

Unusual Intermolecular “Through-Space” *J* Couplings in P–Se Heterocycles

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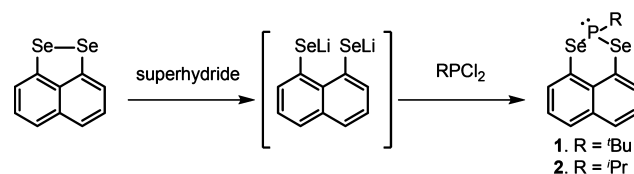
Supporting Information

ABSTRACT: Solid-state NMR spectra of new P–Se heterocycles based on *peri*-substituted naphthalene motifs show the presence of unusual *J* couplings between Se and P. These couplings are between atoms in adjacent molecules and occur “through space”, rather than through conventional covalent bonds. Experimental measurements are supported by relativistic DFT calculations, which confirm the presence of couplings between nonbonded atoms, and provide information on the pathway of the interaction. This observation improves the understanding of *J* couplings and offers insight into the factors that affect crystal packing in solids, for future synthetic exploitation.

Sulfur- and selenium-rich compounds are important in molecular materials since the large, polarizable atoms often support weak interatomic interactions that lead to unusual magnetic or electronic properties.^{1–4} The design of new molecular materials for such applications requires an understanding of weak bonding and repulsive interactions, and we (and others) have previously utilized 1,8 di- (i.e., *peri*-) substituted naphthalene (and acenaphthene) motifs to enable this study.^{5–9} While bond lengths, molecular conformations, and interatomic distances offer some information, these structural parameters are not very sensitive probes of electronic interactions. In contrast, NMR parameters are potentially more sensitive and reliable probes, with the indirect spin–spin (*J*) coupling in particular able to provide insight into chemical bonding. In addition, significant *J* couplings have been observed using solution-state NMR spectroscopy between nuclei that are not formally bonded.¹⁰ For example, we observed large *J* couplings in naphthalenes and acenaphthenes with heavier group 16 (e.g., S, Se, and Te) *peri*-substituents separated by four formal bonds, but at distances smaller than the sum of their van der Waals radii.^{11–16} In previous literature such couplings have been referred to (perhaps erroneously) as “through-space” couplings. Consequently, we will also use this term to refer to couplings between atoms that are not formally bonded, but without implying the nature of the interaction. In this work, solid-state NMR spectroscopy of novel P–Se heterocycles demonstrates the presence of not only intramolecular through-space *J* couplings but also unusual through-space *intermolecular* couplings that direct the three-dimensional solid-state structure, and use periodic DFT calculations to understand their origin.

Two novel selenium phosphorus naphthalenes (**1** and **2**) were prepared following an adapted route,^{17,18} using tertiary phosphines under an oxygen and moisture-free atmosphere, as shown in Scheme 1.

Scheme 1. Synthesis of Naphtho[1,8-*cd*]1,2-diselenole Alkylphosphines



Naphtho[1,8-*cd*]1,2-diselenole was treated with 2 equiv of superhydride, which, when reacted with the corresponding ⁱPr or ^tBu phosphine afforded **1** and **2** in moderate yields (48% and 45%, respectively). Each compound was characterized by solution- and solid-state NMR spectroscopy, single-crystal X-ray diffraction, IR spectroscopy, mass spectrometry, and microanalysis, as described in the Supporting Information. Solution-state ¹³C{¹H} NMR spectra confirm the presence of ^tBu and ⁱPr groups, for **1** and **2**, respectively, and the ³¹P{¹H} solution-state NMR spectra exhibit single resonances at 12.3 and –3.4 ppm. As a result of the low natural abundance of ⁷⁷Se (*I* = 1/2, 7.63%), “satellites” are observed corresponding to ¹*J* ³¹P–⁷⁷Se couplings of 302 Hz for **1** and 276 Hz for **2**. As given in Table 1, the ⁷⁷Se solution-state NMR spectra of **1** and **2** exhibit doublets (centered at 210.2 and 270.2 ppm, respectively) and confirm the magnitude of the ¹*J* ³¹P–⁷⁷Se couplings.

Table 1. Experimental Solution- and Solid-State ⁷⁷Se Chemical Shifts and Se–P *J* Couplings in **1 and **2****

	compound 1		compound 2	
	δ (ppm)	<i>J</i> /Hz	δ (ppm)	<i>J</i> /Hz
solution	210.2	302	270.2	276
solid	176	319	278	c. 300
(9.4 T)	210	340, 270		

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Solid-state ^{77}Se magic-angle spinning (MAS) NMR spectra, acquired at various field strengths using cross-polarization (CP), are shown in Figure 1.

