CARBON–CARBON AND CARBON–CHALCOGEN SPIN–SPIN COUPLING CONSTANTS IN CHALCOGEN-SUBSTITUTED ACETYLENES

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Summary

Carbon–Carbon and carbon–chalcogen spin–spin coupling constants have been determined for chalcogen-substituted phenyl-, alkyl- and silyl-acetylenes. The changes in the C–C couplings involving acetylenic *sp* carbons are explained in terms of the electronegativities of the substituent. The chalcogen-carbon coupling dependence on carbon hybridization previously noted for tellurium derivatives is confirmed.

Introduction

In continuation of our studies of the influence of substituents on C–C coupling constants in variously-substituted acetylenes [1–3], we report here our results for chalcogen substituents. Our main aim was to see whether the general trends reported previously [2] would be observed for a specific group of substituents. Experimental values of C–Se and C–Te coupling constants (measured at natural abundance) are also reported and the factors governing these couplings analysed.

Results

All the spin–spin coupling constants observed in this work are listed in Tables 1–4. Table 1 contains one-bond C–C coupling constants across the C≡C bond and those across C_{sp}–X single bonds, where X = C, H, Si or Sn. Table 1 also, shows values of J(C≡C) calculated by INDO FPT for most of the compounds under study. Table 2 lists values of the couplings J(C–Se) and J(C–Te), and their reduced values K. Table 3 lists two-bond C–C couplings involving carbon atoms of acetylenic fragments. Table 4 lists coupling constants between carbon atoms of the phenyl

TABLE 1

EXPERIMENTAL AND CALCULATED (INDO FPT) VALUES OF NUCLEAR SPIN–SPIN COUPLING CONSTANTS $^1J(C\equiv C)$ AND $^1J(\equiv C-X)$ (X = H, C_{sp^3}, C_{Ar}, Si and Sn) IN CHALCOGEN-SUBSTITUTED ACETYLENES; ALL J VALUES ARE IN Hz

No	Compounds	$^1J_{C\equiv C}$ (exp.)	INDO FPT $^1J_{C\equiv C}$ VALUES				$^1J(\equiv C-X)$
			FC	OD	SD	TOTAL	
1	$CH_3C^\beta\equiv C^\alpha OC_2H_5$ [a]	224.0 [b]	190.51	9.09	5.95	205.55	74.8 [b,c]
2	$HC\equiv COCH_3$ [a]	216.5	190.61	9.35	6.03	205.99	264.3 [d]
3	$(CH_3)_3SiC\equiv COCH_3$ [a]	166.7	135.76	8.76	5.81	150.33	95.6 [e]
4	$(CH_3)_3SnC\equiv COC_2H_5$	151.6 [b]	–	–	–	–	543.4 [b,f]
5	$PhC\equiv CSCH_3$	184.2	153.46	9.21	5.91	168.58	91.2 [g]
6	$(CH_3)_3CC\equiv CSCH_3$ [a]	175.0	163.29	9.32	5.96	178.58	67.1 [c]
7	$(CH_3)_3SiC\equiv CSCH_3$ [a]	134.2	114.14	9.40	5.93	129.47	83.9 [e]
8	$PhC\equiv CSeCH_3$	173.2	–	–	–	–	89.7 [g]
9	$PhC\equiv CTeCH_3$	154.4	–	–	–	–	87.2 [g]

[a] The calculations refer to the compounds $H_3MC\equiv COH$ or $H_3MC\equiv CSCH_3$. [b] Ref. 4. [c] X = C_{sp^3}. [d] X = H. [e] X = Si. [f] X = Sn. [g] X = C_{Ar}.

