1) ^[20]	r_e	0.085(50)	
H ₃ B...NMe ₃	1.617(4)	1.656(3) ^[21] 1.638(10) ^[22]	r_g r_s	0.039(5) 0.021(11)	40(9) ^[23]
H ₃ B...C ₄ H ₉ NO ^[b]	1.605(9)	1.644(6) ^[24]	r_{h1}	0.039(11)	
F ₃ B...NMe ₃	1.58	1.636(4) ^[25] 1.674(4) ^[26]	r_0 r_g	0.056(11) 0.094(11)	32.9
F ₃ B...NH ₃	1.580(1) ^[27,28]	1.673(2) ^[29]		0.093(2)	19.2
F ₃ B...NCH	1.638(2)	2.473(29) ^[30]	r_0	0.835(29)	
F ₃ B...NCCH ₃	1.630(4)	2.011(7) ^[31]	r_0	0.381(8)	5.7
(F ₃ C) ₃ B...CO	1.69(2) ^[c]	1.617(12) ^[32]	r_z	-0.53(23) ^[c]	
Me ₃ B...NMe ₃	1.564	1.69(4) ^[33] 1.698(10) ^[34]	r_0 r_0	0.126(40) 0.134(10)	
Me ₃ Al...OMe ₂	1.940(2)	2.014(24) ^[35]	r_a	0.074(24)	21.9(2)
Me ₃ Al...SMe ₂	2.461 ^[d]	2.55(2) ^[36]	r_a	0.089(20)	18.1(5)
H ₃ Ga...PMe ₃	2.3857(6)	2.443(6) ^[37]	r_{h1}	0.057(6)	
H ₃ Ga...NMe ₃	1.97(9) ^[38]	2.111(2) ^[39] 2.139(4) ^[40]	r_0 r_a	0.141(90) 0.169(90)	
O ₃ S...NH ₃	1.7714(3)	1.957(23) ^[41]	r_0	0.186(23)	19.1
O ₂ S...NHMe ₂	2.003(12) ^[42]	2.335(30) ^[43]	r_s	0.332(32)	10.3
O ₂ S...NMe ₃	2.046(4)	2.260(30) ^[44] 2.285(30) ^[45]	r_s r_0	0.214(30) 0.239(30)	13.4
<i>intramolecular</i>					
FSi(OCH ₂ CH ₂) ₃ N	2.042(1)	2.324(14) ^[46]	r_a	0.282(14)	
F ₃ SiONMe ₂	1.963(1)	2.273(17) ^[47]	r_a	0.310(17)	
ClH ₂ SiONMe ₂	2.028(1)	2.160(7) ^[48]	r_a	0.132(7)	
(F ₃ C)F ₂ SiONMe ₂	1.904(2)	2.112(17) ^[49]	r_{h1}	0.208(17)	
H ₃ Si(CH ₂) ₃ NMe ₂	2.719(2)	2.91(4) ^[50]	r_{h1}	0.191(40)	
1 our work	2.639(1)	2.918(31)	r_e	0.279(31)	
1 MHG, calcd	2.636 ^[e]	2.67(8) ^[e]	r_e	0.034(80)	≈ 8 ^[e]

[a] Uncertainties are given as in the original publications without modification. If missing, they were assumed to be in the last stated digit.

[b] C₄H₉NO = morpholine. [c] Value of very limited quality. [d] Average value. [e] Theoretical estimate by MHG.

Conclusion

MHG raised an interesting point concerning the effect of temperature on the modelling required for data analysis of gas electron diffraction (GED) data, in particular if the objects of study involve weak chemical interactions (WCI). In essence, we have conclusively demonstrated that their reference calculations are not as accurate and reliable as they claim, neither for the solid state nor for the gas phase. We can show that we have not overlooked a substantial contribution of open-chain conformers. On the contrary, we can demonstrate with higher quality theoretical methods, that

