Weak Te,Te Interactions through the Looking Glass of NMR Spin–Spin Coupling**

Michael Bühl,* Fergus R. Knight, Anezka Křístková, Irina Malkin Ondík, Olga L. Malkina, Rebecca A. M. Randall, Alexandra M. Z. Slawin, and J. Derek Woollins

Most of the tools for quantifying the extent of chemical bonding between two atoms are quantum-chemical in nature. None of them are unambiguous, however, and different analyses can lead to conflicting interpretations, even concerning the most fundamental question of whether or not atoms are linked by a chemical bond.1-3 One of the indicators that can be probed experimentally is the indirect spin–spin coupling constant (SSCC). For instance, observation of spin–spin coupling across hydrogen bonds4 has been taken as evidence for covalent contributions to this kind of bonding. For atoms within the same molecule that are close in space, but not linked through a direct formal bond, the question arises, how much of the observed coupling is transmitted through interaction through the overlap of lone pairs (“through-space coupling”). Again, a variety of quantum-chemical tools have been developed to address this question.

A rigid scaffold that is used to achieve such spatial proximity is the naphthalene framework, in which substituents in the peri (1,8) positions have a typical separation of around 3 Å.5 Through-space J(13C,13C) SSCCs, long known for their distance dependence, have been studied in some detail with Te substituents.6 Similarly, J(31P,31P) values in peri-bis(phosphino)naphthalenes have been attributed to through-space coupling,6 and J(77Se,77Se) values in peri-bis(seleno) derivatives have been analyzed in detail through quantum-chemical computations.7 In systematic studies of naphthalene (N) and acenaphthene (A) derivatives with pnictogen and chalcogen atoms in the peri positions, it became apparent that for the heavier congeners, steric repulsion is partly counterbalanced by attractive interactions. In particular with Te substituents, formally nonbonded, “across-the-bay” distances are significantly shorter than the sum of the van-der-Waals radii, which has been traced back to weak donor–acceptor interactions and the onset of 3-center-4-electron (3c4e) bonding.8

For instance in N1 and A1 (Scheme 1), Te–Te distances of around 3.3 Å are observed in the solid state (ca. 0.7 Å below the sum of the vdW radii), and Wiberg bond indices9 (WBI,

![Diagram](image-url)

Scheme 1. Peri-naphthalene ditellurides with formally nonbonded Te atoms.

Because the two Te sites in N1 and A1 are magnetically equivalent in solution, direct observation of J(125Te,125Te) is not possible, but the coupling can be detected as satellites in the 125Te NMR spectrum (see experimental details). With this technique, J(125Te,125Te) values of 2077 and 1750 Hz are...
obtained for N1 and A1, respectively. Neglecting primary and secondary isotope effects, these values correspond to 2505 and 2110 Hz, respectively, in J(125Te,125Te). While the computed value for N1 is again overestimated with respect to the experiment, that for A1 is underestimated, but overall, the predicted tendency is confirmed qualitatively.

To gain deeper insights into the factors that govern the magnitude of these J values, additional computations were performed (Table 1). Typical for NMR properties of heavier elements,[12] the theoretical J couplings are quite sensitive to relativity (compare entries 1–3 in Table 1), level of geometry optimization (compare entries 3 and 4), exchange–correlation functional (compare entries 4 and 5), and rather strongly on the conformation (compare entries 7 and 8).

The conformations of each phenyl group with respect to the naphthalene plane can be classified as roughly perpendicular (A), in-plane (B), or in-between (C), and both can be cis (c) or trans (t) to each other.[8] In the solid, N1 and A1 adopt CCt and AB conformations, respectively (see Figure S1 in the Supporting Information). For the smaller methyl derivatives, for which a CCt conformation would have a representative, Zora-spin-orbit, TZ2P basis employed throughout. [b] Sum of Fermi-contact and spin-dipolar part. [c] Paramagnetic spin-orbit part. [d] Total J coupling. [e] AB conformation.