TABLE 2

CARBON–CHALCOGEN COUPLING CONSTANTS ^nJ IN METHYLCHALCOGEN PHENYLETHYNES AND THEIR REDUCED VALUES K (in 10^{-20} $NA^{-2}m^{-3}$)

$C^\beta\equiv C^\alpha-X-C^{1'}H_3$ (X = ^{77}Se , ^{125}Te , ^{123}Te)
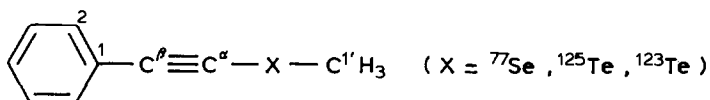
J/K	X		
	^{77}Se [a]	^{125}Te	^{123}Te
$^1J(XC^\alpha)$	−187.4	550.9	456.9
$^1K_{XC^\alpha}$	−32.5	−57.3	−57.3
$^1J(XC^{1'})$	−57.6	151.6	125.8
$^1K_{XC^{1'}}$	−10.0	−15.9	−15.9
$^2J(XC^\beta)$	−35.0	114.1	94.6
$^2K_{XC^\beta}$	−6.1	12.0	12.0
$^3J(XC^1)$	–	6.6	–
$^3K_{XC^1}$	–	0.7	–
$^4J(XC^2)$	–	3.4	–
$^4K_{XC^2}$	–	0.3	–

[a] Negative signs of J(SeC) values adopted from ref. 9,10.

TABLE 3

NUCLEAR SPIN–SPIN COUPLING CONSTANTS $^2J_{C^\alpha_{sp}X}$ (X = C_{sp^3}, C_{Ar}, H and Si) IN METHYLCHALCOGEN SUBSTITUTED ACETYLENES; ALL VALUES ARE GIVEN IN Hz.

No	Compounds	$^2J(C^\alpha_{sp}X)$	$^2J(C^\alpha_{sp}C^{1'}_{sp^3})$
1	$CH_3C^\beta\equiv C^\alpha-OC^{1'}H_2CH_3$	14.8 [a]	–
2	$HC\equiv COCH_3$	59.2	–
3	$(CH_3)_3SiC\equiv COCH_3$	21.2	–
5	$PhC\equiv CSCH_3$	13.0	2.8
6	$(CH_3)_3CC\equiv CSCH_3$	10.3	2.8
7	$(CH_3)_3SiC\equiv CSCH_3$	15.9	2.7
8	$PhC\equiv CSeCH_3$	12.6	2.7
9	$PhC\equiv CTeCH_3$	10.0	–

[a] Ref. 4.

TABLE 4

NUCLEAR SPIN–SPIN COUPLING CONSTANTS $^n J$(CC) IN THE PHENYL RING OF METHYL-SELENO- AND METHYLTELLURO-PHENYLETHYNES

$$4 \left\langle \begin{array}{c} 3 \quad 2 \\ \\ 5 \end{array} \right\rangle \overset{1}{-} C^\beta \equiv C^\alpha - XC^{1'}H_3 \quad (X = S, Se, Te)$$
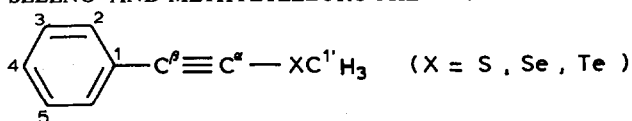
No.	X	$^1 J(C^1 C^2)$	$^1 J(C^2 C^3)$	$^1 J(C^3 C^4)$	$^3 J(C^1 C^4)$	$^3 J(C^2 C^5)$
5	S	59.0	56.7	55.8	8.7	10.5
8	Se	59.1	56.7	56.0	8.7	10.4
9	Te	58.9	56.5	–	8.7	10.4

rings in chalcogen derivatives of phenylethyne. For comparison, data for 1-eth-oxypropyne (1) and 1-trimethylstannyl-2-ethoxyethyne (4) taken from the literature [4] are included in Tables 1 and 3.