a) the abundance of such open-chain conformers with larger N...Te distances is almost negligible and b) even if they existed, they would have a very small effect on the refined N...Te distance from GED. We have also shown that the suggested H0-tuning of the GFN methods does not substantially change the values of vibrational corrections $r_a - r_e$. However, we have found that alternative routes for vibrational calculations using analytical harmonic and numerical cubic force fields at higher levels (PBE0-D3BJ/def2-TZVP) yield a value for $r_e(\text{N}\cdots\text{Te}) = 2.852(25)$ Å, which is slightly smaller than in our original work (2.918(31) Å). This value is still well within the reported experimental error, but it is far from the "reference" value of 2.67(8) Å predicted by MHG. The error for this value, $r_e(\text{N}\cdots\text{Te}) = 2.852(25)$ Å, was calculated by taking into account the inaccuracy in the calculated vibrational amplitudes and corrections and was calculated using the direct Monte-Carlo method (MC). This GED investigation was performed at the best level currently available. However, effects related to (a) uncertainties in the scattering factors, (b) multicenter scattering, (c) multi-dimensional large-amplitude motions, (d) electron scattering from finite sample volume may be present. We assume these effects play a minor role compared to those from vibrations. Future development of the GED method should clarify this.

By placing our results into a broader chemical context, we have compared the phase-dependent behaviour of the weak N...Te interaction in **1** with a number of other weakly bound systems. This shows that a gas/solid difference for interactions as weak as the N...Te interaction in **1** ($r_{\text{gas}} - r_{\text{solid}} = 0.279(31)$ Å) can be expected to be substantially larger than the 0.034(80) Å predicted by MHG.

The whole case clearly demonstrates how much experiment and theory are meanwhile interdependent and dependent on one another, and how much both can benefit in their development if data and methods are mutually referenced. This is in particular true for systems involving heavy elements, for which the validation of theoretical methods is often still inadequate and for which reliable experimental values are still scarce, and it is an even greater problem for weak chemical interactions involving heavy elements. It is also apparent that knowledge of the differences between molecular structures in different phases is still very incomplete.

Computational Details

Potential energy scans with DFT in the conformational search and calculations of harmonic and cubic force fields for the use in perturbation theory were performed using Gaussian 16.^[51] Optimizations of conformers and frequency calculations were done at the PBE0-D3BJ/def2-QZVPP level with m4 integration grid and with RI approximation as implemented in Turbomole 7.4.1.^[52] The SCF convergence criterion scfconv was set to 7 and 8 in optimizations and frequencies calculations, respectively. Single-point DLPNO-CCSD(T) energies were calculated in Orca 4.2.1^[53] with the RI-JK approximation and TightSCF and TightPNO options. PIMD simulations in the PIGLET variant with 1 fs time step were performed as implemented in the CP2K 9.0 (develop-

ment version git:6d312f7) code^[54] with preliminary testing and validation of its functionality. Gradients in these simulations were computed using the GFN1 approximation^[12] with tuned N···Te term, as recommended by MHG: GFN1(0.9). Calculations of vibrational interatomic amplitudes and corrections from the PIMD trajectories were performed with the Qassandra 1.0-7 program.^[55] Amplitudes and corrections at the level of perturbation theory^[5] were calculated from the PBE0-D3BJ/def2-TZVP optimized geometry and harmonic and cubic force fields using VibModule program.^[56] All vibrational calculations and PIMD simulations were done for the average experimental temperature $T=444(1)$ K. All kinds of GED data processing including refinements, data simulations and Monte-Carlo sampling were performed with the UNEX program.^[57]

Acknowledgements

We are grateful to Dr. J.-M. Mewes (Bonn) for cooperating on this topic in order to allow for a clear scientific debate. This work was funded by DFG (German Research Foundation) in the Priority Program SPP1807 “Control of London dispersion in molecular chemistry”, grant MI477/28-2, project no. 271386299), the core facility GED@BI (grant MI477/35-1, project no. 324757882) and a grant to Yu.V.V (VI 713/1-2, project no. 243500032). The authors gratefully acknowledge computing time provided by the DFG-funded HPC facilities at the Universität zu Köln (funding number: INST 216/512/1FUGG). Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

