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Influence of Substituents on Carbon-Carbon Coupling Constants in Substituted Acetylenes*

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Indirect spin-spin carbon-carbon coupling constants across a triple bond have been calculated using the DFT method in a large series of substituted acetylenes and compared with those determined experimentally. The DFT calculated coupling data not only follow the trends observed for the experimental results but also the absolute $^{1}J_{CC}$ values are very well reproduced (in most cases within several Hz). It has been found that the magnitude of the coupling is strongly dependent on the electronegativity of the first atom of the substituent attached to the triple bond which is described by the equation: $^{1}J_{XC\equiv CY}$ (TOTAL) = 25.9 E_XE_Y + 5.4. The smallest $^{1}J_{C\equiv C}$ coupling calculated for Li_2C_2 is 31.6 Hz and the largest one for C_2F_2 420.9 Hz, which reflects the dramatic changes occurring in the electronic structure of the triple bond upon substitution. A rough linear correlation has been found between the ln $^{1}J_{C\equiv C(DFT)}$ and the DFT optimized bond lengths, $r_{C\equiv C}$. Additionally, the couplings across one Csp^3–Csp and Csp^2(arom)–Csp single bonds and those across two **C**sp^3–C≡**C** and **C**sp^2(arom)C≡**C** bonds have been derived and discussed.

Key words: substituted acetylenes, spin-spin carbon-carbon coupling constants, substituent effects, bond lengths, DFT calculations

A growing interest has been observed in the last few years in *ab initio* and/or DFT calculations of carbon-carbon spin-spin coupling constants across one bond and numerous important papers on this topic have been recently published [1–9].

However, while a lot of attention has been paid to unsubstituted hydrocarbons such as acetylene [1–4], cyclopropane [5], cyclopropene [6,7] and some strained bicyclomolecules [8,9], the papers devoted to the effects of substituents on $^{1}J_{CC}$ couplings are rather scarce [10,11]. The main reason is that the calculations of J couplings for large molecules are still beyond the scope of the methods based strictly on the *ab initio* approach.

The deMon program has recently been developed by the Malkins and Salahub [12], based on the density functional theory. Within this methodology, three contributions are taken into account, *i.e.* the Fermi contact contribution (FC), the paramagnetic spin-orbit (PSO) and the diamagnetic spin-orbit (DSO) contributions. The spin-dipolar (SD) term is neglected within this approach. The FC term is calculated by finite perturbation theory (FPT), the PSO contribution is obtained using the sum-over-states density functional perturbation theory (SOS-DFPT) and the DSO term is obtained by

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*Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

numerical integration. The program allows one to calculate the coupling constants and chemical shifts for relatively large molecules in a reasonable computing time. This is its important feature since the studies on the influence of substituents on the NMR parameters require that various and often quite large substituents should be introduced into the molecule. Moreover, as will be shown in further parts of our work, agreement between the calculated and experimental values can be achieved provided that the corresponding data are obtained for precisely the same molecules. This seems to be a rather trivial statement but one should remember that the synthesis of the appropriate small model compounds and performing long lasting measurements for them may often be difficult or in some cases even impossible. It is therefore quite a natural practice that the synthesis and measurements are performed for larger and more stable compounds, whereas the calculations are carried out for smaller molecules in order to save the computing time. It is tacitly assumed in such cases that the additional substituents such as the methyl groups, for example, do not influence the results significantly. This, however, may lead to quite large discrepancies between the calculated and experimental data.

Recently, a large number of variously substituted derivatives of acetylene have been synthesized by us and the ${}^1J_{C\equiv C}$ couplings measured for them [13–18]. The smallest experimental coupling value, ${}^1J_{CC}$ of 56.8 Hz, was determined by us for the $(C_2H_5)_3SiC\equiv CLi$ derivative [13] and the largest one, ${}^1J_{CC}$ of 224.3 Hz was found by Sebald and Wrackmeyer [19] for $CH_3C\equiv COC_2H_5$. This set of data together with some results published in the literature [19] provides an excellent experimental basis for a comparison with the theoretically calculated couplings.

The DFT calculations performed for this large group of compounds and for a series of the compounds, which are not easily accessible synthetically, such as lithio- and fluoroacetylene substituted acetylenes, allowed us to shed a new light on the influence of substituents on the magnitude of the spin-spin couplings across the triple bond in substituted acetylenes and on the mechanism governing this phenomenon.