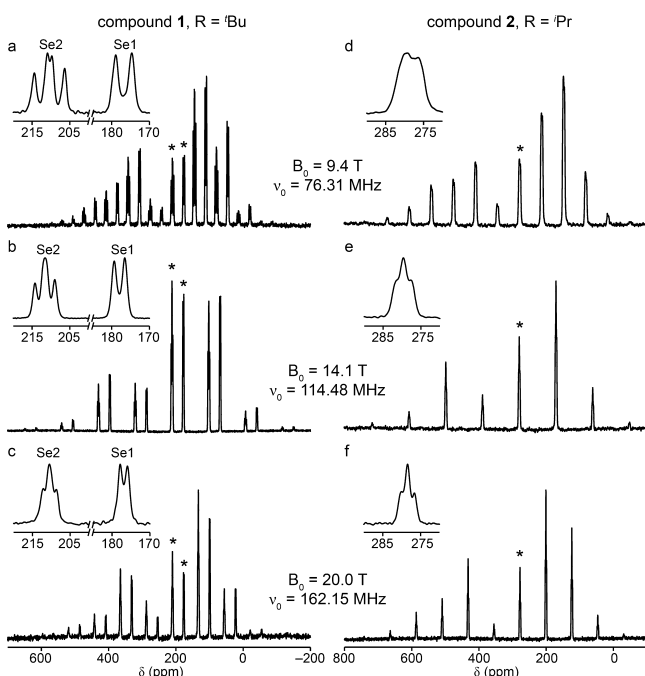


Figure 1. ^{77}Se CP MAS NMR spectra of **1** and **2**, at (a, d) 9.4 T (5 kHz), (b, e) 14.1 T (12.5 kHz), and (c, f) 20.0 T (12.5 kHz).

In each case, a significant sideband manifold is observed as a result of the chemical shift anisotropy (CSA). The positions of the isotropic centerbands (*) were determined by acquiring additional spectra at a faster MAS rate. For **1**, two isotropic signals are easily distinguished, as shown in Table 1, centered around 176 and 210 ppm at 9.4 T (5 kHz MAS), resulting from the two Se in the molecule, which are distinct as a result of the crystal packing. In contrast, for **2**, a single isotropic resonance appears to be observed (at *c.* 278 ppm at 9.4 T). As shown in the (inset) expansions, multiplet structures are observed for the centerbands. At all fields, the centerbands for **1** show a clear doublet for the Se at 176 ppm, but what appears to be a “doublet of doublets” for the Se at 210 ppm. The doublet splitting for the Se at 176 ppm is *c.* 319 Hz (9.4 T), in relatively good agreement with the 1J ^{31}P – ^{77}Se couplings observed in solution. Multiple-field measurements enable two couplings of *c.* 340 and *c.* 270 Hz, to be determined for the signal at 210 ppm. In contrast, for **2**, a broadened, overlapped line shape is seen at lower field strengths, resolving into a pattern containing two closely spaced doublets at higher field strengths, with J couplings of *c.* 300 Hz (see Supporting Information). The origin of the coupling patterns observed is not immediately clear. A significant 1J coupling to ^{31}P would be expected for all Se, but while (through-space) J couplings between *peri*-substituted group 16 elements have been observed in solution (150–400 Hz for Se, and up to 4000 Hz for Te),^{10–16} the low natural abundance of ^{77}Se would not produce the multiplet patterns observed. It should also be noted that the exact chemical shifts vary between each of the different experimental measurements; however, the different spinning speeds and rotor sizes used will result in different temperatures (arising from frictional heating) for the measurements. Variable-

temperature experiments at one field strength confirmed that both shifts and couplings show a small temperature dependence (see Supporting Information), probably as a result of motion of the alkyl chain.