- [1] J.-M. Mewes, A. Hansen, S. Grimme, *Angew. Chem. Int. Ed.* **2021**, *60*, <https://doi.org/10.1002/anie.202102679>; *Angew. Chem.* **2021**, *133*, <https://doi.org/10.1002/ange.202102679>.
- [2] T. Glodde, Yu. V. Vishnevskiy, L. Zimmermann, H.-G. Stamm-ler, B. Neumann, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2021**, *60*, 1519–1523; *Angew. Chem.* **2021**, *133*, 1542–1546.
- [3] K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.* **1997**, *30*, 57–64.
- [4] a) J. Vogt, N. Vogt, R. Rudert, E. Popov, S. Schlagenhauf, K. Deutzmann, R. Kramer, *Struct. Chem.* **2015**, *26*, 1725–1727; b) J. Vogt, N. Vogt, *Asian J. Spectrosc.* **2010**, *67*–73.
- [5] V. A. Sipachev, *J. Mol. Struct.* **2004**, *693*, 235–240.
- [6] a) K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, J. F. Stanton, *J. Chem. Phys.* **2001**, *114*, 6548–6556; b) D. Cremer, E. Kraka, Y. He, *J. Mol. Struct.* **2001**, *567*–568, 275–293.
- [7] H. H. Nielsen, *Rev. Mod. Phys.* **1951**, *23*, 90–136.
- [8] M. K. Kesharwani, B. Brauer, J. M. L. Martin, *J. Phys. Chem. A* **2015**, *119*, 1701–1714.
- [9] G. Katzer, A. F. Sax, *J. Phys. Chem. A* **2002**, *106*, 7204–7215.
- [10] D. A. Wann, A. V. Zakharov, A. M. Reilly, P. D. McCaffrey, D. W. H. Rankin, *J. Phys. Chem. A* **2009**, *113*, 9511–9520.
- [11] R. A. Bonham, M. Fink, *High-Energy Electron Scattering*, Van Nostrand Reinhold, New York, **1974**.
- [12] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009.
- [13] Yu. V. Vishnevskiy, J. Schwabedissen, A. N. Rykov, V. V. Kuznetsov, N. N. Makhova, *J. Phys. Chem. A* **2015**, *119*, 10871–10881.
- [14] P. Rakesh, H. B. Singh, R. J. Butcher, *Acta Crystallogr. Sect. E* **2012**, *68*, o214.
- [15] L. Engman, A. Wojton, B. J. Oleksyn, J. Sliwinski, *Phosphorus Sulfur Silicon Relat. Elem.* **2004**, *179*, 285–292.
- [16] T. Chakraborty, H. B. Singh, R. J. Butcher, *Acta Crystallogr. Sect. E* **2009**, *65*, o2562–o2563.
- [17] J. E. Drake, M. B. Hursthouse, M. Kulcsar, M. E. Light, A. Silvestru, *J. Organomet. Chem.* **2001**, *623*, 153–160.
- [18] A. Gupta, R. Deka, S. Raju, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.* **2019**, *894*, 10–17.
- [19] E. W. Hughes, *J. Am. Chem. Soc.* **1956**, *78*, 502–503.
- [20] J. Demaison, J. Lievin, A. G. Császár, C. Gutle, *J. Phys. Chem. A* **2008**, *112*, 4477–4482.
- [21] K. Iijima, N. Adachi, S. Shibata, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3269–3273.
- [22] P. Cassoux, R. L. Kuczkowski, P. S. Bryan, R. C. Taylor, *Inorg. Chem.* **1975**, *14*, 126.
- [23] W. Kasten, H. Dreizler, R. L. Kuczkowski, *Z. Naturforsch.* **1985**, *40a*, 1262–1264.
- [24] A. M. Ja’o, D. A. Wann, C. D. Rankine, M. I. J. Polson, S. L. Masters, *Aust. J. Chem.* **2020**, *73*, 794–802.
- [25] P. Cassoux, R. L. Kuczkowski, A. Serafim, *Inorg. Chem.* **1977**, *16*, 3005.
- [26] K. Iijima, S. Shibata, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 711–715.
- [27] D. Göbbels, G. Meyer, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1799–1805.
- [28] S. Mebs, S. Grabowsky, D. Förster, R. Kickbusch, M. Hartl, L. L. Daemen, W. Morgenroth, P. Luger, B. Paulus, D. Lenz, *J. Phys. Chem. A* **2010**, *114*, 10185–10196.
- [29] D. Fujiang, P. W. Fowler, A. C. Legon, *J. Chem. Soc. Chem. Commun.* **1995**, 113.
- [30] S. Reeve, W. A. Burns, F. J. Lovas, R. D. Suenram, K. R. Leopold, *J. Phys. Chem.* **1993**, *97*, 10630.
- [31] M. A. Dvorak, R. S. Ford, R. D. Suenram, F. J. Lovas, K. R. Leopold, *J. Am. Chem. Soc.* **1992**, *114*, 108.
- [32] G. Feng, Q. Gou, L. Evangelisti, J.-U. Grabow, W. Caminati, *J. Mol. Spectrosc.* **2017**, *335*, 80–83.
- [33] P. M. Kuznesof, R. L. Kuczkowski, *Inorg. Chem.* **1978**, *17*, 2308.
- [34] S. W. Hunt, D. L. Shelley, K. R. Leopold, *J. Mol. Spectrosc.* **2012**, *281*, 9–12.
- [35] A. Haaland, S. Samdal, O. Stokkeland, J. Weidlein, *J. Organomet. Chem.* **1977**, *134*, 165.
- [36] L. Fernholt, A. Haaland, M. Hargittai, R. Seip, J. Weidlein, *Acta Chem. Scand. A* **1981**, *35*, 529–535.
- [37] C. Y. Tang, R. A. Coxall, A. J. Downs, T. M. Greene, L. Kettle, S. Parsons, D. W. H. Rankin, H. E. Robertson, A. R. Turner, *Dalton Trans.* **2003**, 3526–3533.
- [38] D. F. Shriver, C. E. Nordman, *Inorg. Chem.* **1963**, *2*, 1298.
- [39] J. R. Durig, K. K. Chatterjee, Y. S. Li, M. Jalilian, A. J. Zozulin, J. D. Odom, *J. Chem. Phys.* **1980**, *73*, 21.
- [40] P. T. Brain, H. E. Brown, A. J. Downs, T. M. Greene, E. Johnsen, S. Parsons, D. W. H. Rankin, B. A. Smart, C. Y. Tang, *J. Chem. Soc. Dalton Trans.* **1998**, 3685–3691.
- [41] M. Canagaratna, M. E. Ott, K. R. Leopold, *Chem. Phys. Lett.* **1997**, *281*, 63–68.
- [42] J. A. Phillips, D. Britton, K. R. Leopold, *J. Chem. Crystallogr.* **1996**, *26*, 533–538.
- [43] J. J. Oh, K. W. Hillig, R. L. Kuczkowski, *J. Phys. Chem.* **1991**, *95*, 7211–7216.
- [44] D. L. Fiacco, A. Toro, K. R. Leopold, *Inorg. Chem.* **2000**, *39*, 37–43.