Additionally, we also discuss the influence of substituents on ${}^1J_{C\text{-}C\equiv}$ and ${}^2J_{C\text{-}C\equiv C}$ couplings in alkyl and phenylacetylenes. The data for the latter are rather scarce in the literature.

RESULTS AND DISCUSSION

As the first step we decided to perform the calculations for those compounds for which the experimental data are available; these were substituted methyl-, *t*-butyl-, trialkylsilyl- and phenylacetylenes. Most of the calculations were performed for exactly the same molecules for which the experimental ${}^1J_{CC}$ values had been obtained. This allowed us to check the reliability of the calculated ${}^1J_{C\equiv C}$ values. In some cases, however, due to the convergence problems (compounds with substituents bearing ethyl, *n*-butyl or Ph groups) we had to limit the calculations to the compounds with the methyl groups. In the case of the stannyl derivatives the $SnBu_3$ groups had to be replaced by the SnH_3 ones. All geometries used were DFT optimized. The DFT ${}^1J_{C\equiv C}$ data and the corresponding experimental $^1J_{C\equiv C}$ values for this group of compounds are presented in Table 1. For comparison, the same Table includes the couplings for the corresponding H_nX (X = C, N, P, Si, Ge, Sn, n = 2, 3) derivatives for which experimental data have not been determined.

Table 1. DFT calculated and experimental $^1J(C\equiv C)$ couplings in substituted methyl-(*t*-butyl), silyl- and phenylacetylenes (all values in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	$^1J(C\equiv C)^{a)}$ exp.
1a	$H_3SiC\equiv CLi$	0.56	0.04	57.09	57.69	
1b	$Me_3SiC\equiv CLi$	–0.25	0.05	55.25	55.06	56.8 [13]
2a	$H_3SiC\equiv CSnH_3$	3.80	0.19	94.95	98.94	
2b	$Me_3SiC\equiv CSnH_3$	3.26	0.21	89.12	92.59	94.0 [13]
3a	$H_3SiC\equiv CSiH_3$	3.14	0.11	103.69	106.94	
3b	$Me_3SiC\equiv CSiMe_3$	2.15	0.14	94.81	97.10	101.4 [14]
4a	$H_3SiC\equiv CPH_2$	4.70	0.13	118.68	123.51	
4b	$Me_3SiC\equiv CPMe_2$	3.45	0.16	105.61	109.22	115.2 [15]
5a	$H_3SiC\equiv CH$	5.26	0.06	137.03	142.35	
5b	$Me_3SiC\equiv CH$	4.62	0.08	127.84	132.54	131.8 [16]
6a	$H_3SiC\equiv CSMe$	5.65	0.17	137.68	143.50	
6b	$Me_3SiC\equiv CSMe$	5.30	0.18	126.91	132.39	134.2 [15]
7a	$H_3SiC\equiv CMe$	5.00	0.12	139.44	144.57	
7b	$Me_3SiC\equiv CMe$	4.53	0.14	131.23	135.89	136.7 [13]
8a	$H_3SiC\equiv CBr$	9.36	0.24	145.04	154.64	
8b	$Me_3SiC\equiv CBr$	9.17	0.25	129.92	139.35	143.2 [13]
9a	$H_3SiC\equiv CCl$	9.05	0.18	159.05	168.28	
9b	$Me_3SiC\equiv CCl$	8.87	0.20	143.61	152.68	155.3 [13]
10a	$H_3SiC\equiv COMe$	7.62	0.20	173.47	181.30	
10b	$Me_3SiC\equiv COMe$	7.43	0.22	160.21	167.86	166.7 [15]
11a	$MeC\equiv CSnH_3$	5.36	0.20	129.10	134.66	
11b	$MeC\equiv CSnMe_3$	4.96	0.21	121.21	126.38	127.6 [19]
12a	$MeC\equiv CGeH_3$	5.63	0.19	141.50	147.32	
12b	$MeC\equiv CGeMe_3$	5.03	0.20	131.96	137.19	137.3 [16]
13	$MeC\equiv CH$	6.67	0.07	177.46	184.20	175.0 [16]
14	$t\text{-}BuC\equiv CH$	6.18	0.10	168.24	174.52	168.7 [16]
15	$t\text{-}BuC\equiv CMe$	6.30	0.16	172.44	178.90	174.0 [16]
16a	$MeC\equiv CSMe$	7.30	0.18	183.84	191.31	
16b	$t\text{-}BuC\equiv CSMe$	7.04	0.21	172.79	180.04	175.0 [15]
17a	$MeC\equiv CBr$	10.67	0.24	203.92	214.83	
17b	$t\text{-}BuC\equiv CBr$	10.55	0.28	188.36	199.19	190.6 [13]