Discussion

According to the theory developed by Ramsey [6], three processes are involved in spin–spin coupling interaction: namely orbital–dipole (OD), spin–dipole (SD), and Fermi contact contributions (FC). Both OD and SD terms are proportional to the product of the values $\langle r_i^{-3} \rangle$, where r_i is the separation of the valence p.electrons from the nucleus i. The contact process depends upon the product of the s electron densities at the coupled nuclei. We have shown recently [2,5] that in Group IV derivatives of acetylene (i) the magnitude of the spin–spin coupling constant $^1 J(C\equiv C)$ is governed by electronegativity of the substituent bonded to the triple $C\equiv C$ bond, (ii) the changes in $^1 J(C\equiv C)$ values are governed mainly by changes in the Fermi contact term, [5], and (iii) the OD and SD terms are not negligible, but their sum does not amount to more than 10% of the Fermi contact term [5]. Moreover, it was shown [2] that the Egli and Philipsborn formula [7] can be applied to this group of compounds. With chalcogen substituent present it can be expected that owing the presence of two lone electron pairs on O, S, Se and Te atoms the $n-\pi$ conjugation effect may also become important:

$$R-\overline{\underline{X}}-C\equiv CH \leftrightarrow R-\overset{+}{\underline{X}}=C=\overset{-}{C}H$$
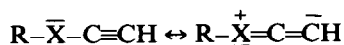
Should this be the case, the trends and regularities observed for the Group IV substituted acetylenes would not hold for the Group VI derivatives. Thus an analysis of the $^1 J(C\equiv C)$ data should throw light on the role played by the canonical structures in spin–spin interaction.

It is convenient to examine the results obtained for the $^1 J(C\equiv C)$ values with the compounds under study divided into three groups. The first group consists of the alkyl, hydrogen, silyl and stannyl derivatives of alkoxyethynes (1–4), the second of phenyl, alkyl and silyl derivatives of methylthioethyne (5–7) and the third of the methylthio (5), methylseleno (8) and methyltelluro (9) derivatives of phenylethyne. In all three groups one substituent attached to an acetylenic fragment is kept constant while the other is varied. In all cases a dependence of $^1 J(C\equiv C)$ upon the electronegativity E_x of the substituent is evident. Increasing electronegativity causes

an increase of the coupling across a triple C≡C bond. Thus, in the third group, the highest $^1J(C≡C)$ is found for 1-methylthio-2-phenylethyne (5) (184.2 Hz), a somewhat lower value for 1-methylseleno-2-phenylethyne (8) (173.2 Hz) and the lowest (154.4 Hz) for 1-methyltelluro-2-phenylethyne (9). The E_x values on Pauling's scale for S, Se and Te are 2.58, 2.55 and 2.1, respectively [8]. A similar trend is observed for the couplings $^1J(C≡C)$ in 1-methoxy- (3) (166.7 Hz) and 1-methylthio- (7) (134.2 Hz) -2-trimethylsilylethynes.

Furthermore, the measured one-bond C–C coupling constants obey with high accuracy the Egli and Philipsborn equation (eq. 1) where the I factors are square

$$^1J(C_A≡C_B) = I_{C_A} \times I_{C_B}, \tag{1}$$

roots of the $^1J(C≡C)$ values in symmetrically substituted compounds or are calculated as a multiple of $^1J(C_A≡C_B)$ and the already determined factor I [7]. Thus, e.g., the $^1J(C≡C)$ values for 3 and 7 and the factor I_{Alk_3SiCsp} (10.07 $\sqrt{Hz}$) determined earlier [2] can be used to calculate the $I_{AlkOCsp}$ and $I_{AlkSCsp}$ factors, which are 16.55 $\sqrt{Hz}$ and 13.33 $\sqrt{Hz}$, respectively. These multiplied by the factors I_{CH_3Csp} [2], I_{HCsp} [2], I_{Alk_3SnCsp} [1] and $I_{t\text{-}BuCsp}$ * gave $^1J(C≡C)$ values of 224.6 Hz for 1, 216.3 Hz for 2, 154.5 Hz for 4 and 172.6 Hz for 6. These estimated J values are in remarkably good agreement with those determined experimentally (see Table 1).