Figure 2 shows ^{77}Se MAS NMR spectra, acquired with ^1H and ^{31}P decoupling. When all couplings to ^{31}P are removed,

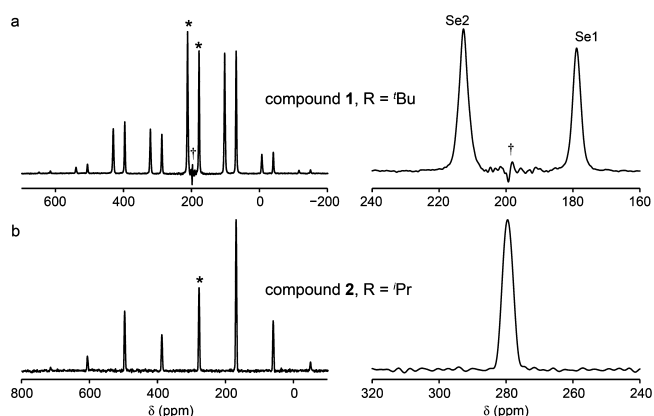


Figure 2. ^{77}Se CP MAS NMR spectra of (a) **1** and (b) **2**, at 14.1 T (114.5 MHz, 12.5 kHz), with ^{31}P decoupling. † denotes an artifact from multiple-channel decoupling.

two single resonances corresponding to two distinct Se species for **1** and one resonance (containing two overlapped signals) for **2** are observed, confirming the multiplet patterns result from the presence of multiple couplings to ^{31}P . From these decoupled spectra it is possible to obtain the complete ^{77}Se CSA parameters, which are given in the Supporting Information. Note that the corresponding ^{31}P – ^{77}Se J couplings are not resolved in the ^{31}P MAS NMR spectra (Supporting Information), owing to the broader lines observed in the solid state and the low abundance of ^{77}Se .

The crystal structures for **1** and **2** (obtained using single-crystal diffraction) provide insight into the origin of the NMR spectra observed. As shown in Figure 3 (and Supporting

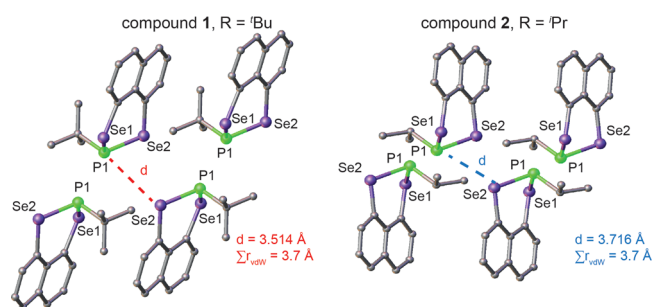


Figure 3. Packing motifs for **1** and **2**, showing the shortest intermolecular Se–P distances.

Information), in each case chains of molecules are seen, but the different size of the alkyl groups results in a different packing motif. For **1**, a very short *intermolecular* Se2–P distance of 3.514 Å is found (notably within the sum of the van der Waals radii), while the corresponding Se1–P distance is 4.095 Å. In contrast, for **2**, two more similar distances, 4.017 and 3.716 Å, are observed for Se1–P and Se2–P, respectively. This suggests that the CP MAS spectrum of **1** contains an additional J coupling to ^{31}P , which must be both “through space” and, remarkably, between different molecules, i.e., *intermolecular*.

Although, as described above, through-space couplings have been observed for molecules in solution,¹⁰ relatively few through-space J couplings have been observed in the solid state (partly as a result of the inherently broader lines obtained). A number of *intramolecular* couplings between *peri*-substituted atoms (and others similarly forced close in space) have been observed, notably for P, Se, and Te,^{14,19–21} and work by Ashbrook and co-workers determined the presence of a through-space ^{19}F – ^{19}F interaction in fluorinated clinohumite, $4\text{Mg}_2\text{SiO}_4\cdot\text{Mg}(\text{F},\text{OH})_2$.²² However, the observation of an *intermolecular* through-space J coupling in a solid remains extremely unusual, if not unique. (Note intermolecular couplings via hydrogen bonds have been observed for small organic molecules.^{23,24})

In order to support the conclusions of the solid-state NMR experiments, and to gain insight into the nature of the interactions observed, periodic planewave density functional theory (DFT) calculations were carried out using the CASTEP code²⁵ (see Supporting Information). J coupling calculations, performed at the scalar-relativistic levels of theory using the ZORA method, are given in Table 2.^{26,27} ZORA was found to

Table 2. J Couplings (Hz) (TB = formally through bond, TS = formally through space) in **1** and **2** Predicted by DFT at the Scalar-Relativistic ZORA Level of Theory^a

	Type	1	2
Se1–P	TB	–289.7	–271.6
Se1–P	TS	66.6	64.1
Se2–P	TB	–324.0	–261.4
Se2–P	TS	348.0	109.1
P–P	TS	147.6	11.5
Se1–Se2	TB	13.9	29.4
Se1–Se2	TS	23.5	19.8
Se1–Se1	TS	123.7	136.3
Se2–Se2	TS	75.3	1.7

^aValues given are the largest coupling of that type.

make a small difference in the predicted couplings, generally resulting in an increase. However, ZORA and nonrelativistic calculations do predict a different order for the Se2–P through-bond and through-space couplings.