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The first of the 2D plots represents the potential energy, with the minimum labeled as CCt. There is a huge flat area within just 1 kcal mol\textsuperscript{-1} (light yellow) which extends well into what would be classified as AB conformation, consistent with the structural variety observed in the solid for different members of this family.[8] The second of the 2D plots represents the J coupling surface, which looks quite different. Here, a structure with CCt conformation would have a J value of around 2500 Hz, similar to what is found for N1; a structure in the AB region would be much lower (ca. 1500 Hz). This situation is reminiscent of that in the Se congeners, although the J(\textsuperscript{77}Se,\textsuperscript{77}Se) values computed for the corresponding stationary points are much smaller.[7,13]
space around them). Because the $J$ coupling changes so dramatically with the conformations (bottom of Figure 1), it is a sensitive probe into structure and dynamics of this kind of system.

A mean $J^{(125\text{Te},125\text{Te})}$ value of more than 2500 Hz, as observed for N1, is quite large for a $J$ coupling between formally nonbonded Te atoms. The largest SSCC between bonded Te atoms is, to our knowledge, $J^{(125\text{Te},125\text{Te})} = 4395$ Hz in Te$_2$$^2$-$^2$.[15] Similar values can be reached in N1a (Figure 1) and are even exceeded in one of the instantaneous MD snapshots. Why are these formal $J$ couplings so large? When the naphthalene moiety in the B3LYP geometry of N1 is deleted and the Te atoms capped with H atoms, the computed $J$ value even increases from 2779 Hz to 3101 Hz. Transmission through the intermittent TeC- and CC-bonds thus plays only a minor role.

The same conclusion can be drawn from analysis of the Te–Te coupling pathway in N1a through inspection of the coupling deformation density (CDD).[16] Reminiscent of the situation in $J$(P,P) couplings ($n = 2,3$),,[16] the overlap of the lone pairs (lps) is the determining mechanism, rather than transmission through the organic framework (Figure 2). The CDD topology was obtained for the first time at a relativistic level (the first order Douglas-Kroll-Hess, DKH-1). Because it is very similar to its nonrelativistic counterpart (see Figure S3 in the Supporting Information), the analysis of $J^{(125\text{Te},125\text{Te})}$ performed at the nonrelativistic level should give a qualitatively correct picture. At the nonrelativistic BP level, the total calculated FC part of $J^{(125\text{Te},125\text{Te})}$ is 2038 Hz, the largest part of which (in a localized MO formalism with Pipek-Mezey localization[20]) stems from the two “sp-like”[19] Te lone pairs (+2359 Hz in total), with smaller contributions from the four Te–C bonds (−301 Hz) and negligible ones from the two “p-type” Te lone pairs (21 Hz, see Figure S4 in the Supporting Information).

It is noteworthy that the Te,Te coupling path in the CDD analysis extends noticeably into the “dead ends” of the Te–C(Me) bonds, rather than the conjugated aromatic moiety.

This may be taken as evidence for the importance of the lp(Te)–o*(TeC) interaction that is responsible for the onset of 3c4e bonding and the noticeable WBI.[8,19] In this context, it is interesting to note that at the same nonrelativistic level, a bond-critical point is located between the two Te atoms in N1a in an atoms-in-molecules analysis.[20]

The variation in the computed $J$ values can be rationalized through the extent of overlap between the densities of the Te lone pairs (Figure S5). Compared to typical “through-space” $J$(P,P) couplings, the Te,Te couplings of this study are larger by at least one order of magnitude.[13] From computed valence s-orbital densities (see the Supporting Information) and the gyromagnetic ratios, one would expect Te,Te couplings to be approximately seven times larger than the corresponding $J$(P,P). Further enhancement is likely due to the increased polarizability and the onset of multicenter bonding in the Te systems.

In the course of our studies, we noticed that the mesityl derivative A1a showed an even larger Te,Te coupling than N1 or A1, namely $J^{(125\text{Te},125\text{Te})} = 3398$ Hz. This value led us to suspect that, unlike A1 with its AB conformation,[8] A1a would rather adopt a CCt conformation, an expectation that was borne out in a subsequent structure determination by X-ray crystallography (Figure 3).[21] These findings underscore the potential of Te,Te-coupling constants as an analytical tool.

Figure 2. Total coupling deformation density (CDD) in N1a. (DKH-1/BP/Hirao/II level, isosurfaces plotted for CDD = 6.0).