INDO FPT calculations of $^1J(C≡C)$ have been performed for most of the compounds studied, The calculated values are in most cases lower than the experimental ones, but the agreement is reasonable especially for compounds 6 and 7 involving second row substituents. Two important observations can be made. First, in all cases the magnitude of the $^1J(C≡C)$ is governed by the Fermi contact contribution. Although orbital–dipole (OD) and spin–dipole (SD) terms are not negligible, they together account for roughly only 7 to 12% of the total $^1J(C≡C)$ value. Secondly, only the FC term reflects the changes in the experimental coupling constants $^1J(C≡C)$ both OD and SD terms remaining constant through the whole series.

All these observations lead to the conclusion that the mesomeric interactions are of minor importance in the compounds under study at least as far as the magnitude of $^1J(C≡C)$ is concerned. The electronegativity of substituent remains the main influence on $^1J(C≡C)$.

The second set of data derived in this work involves the coupling constants $^1J(C–Se)$ and $^1J(C–Te)$ (Table 2). These are of particular interest since an understanding of the factors which govern them may shed some light on the behaviour of $^{13}C–^{17}O$ and $^{13}C–^{33}S$ couplings [9]. The latter are very important as electron density indicators, but are extremely difficult to determine experimentally owing to the unfavourable magnetic properties of both the ^{17}O and ^{33}S nuclei.

No attempt was made in this work to determine the sign of the coupling constants, but a negative sign for $^1J(C–Se)$ couplings has been adopted from literature data [9,10].

The value of $^1J(C^α–Te)$ for 1-metyltelluro-2-phenylethyne (9) (550.9 Hz) is in the usual region for ^1J values between acetylenic sp carbons and tellurium determined for other tellurium acetylene derivatives [11]. The $^1J(C^α–Se)$ coupling constant

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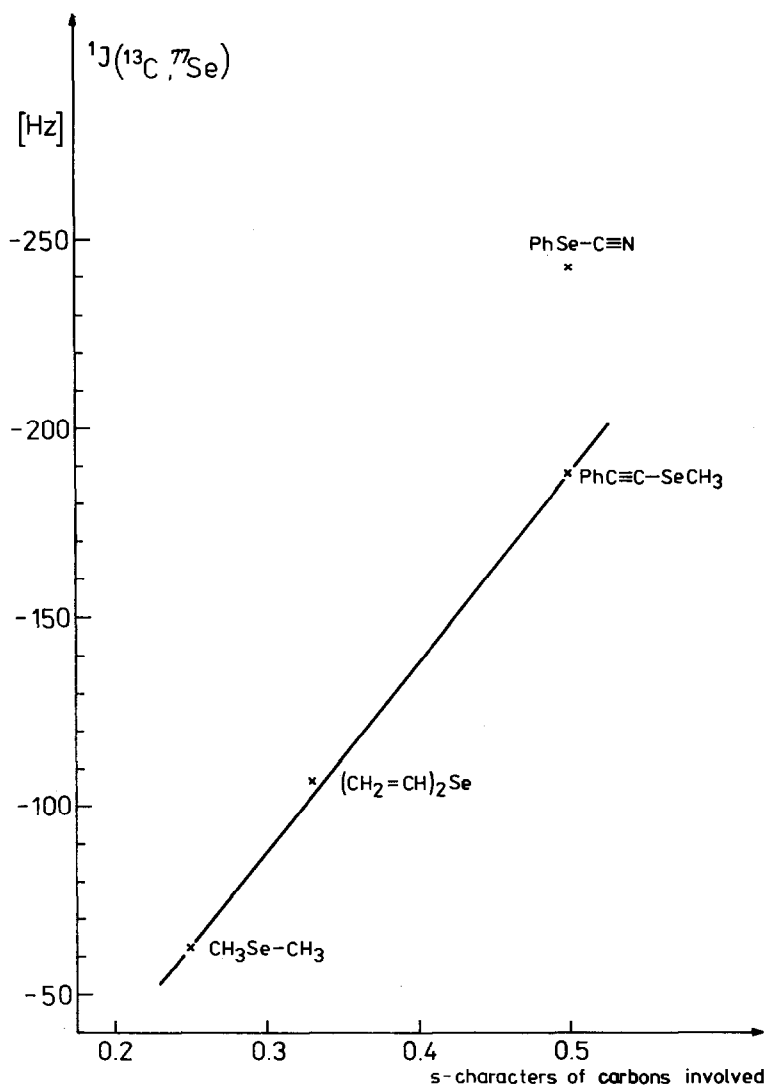* Calculated using $^1J(C≡C)$ for $(C_2H_5)_3SiC≡CC(CH_3)_3$ (130.4 Hz) and the I_{Alk_3SiCsp} factor [2].