For **1**, two major Se2–P couplings were predicted. A through-bond coupling (i.e., to P in the same molecule) of –324.0 Hz was found, along with a 348.0 Hz through-space coupling (i.e., to P in a neighboring molecule). These are in reasonable quantitative agreement with the two experimental couplings, *c.* 340 Hz and *c.* 270 Hz. Only one major Se1–P coupling was found, predicted to be –289.7 Hz (through bond), in good agreement with the single experimental coupling of *c.* 319 Hz. For **2**, each Se site exhibited only one major coupling to P. Se1–P was predicted to be –271.6 Hz, and Se2–P was predicted to be –261.4 Hz, both in good agreement with the experimental range of 280 to 290 Hz. The predicted *peri*- through-bond Se–Se couplings were small in both compounds, whereas large through-space Se1–Se1 couplings of 123.7 and 136.3 Hz were predicted in **1** and **2**, respectively. However, these are not easy to observe in solids, owing to the low abundance of ^{77}Se . The dominant J coupling mechanism in all the Se–P couplings was shown to be the Fermi contact interaction, indicating that, although formally “through space”, there is a significant electronic interaction present.¹⁰ To investigate the pathway of the through-space

couplings, the coupling deformation density (CDD)²⁸ (see Supporting Information) was calculated, as shown in Figure 4.

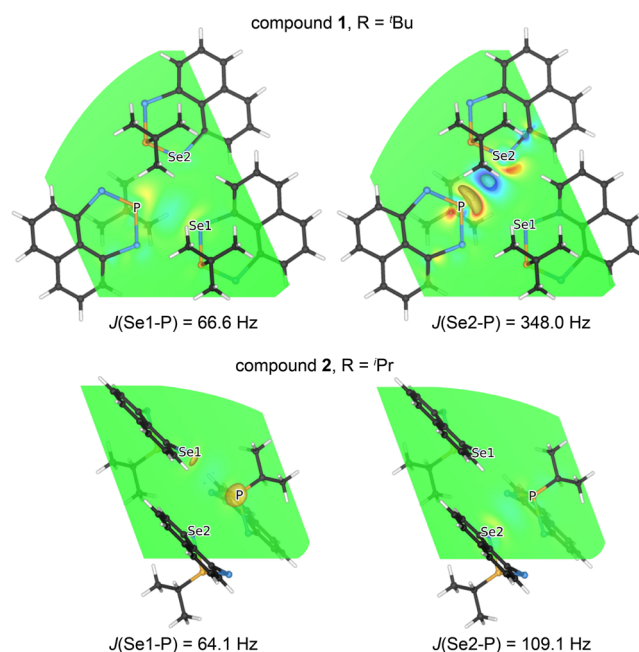


Figure 4. Coupling deformation density (CDD) of the Se1–P and Se2–P through-space J couplings in **1** and **2**, shown with isosurfaces on the same scale.

The CDD demonstrates that the large Se2–P coupling in **1** proceeds by the overlap of the P and Se2 lone pairs, while the P and Se1 lone pairs do not overlap as significantly resulting in a smaller through-space coupling. In **2**, both overlaps are weak and there is little observable CDD.