Table 1 (continuation)

18a	$MeC\equiv CNH_2$	8.06	0.16	215.09	223.32	
18b	$MeC\equiv CNEt_2$	7.15	0.21	209.48	216.83	204.0 [19]
19a	$MeC\equiv CCl$	10.43	0.19	218.93	229.54	
19b	t-$BuC\equiv CCl$	10.20	0.22	204.01	214.43	204.8 [15]
20a	$MeC\equiv COMe$	9.47	0.21	232.63	242.31	
20b	$MeC\equiv COEt$	9.39	0.21	231.97	241.57	224.3 [19]
21a	$PhC\equiv CSiH_3$	4.39	0.15	139.80	144.34	
21b	$PhC\equiv CSiMe_3$	3.90	0.16	131.36	135.42	136.9 [15]
22a	$PhC\equiv CPH_2$	5.52	0.17	157.55	163.24	
22b	$PhC\equiv CPMe_2$	4.80	0.18	149.34	154.32	154.1 [17]
23	$PhC\equiv CH$	6.27	0.10	177.73	184.10	172.3 [this work]
24	$PhC\equiv CMe$	6.14	0.15	180.84	187.14	181.2 [this work]
25	$PhC\equiv CSMe$	6.39	0.20	183.41	190.01	184.2 [15]
26	$PhC\equiv CBr$	9.89	0.27	203.92	214.09	202.5 [13]
27a	$PhC\equiv CNH_2$	7.14	0.19	214.62	221.96	
27b	$PhC\equiv CNMe_2$	6.16	0.22	211.06	217.44	204.3 [15]
28	$PhC\equiv CCl$	9.66	0.22	218.69	228.57	216.0 [13]
29	$H_3SnC\equiv CSnH_3$	4.19	0.27	80.14	84.60	81.0 [16]
30a	$H_3SnC\equiv CH$	5.50	0.14	125.73	131.38	
30b	$Me_3SnC\equiv CH$	5.50	0.15	117.63	122.89	122.0 [16]
31a	$H_3GeC\equiv CH$	5.81	0.13	138.30	144.24	
31b	$Me_3GeC\equiv CH$	5.24	0.14	127.77	133.15	132.5 [15]
32	$Me_3SnC\equiv COMe$	7.70	0.29	146.05	154.04	151.6 [19]

[a] Experimental values for the compounds with substituents Et_3Si (**1b**, **3b**, **4b**, **5b**), Me_3Sn (**2b**), PPh_2 (**4b**), $P(n\text{-}Bu_2)$ (**22b**), NEt_2 (**27b**), n-Bu_3Sn (**29**), Et_3Ge (**31b**), OEt (**32**).

In Table 2 the coupling constants for lithio and fluoro derivatives of acetylene, methyl-, *t*-butyl-, trimethylsilyl- and phenylacetylene are collected. Most of these compounds are not available synthetically and the calculations are the most convenient source of the information on the magnitude of $^1J_{C\equiv C}$ in their case. This particularly concerns the fluoro derivatives.

Table 2. DFT $^1J(C\equiv C)$ couplings in the lithio and fluoro derivatives of acetylene and of methyl-(*t*-butyl), silyl- and phenylacetylenes (in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	$^1J(C\equiv C)$ exp.
33	$HC\equiv CH$	7.02	0.01	175.81	182.85	171.5 [21]
34	$HC\equiv CLi$	2.44	–0.01	73.50	75.93	
35	$HC\equiv CF$	12.29	0.16	257.03	269.47	
36	$LiC\equiv CLi$	–0.83	–0.04	32.51	31.64	

Table 2 (continuation)

37	FC≡CF	15.84	0.29	404.78	420.91	
1b	Me$_3$SiC≡CLi	–0.25	0.05	55.25	55.96	56.8 [13]
38	Me$_3$SiC≡CF	10.84	0.22	168.97	180.04	
39	MeC≡CLi	2.46	0.05	75.49	78.00	
40	MeC≡CF	12.30	0.21	260.02	272.53	
41	*t*-BuC≡CLi	1.94	0.08	69.62	71.63	
42	*t*-BuC≡CF	12.14	0.25	240.91	253.29	
43	PhC≡CLi	1.58	0.07	75.96	77.62	
44	PhC≡CF	11.70	0.24	260.07	272.01	

Tables 3 and 4 contain the data for the couplings across single Csp^3–Csp and Csp^2(arom)–Csp bonds and in Tables 5 and 6 the corresponding CC couplings across two bonds are included.