Fig. 1. The relationship between ^1J(C–Se) values and s-characters of the carbons involved, in seleno substituted compounds.

determined in this work for 1-methylseleno-2-phenylethyne (**8**) (-187.4 Hz) is the first for coupling between selenium and acetylenic carbon. The only coupling of a related type is that for PhSe–C≡N (-242.0 Hz) [10].

A plot of the J(C–Se) values for CH_3SeCH_3 (-62.0 Hz [10]), $(CH_2{=}CH)_2Se$ (-106.3 Hz [10]) and compound **8** against the s-characters of carbons (Fig. 1) shows that spin–spin coupling constants between carbon ^{13}C and selenium ^{77}Se depend linearly upon the hybridization of carbon atoms. An analogous linear relationship was previously noted for derivatives of tellurium [11]. This provides evidence that in both cases the ^1J(Chalc-C) depends mainly on the Fermi contact term provided that there is no other influence on the chalcogen atom. If the other coupling terms (OD,

TABLE 5

$^1K_{\text{Chalc-C}}$ IN 10^{-20} $NA^{-2}m^{-3}$ [a]

Chalcogen	C_{sp^3}	C_{sp^2}	C_{sp}
O	(−4.0)	(−6.8)	(−9.0)
S	(−5.5)	(−9.8)	(−14.8)
Se	−10.8 [b]	−18.4 [d]	−32.5
Te	−16.4 [c]	−29.9 [e]	−57.3

[a] The negative signs are based on ref. 9. [b-e] Calculated using: [b] $^1J(\text{Se-CH}_3)$ in $(\text{CH}_3)_2\text{Se}$ [10]; [c] $^1J(\text{Te-CH}_3)$ in $(\text{CH}_3)_2\text{Te}$ [14]; [d] $^1J(\text{Se-C}_{sp^2})$ in $(\text{CH}_2=\text{CH})_2\text{Se}$ [10]; [e] $^1J(\text{Te-C}_{sp^2})$ in $(\text{CH}_2=\text{CH})_2\text{Te}$ [11].

SD) cannot be neglected they must also depend on the percentage of s-characters of carbons involved in the C–Se and C–Te bonds. Thus it can be predicted that $^1J(\text{C–O})$ and $^1J(\text{C–S})$ will also behave analogously.

A comparison of couplings between different nuclei can be made by using the corresponding reduced coupling constants, K, which are independent of magnetic properties of the nuclei coupled. It has been shown by Reeves [12] that the square roots of the reduced K_{X-Y} couplings, where Y is kept constant and X varies vertically along the Periodic Table, are linearly related to the atomic number of X, and this is generally true provided that the orbital hybridization at X and Y are strictly preserved [12]. This approach was used by Galasso et al. [9], who estimated K_{C-S} and K_{C-O} for furan and thiophene by extrapolating the experimental K_{C-Se} and K_{C-Te} values for selenophene and tellurophene, respectively. On the assumption that the Reeves relationship [12] also holds for the compounds studied in the present work we estimated the reduced couplings of oxygen and sulphur with sp^3, sp^2, and sp carbon atoms. The results are listed in Table 5.