- [45] J. J. Oh, M. S. LaBarge, J. Matos, J. W. Kampf, K. W. Hillig, R. L. Kuczkowski, *J. Am. Chem. Soc.* **1991**, *113*, 4732–4738.
- [46] G. Forgács, M. Kolonits, I. Hargittai, *Struct. Chem.* **1990**, *1*, 245–250.
- [47] N. W. Mitzel, U. Losehand, A. Wu, D. Cremer, D. W. H. Rankin, *J. Am. Chem. Soc.* **2000**, *122*, 4471–4482.
- [48] N. W. Mitzel, U. Losehand, *J. Am. Chem. Soc.* **1998**, *120*, 7320–7327.
- [49] N. W. Mitzel, K. Vojinović, R. Fröhlich, T. Foerster, D. W. H. Rankin, *J. Am. Chem. Soc.* **2005**, *127*, 13705–13713.
- [50] M. Hagemann, R. J. F. Berger, S. Hayes, H.-G. Stammler, N. W. Mitzel, *Chem. Eur. J.* **2008**, *14*, 11027–11038.
- [51] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16 Revision B.01*; Gaussian Inc. Wallingford CT, **2016**.
- [52] S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Vora, F. Weigend, A. Wodyński, J. M. Yu, TURBOMOLE: Modular Program Suite for Ab Initio Quantum-Chemical and Condensed-Matter Simulations, *J. Chem. Phys.* **2020**, *152*, 184107.
- [53] F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [54] J. Hutter, M. Iannuzzi, F. Schiffmann, J. VandeVondele, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2014**, *4*, 15–25.
- [55] Yu. V. Vishnevskiy, D. Tikhonov, *Theor. Chem. Acc.* **2016**, *135*, 88.
- [56] Yu. V. Vishnevskiy, Yu. A. Zhabanov, *J. Phys. Conf. Ser.* **2015**, *633*, 012076.
- [57] Yu. V. Vishnevskiy, UNEX version 1.6, <http://unexprog.org> (accessed Apr 1, 2021).

Manuscript received: April 9, 2021

Version of record online: May 3, 2021