Table 3. DFT and experimental ^1J(CspCsp^3) couplings in substituted methyl and *t*-butylacetylenes (in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	^1J(CspCsp^3) exp.
39	MeC≡CLi	–1.68	0.14	58.04	56.51	–
41	*t*-BuC≡CLi	–2.06	0.27	56.66	54.88	–
11b	MeC≡CSnMe$_3$	–1.84	0.18	62.75	61.09	62.2 [19]
7b	MeC≡CSiMe$_3$	–1.89	0.16	63.86	62.13	63.5 [13]
12b	MeC≡CGeMe$_3$	–1.83	0.18	64.04	62.39	62.5 [this work]
16b	*t*-BuC≡CSMe	–2.12	0.29	66.91	65.08	67.1 [18]
17b	*t*-BuC≡CBr	–2.03	0.30	66.59	64.86	67.0 [13]
24	MeC≡CPh	–1.82	0.17	70.33	68.68	68.9 [this work]
13	MeC≡CH	–1.75	0.15	68.34	66.75	–
14	*t*-BuC≡CH	–2.03	0.28	64.79	63.03	62.1 [19]
15	*t*-BuC≡CCH$_3$	–1.92	0.29	67.40	65.77	68.3 [13]
18b	MeC≡CNEt$_2$	–1.56	0.18	76.27	74.88	70.0 [19]
19b	*t*-BuC≡CCl	–1.99	0.30	68.23	66.54	68.5 [this work]
20b	MeC≡COEt	–1.48	0.17	77.77	76.47	74.8 [19]
40	MeC≡CF	–1.50	0.17	77.36	76.03	–
42	*t*-BuC≡CF	–1.79	0.30	71.90	70.41	

An inspection of the $^1J_{CC}$ data presented in Table 1 shows that the DFT $^1J_{CC}$ values not only very well follow the trends observed for the experimental ^1J(CC) couplings but in most cases also the absolute values are reproduced within several Hz.

Table 4. DFT calculated and experimental ^{1}J(CspCsp^{2}arom.) couplings in substituted phenylacetylenes (in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	^{1}J(CspCsp^{2}arom.) exp.
43	$\mathrm{PhC{\equiv}CLi}$	–3.15	0.25	81.61	78.72	–
21b	$\mathrm{PhC{\equiv}CSiMe_3}$	–3.05	0.28	88.06	85.28	84.5 [this work]
22b	$\mathrm{PhC{\equiv}CPMe_2}$	–3.18	0.28	91.55	88.64	86.8 [17]
23	$\mathrm{PhC{\equiv}CH}$	–2.84	0.26	93.28	90.70	88.5 [this work]
24	$\mathrm{PhC{\equiv}CCH_3}$	–2.84	0.27	95.57	93.00	91.2 [this work]
25	$\mathrm{PhC{\equiv}CSMe}$	–3.24	0.28	96.29	93.33	91.2 [18]
26	$\mathrm{PhC{\equiv}CBr}$	–2.91	0.29	96.91	94.29	92.0 [13]
27b	$\mathrm{PhC{\equiv}CNMe_2}$	–3.24	0.28	101.87	98.92	95.8 [17]
28	$\mathrm{PhC{\equiv}CCl}$	–2.85	0.28	98.71	96.14	93.6 [13]
44	$\mathrm{PhC{\equiv}CF}$	–2.62	0.28	103.55	101.22	–