Figure 3. The crystal structure of 5,6-bis(mesityltelluro)acenaphthene (A1a, H atoms omitted for clarity), including the key dihedral angles for classification as CCt conformation. See the Supporting Information for further details.

In summary, a combination of NMR and DFT techniques has been used to study the interactions between formally nonbonded, but spatially close Te atoms. Weak donor–acceptor interactions in the peri-naphthalene system, which mark the onset of 3c4e bonding, reinforce the Te,Te couplings and lead to unusually large $J^{(125\text{Te},125\text{Te})}$ values. This property turns out to be a sensitive probe (“looking glass”), not only into the electronic structure underlying the bonding situation, but also into the particular conformations that ensue. In the broader context of well-known through-space spin–spin coupling, this conformational aspect is a new facet worth exploring. Studies are under way to probe how substituents at the phenyl rings can modulate the bonding and the concomitant NMR properties, ever broadening our knowledge of the very foundation of chemistry, the chemical bond.
**Experimental Section**

Geometry optimizations and Born–Oppenheimer MD simulations were carried out at the B3LYP/6-31G* level (augmented SDD on Te), $J$ values computed\(^{[35]}\) at the ZORA-Spinorbit/BP86/TZ2P level (which has performed well for the computation of SSCCs involving fourth-row and heavier elements)\(^{[35]}\) or at the nonrelativistic BP86 level (TZVP on Te, IGLO-II on C,H).\(^{[35]}\) 123Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with $\delta$(Te) referenced to external diphenyl ditelluride. $^{127}$Te NMR (70.7 MHz, 25°C. PhTe-TePh): $\delta$ = 620.3 ppm (s, $J$(125Te,127Te) = 2077.4 Hz). A1 (CDCl3): $\delta$ = 586.6 ppm (s, $J$(125Te,127Te) = 1750.4 Hz; see Figure S8 in the Supporting Information for the spectra), A1a (CDCl3): $\delta$ = 362.9 ppm (s, $J$(125Te,127Te) = 2818.5 Hz; see Supporting Information for experimental details).

Received: July 26, 2012
Revised: November 14, 2012
Published online: January 23, 2013

**Keywords:** naphthalenes · quantum-chemical computation · tellurium · through-bond interactions · through-space interactions

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[14] The reasonably good accord between the ZSO/BP/B3LYP result for $\text{N}_{1}$ (2779 Hz, Table 1) with the experimental result (2505 Hz) may thus be somewhat random.
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[19] If the FC part of $\text{J}$(125Te,125Te) in $\text{N}_{1}$ is subjected to an NBO analysis (J. Autschbach, *J. Chem. Phys.* 2008, 128, 164112) at the scalar ZORA level, the $J$ coupling is clearly dominated by the four lone pairs, with the two “sp-type” and “p-type” lone pair NLMOs contributing each at about 1000 Hz and 400 Hz, respectively. A similar picture is obtained for the FC part of $\text{J}$(125Te,125Te) in $\text{N}_{1}$ in a natural $J$ coupling analysis (S. J. Wilkens, W. M. Westler, J. L. Markley, F. Weinhold, *J. Am. Chem. Soc.* 2001, 123, 12026–12036) at the nonrelativistic BP level, where roughly half of the $J$ coupling is indicated to come from the Lewis structure, the other half from delocalization. The Lewis and total NLMO contributions are dominated by the “sp” lone pairs, whereas the single largest delocalization contributions stem from the “sp-type” $\text{p}(\text{Te})$–$\text{o}(\text{TeC})$ interactions (ca. 400 Hz each).

The *Quantum Theory of Atoms in Molecules* (Eds.: C. F. Matta, R. J. Boyd), Wiley-VCH, Weinheim, 2007: for the critical point in $\text{N}_{1}$, $\rho$ and $\nabla \rho$ values are 0.022 au and 0.033 au, respectively, that is, around 20% and 100%, respectively, of the corresponding values for the Te–C bonds; very similar values are obtained for $\text{N}_{1}$.

This is the only minimum that can be located for $\text{A}_{1}$ at the B3LYP level (computed $J$ value of 2738 Hz); apparently, the Me substituents help to sample the area of maximum $J$ in space (around 150°/150° in Figure 1).

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