We have demonstrated the presence of unusual through-space J couplings in new *peri*-substituted naphthalene-based heterocycles. In addition to the known through-space couplings between the *peri*-substituted Se atoms, *intermolecular* heteronuclear J couplings between ^{77}Se and ^{31}P were observed. Experimental measurements were supported by relativistic DFT calculations, which verified the presence of these through-space interactions, and provided insight into the coupling mechanism. This work adds to the range of weak interactions that can be utilized to direct structure, and may lead to unusual physical properties that can be exploited further in the future.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic details, experimental methods, diffraction structures, solid-state ^{13}C , ^{31}P , and ^{77}Se NMR spectra, and more information on DFT and CCD calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03353.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Stingelin-Stutzmann, N. *Nat. Mater.* **2008**, *7*, 171.
- (2) Semenov, N. A.; Pushkarevsky, N. A.; Lonchakov, A. V.; Bogomyakov, A. S.; Pritchina, E. A.; Suturina, E. A.; Gritsan, N. P.; Konchenko, S. N.; Mews, R.; Ovcharenko, V. I.; Zibarev, A. V. *Inorg. Chem.* **2010**, *49*, 7558.
- (3) Cozzolino, A. F.; Whitfield, P. S.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2010**, *132*, 17265.
- (4) Alberola, A.; Less, R. J.; Pask, C. M.; Rawson, J. M.; Palacio, F.; Oliete, P.; Paulsen, C.; Yamaguchi, A.; Farley, R. D.; Murphy, D. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4782.
- (5) Knight, F. R.; Fuller, A. L.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2010**, *16*, 7503.
- (6) Kilian, P.; Knight, F. R.; Woollins, J. D. *Chem.—Eur. J.* **2011**, *17*, 2302.
- (7) Aschenbach, L. K.; Knight, F. R.; Randall, R. A. M.; Cordes, D. B.; Baggott, A.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2012**, *41*, 3141.
- (8) Zhang, S.; Wang, X.; Su, Y.; Qiu, Y.; Zhang, Z.; Wang, X. *Nat. Commun.* **2014**, *5*, 4127.
- (9) Zhang, S.; Wang, X.; Sui, Y.; Wang, X. *J. Am. Chem. Soc.* **2014**, *136*, 14666.
- (10) Hierso, J. C. *Chem. Rev.* **2014**, *114*, 4838.
- (11) Knight, F. R.; Randall, R. A. M.; Athukorala Arachchige, K. S.; Wakefield, L.; Griffin, J. M.; Ashbrook, S. E.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chem.* **2012**, *51*, 11087.
- (12) Bühl, M.; Knight, F. R.; Křístková, A.; Malkin Ondik, I.; Malkina, O. L.; Randall, R. A. M.; Slawin, A. M. Z.; Woollins, J. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 2495.
- (13) Diamond, L. M.; Knight, F. R.; Athukorala Arachchige, K. S.; Randall, R. A. M.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2014**, 1512.
- (14) Stanford, M. W.; Knight, F. R.; Athukorala Arachchige, K. S.; Sanz Camacho, P.; Ashbrook, S. E.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2014**, *43*, 6548.
- (15) Knight, F. R.; Diamond, L. M.; Athukorala Arachchige, K. S.; Sanz Camacho, P.; Randall, R. A. M.; Ashbrook, S. E.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2015**, *9*, 3613.
- (16) Knight, F. R.; Fuller, A. L.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2010**, *16*, 7617.
- (17) Baudler, M.; Moog, A.; Glinka, K.; Kelsch, U. *Z. Naturforsch.* **1973**, *28*, 263.
- (18) Fuller, A. L.; Knight, F. R.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2010**, *2010*, 4043.
- (19) Wiegand, T.; Eckert, H.; Ren, J.; Brunklaus, G.; Fröhlich, R.; Daniliuc, C. G.; Lubbe, G.; Bussmann, K.; Kehr, G.; Erker, G.; Grimme, S. *J. Phys. Chem. A* **2014**, *118*, 2316.
- (20) Wiegand, T.; Eckert, H.; Ekkert, O.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *J. Am. Chem. Soc.* **2012**, *134*, 4236.
- (21) Athukorala Arachchige, K. S.; Sanz Camacho, P.; Ray, M. J.; Chalmers, B. A.; Knight, F. R.; J, M.; Ashbrook, S. E.; Bühl, M.; Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *Organometallics* **2014**, *33*, 2424.
- (22) Griffin, J. M.; Yates, J. R.; Berry, A. J.; Wimperis, S.; Ashbrook, S. E. *J. Am. Chem. Soc.* **2010**, *132*, 15651.
- (23) Brown, S. P.; Perez-Torrallba, M.; Sanz, D.; Claramunt, R. M.; Emsley, L. *J. Am. Chem. Soc.* **2002**, *124*, 1152.
- (24) Pham, T. N.; Masiero, S.; Gottarelli, G.; Brown, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 16018.
- (25) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. *Z. Kristallogr.* **2005**, *220*, 567.
- (26) Joyce, S. A.; Yates, J. R.; Pickard, C. J.; Mauri, F. *J. Chem. Phys.* **2007**, *127*, 204107.
- (27) Green, T. F. G.; Yates, J. R. *J. Chem. Phys.* **2014**, *140*, 234106.
- (28) Malkina, O. L.; Malkin, V. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4335.