It is evident that the values of $K_{\text{Chalc-C}}$ decrease in the order Te, Se, S and O, which is in an accord with the trend predicted by an independent theoretical analysis [9,13]. Though it is obvious that such "extrapolation" must be regarded with the greatest caution and the results are only tentative, we believe that the $^1K_{CO}$ and $^1K_{CS}$ values displayed in the Table 5 at least indicate the range in which the couplings will appear. It is also reassuring that our results for $^1K_{C_{sp^2}-S}$ and $^1K_{C_{sp^2}-O}$ couplings agree with those calculated by Galasso et al., for chalcogen pentaheterocycles [9].

The data available are too limited to allow analysis of the influence of the electronegativity of the substituents in this set of couplings. However, it is noteworthy that $^1J(\text{Se–CH}_3)$ in $\text{PhC}\equiv\text{CSeCH}_3$ (8) (−57.6 Hz) and $^1J(\text{Te–CH}_3)$ in $\text{PhC}\equiv\text{CTeCH}_3$ (9) (151.6 Hz) are consistently smaller than the corresponding values for the related dimethylchalcogens (−62.0 Hz [10] and 157.5 Hz [14], respectively). This means that increase in the electronegativity of substituent ($E_{C_{sp}} > E_{C_{sp^3}}$) causes a decrease in $J_{\text{Chalc-C}}$. This is unusual, an increase of electronegativity of substituent normally causing an increase in J [15] (see also the discussion of the other couplings in this work).

The remaining couplings determined for the studied compounds can be divided into two groups, those involving acetylenic carbons i.e. $^1J(\text{C}^\beta_{sp}\text{X})$ (Table 1) and $^2J(\text{C}^\alpha_{sp}\text{X})$ values (Table 3) where X denotes the H, C and Si nuclei, and those involving $J(\text{CC})$ couplings in the phenyl ring (Table 4). Analysis of the data for the

couplings to the acetylenic carbons shows that in both cases the contants follow the usual trend and depend upon the electronegativity of the chalcogen atom attached to the acetylenic α-carbon. A decrease in the substituent electronegativity causes a decrease of the corresponding coupling constant, as can be seen from a comparison of the ^1J values in **5**, **8** and **9**, and **3** and **7**, for example.

An analysis of C–C couplings in the phenyl ring shows that they are only slightly different from the value characteristic of the unsubstituted aromatic ring (^1J(CC) in benzene 55.9 Hz [16]). It means that the influence of the chalcogen substituent is limited to the acetylenic moiety and it is not transmitted further to the carbons of the phenyl ring.

Experimental

All compounds studied were prepared by general methods (slightly modified in some cases *) as described in refs. 17 (compds. **2**, **5–9**) and 18 (compd. **3**).

The proton-decoupled ^{13}C NMR spectra were recorded with natural abundance samples using a Varian XL-200 spectrometer. The calculations of the coupling constants were based on the self-consistent perturbation approach within the INDO framework. A modified version of the Blizzard–Santry program [19] with values of 4.0318 and 1.6920 a.u. for $S_C^2(0)$ and $\langle r^{-3} \rangle_e$, respectively, was used. Standard geometries of the compounds were taken from ref. 20. To save computer time calculations on the Me$_3$M derivatives with M = C, Si, Sn were actually carried out only for the parent compounds $H_3MC{\equiv}COH$ and $H_3MC{\equiv}CSCH_3$.

Acknowledgements

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* For preparation of **3**, **5**, **6** and **7**, a solution of BuLi in hexane was used instead of the Grignard reagent or LiNH$_2$ in liquid ammonia.

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