The Signs of Nuclear Spin–Spin Coupling Constants Involving Selenium: the Effect of Electron Lone Pairs

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Summary The signs of coupling constants involving selenium are usually unaffected by changes in the valency of selenium, but if all the selenium electron lone pairs are used for bonding there may be a sign inversion.

Coupling constants between ^{31}P and ^{1}H or ^{13}C usually alter substantially and often change sign as the substituents and valence of the phosphorus atom are changed.[1] By contrast most analogous coupling constants involving ^{77}Se vary much less, and sign changes are unknown in the limited range of species which has been studied hitherto.[2–4] We now report heteronuclear magnetic double resonance experiments done on a wider range of molecules which show that in certain circumstances changes of sign do occur, and which suggest that there are close parallels between couplings involving phosphorus and those involving selenium.

The data of the table were obtained by standard $^{1}H-\{^{13}C\}$ and $^{1}H-\{^{77}Se\}$ double resonance experiments upon samples containing the isotopes ^{13}C and ^{77}Se in natural abundance. (1·1 and 7·5% respectively).

Table

	Compound	$^{n}J(^{77}Se \cdots {}^{1}H)^{c}$ (in Hz)	$^{n-1}J(^{77}Se \cdots {}^{13}C)^{c}$ (in Hz)	$^{n+1}J(^{77}Se \cdots {}^{1}H)^{c}$ (in Hz)	n	Number of Se lone pairs	Reference
1	$EtSe^{-}Na^{+}$	+ 7·5 ± 2·0		+12·3 ± 0·3	2	3	[a]
2	MeSeH	+10·5 ± 0·2	−48 ± 10		2	2	2
3	Me_2Se	+10·5 ± 0·2	−62 ± 1		2	2	3
4	Me_2Se_2	+11·9 ± 0·2	−75		2	2	3
5	EtSeH	+13·0 ± 0·5		+10·5 ± 0·5	2	2	[a]
6	Et_2Se	+10·7 ± 0·2		+10·8 ± 0·2	2	2	[a]
7	Et_2Se_2	+15·4 ± 0·3		+ 9·3 ± 0·3	2	2	[a]
8	$Me_3Se^{+}I^{-}$	+ 9·3 ± 0·2	−50 ± 3		2	1	3
9	$Et_3Se^{+}I^{-}$	+ 7·5 ± 1·0		+17·4 ± 0·5	2	1	[a]
10	Et_2SeBr_2	+ 5·3 ± 0·5		+17·2 ± 0·2	2	1	[a]
11	$MeSeO_2H$	(+)13·5 ± 0·2[b]			2	1	4
12	$EtSeO_2H$	+16·5 ± 0·5		+12·8 ± 0·3	2	1	[a]
13	$(MeO)_2SeO$	(+)7·6 ± 0·2	(+) 0·9 ± 0·4		3	1	[a]
14	$MeSeO_3^{-}K^{+}$	(−)8·8 ± 0·2			2	0	[a]
15	$EtSeO_3^{-}K^{+}$	− 3·6 ± 0·2		+37·9 ± 0·2	2	0	[a]
16	$(MeO)_2SeO_2$	+25·0 ± 0·2	−12·6 ± 1·0		3	0	[a]

[a] This work. [b] Parentheses indicate that the sign is assumed to be the same as in a closely related compound. [c] n is defined in column Six.

For the ethyl compounds the signs are relative to $^{3}J(H \cdots H)$ which is known to be positive,[5] and for the methyl compounds they are relative to $^{1}J(^{13}C–H)$ (positive) except in $(MeO)_2SeO$ in which $^{2}J(^{13}C \ldots {}^{77}Se)$ was too small to permit a reliable sign determination. In $(PhCH_2O)_2SeO$ however, $^{3}J(^{77}Se \ldots H)$ was found to be of opposite sign to the coupling between the magnetically inequivalent geminal protons which is known to be negative, so a positive value is assigned to $^{3}J(^{77}Se \cdots H)$ in $(MeO)_2SeO$.

It is apparent that $^{3}J(^{77}Se \cdots H)$ is always positive; this is analogous to the situation in phosphorus compounds in which only a specific geometrical relationship can lead to a (small) negative $^{3}J(^{31}P \cdots H)$. Provided that the selenium atom retains at least one electron lone pair the coupling constants $^{2}J(^{77}Se \cdots H)$, $^{2}J(^{77}Se \cdots {}^{13}C)$, and $^{1}J(^{77}Se \cdots {}^{13}C)$ are positive, positive, and negative respectively, regardless of the valence and co-ordination number of the selenium atom. The analogous coupling constants involving ^{31}P generally have these signs only in trico-ordinate phosphorus(III) compounds. In phosphorus(V) compounds, in which there are no lone pairs, these signs are inverted, and species **14**—**16** (see Table) display similar behaviour, thus showing the parallel between phosphorus and selenium coupling constants. Dominance of the coupling mechanism by the Fermi contact interaction will lead to positive one-bond and negative two-bond coupling constants provided the *s* overlap integral for the appropriate P–C or Se–C bond is reasonably large, and this will be the case when there are no lone pairs on phosphorus or selenium.[6]

However when the phosphorus or selenium atom has at least one lone pair this will have most of the phosphorus or selenium *s*-character, and that of the hybrids used to form the bonds will be low so that the *s*-overlap integral will be small. This is the situation found in most selenium compounds and therefore $^{2}J(^{77}Se \cdots H)$ and $^{2}J(^{77}Se \cdots {}^{13}C)$ are normally positive. But in the species 14—16 with no selenium lone pairs the geminal coupling to selenium is negative as is found for the majority of geminal coupling constants including those involving phosphorus(V). We can further predict that in 14 and 15 $^{1}J(^{77}Se—{}^{13}C)$ will be positive.

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