Table 5. DFT calculated and experimental ^{2}J(CspCsp^{3}) couplings in substituted methyl and *t*-butylacetylenes (in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	^{2}J(CspCsp^{3}) exp.
39	$\mathrm{MeC{\equiv}CLi}$	–0.23	–0.16	2.33	1.94	–
41	*t*-$\mathrm{BuC{\equiv}CLi}$	–0.10	–0.10	2.11	1.91	–
3b	$\mathrm{MeC{\equiv}CSiMe_3}$	–0.26	–0.12	9.20	8.82	8.5 [13]
12b	$\mathrm{MeC{\equiv}CGeMe_3}$	–0.22	–0.09	8.9	8.61	7.6 [this work]
16a	*t*-$\mathrm{BuC{\equiv}CSMe}$	–0.12	–0.06	11.30	11.12	10.3 [18]
17b	*t*-$\mathrm{BuC{\equiv}CBr}$	0.07	–0.03	11.82	11.85	10.6 [13]
24	$\mathrm{MeC{\equiv}CPh}$	–0.20	–0.12	13.76	13.43	11.9 [this work]
13	$\mathrm{MeC{\equiv}CH}$	–0.11	–0.16	13.70	13.42	–
14	*t*-$\mathrm{BuC{\equiv}CH}$	–0.15	–0.10	11.41	11.16	12.0 [19]
15	*t*-$\mathrm{BuC{\equiv}CCH_3}$	–0.15	–0.08	11.95	11.72	10.8 [13]
18b	$\mathrm{MeC{\equiv}CNEt_2}$	–0.14	–0.11	16.68	16.44	–
19b	*t*-$\mathrm{BuC{\equiv}CCl}$	0.03	–0.06	13.07	13.04	11.8 [this work]
20a	$\mathrm{MeC{\equiv}COMe}$	–0.02	–0.12	17.51	17.37	14.8 [19]
40	$\mathrm{MeC{\equiv}CF}$	0.15	–0.12	18.78	18.82	–
42	*t*-$\mathrm{BuC{\equiv}CF}$	0.15	–0.06	15.29	15.34	–

Table 6. DFT calculated and experimental ^2J(CspCsp^{2}arom.) couplings in substituted phenylacetylenes (in Hz).

No.	Compound	PSO	DSO	FC	TOTAL	^2J(CspCsp^{2}arom.) exp.
43	PhC≡CLi	0.32	–0.11	4.14	4.35	–
21b	PhC≡CSiMe$_3$	–0.06	–0.08	10.55	10.41	13.8 [this work]
22b	PhC≡CPMe$_2$	–0.05	–0.07	11.98	11.86	–
23	PhC≡CH	–0.08	–0.11	15.13	14.93	12.6 [this work]
24	PhC≡CCH$_3$	–0.09	–0.09	15.52	15.34	13.6 [this work]
25	PhC≡CSMe	–0.03	–0.07	15.22	15.11	13.0 [18]
26	PhC≡CBr	0.11	–0.04	16.43	16.49	13.6 [13]
27b	PhC≡CNMe$_2$	–0.10	–0.07	18.47	18.30	16.1 [17]
28	PhC≡CCl	0.03	–0.07	17.83	17.79	14.9 [13]
44	PhC≡CF	–0.04	–0.07	20.77	20.74	–

On the one hand, this good agreement between the DFT and experimental data can be used as a proof that the applied theory is good enough, but on the other one can argue that the $^1J_{CC}$ coupling values measured in solution are close to those in isolated molecules. It is worth noting that this is not always the case. It has been shown quite recently by Jackowski *et al.* [20] that the $^1J_{CC}$ coupling value quite significantly may depend on the polarity of the solvent and on the phase. Therefore, the differences larger than 10 Hz observed between the calculated and experimental $^1J_{C\equiv C}$ values in several compounds such as the methoxy (**20b**) and amino (**18b**) derivatives of propyn-1, may be caused not by some inadequacies of the theoretical method but also by the fact the coupling values measured in solution are too low. However, even these discrepancies of *ca.* 13 to 17 Hz constitute less than 10% of the total $^1J_{C\equiv C}$ value. The equation including all the compounds for which both experimental and calculated $^1J_{C\equiv C}$ values are available is given below and shown in Fig. 1:

$$^1J_{C\equiv C\ (DFT)} = 0.887\ ^1J_{C\equiv C\ (exp)} + 14.3; \qquad n = 32;\ r = 0.997;\ s.d. = \pm 3.1 \qquad (1)$$

An analysis of the data presented in Tables 1 and 2 shows that the Fermi contribution is the main factor which determines the coupling value. The two remaining contributions, *i.e.* paramagnetic (PSO) and diamagnetic (DSO) spin-orbital contributions are drastically smaller, the DSO being almost negligible. The FC term is clearly dependent on the electronegativity of the first atom of the substituent attached to the triple bond. However, the β-substituents cannot be neglected since even the introduction of β-methyl groups into this position causes a decrease of $^1J_{C\equiv C}$ values by *ca.* 10 to 20 Hz (compare the results for pairs **a** and **b** in Tables 1 and 2).

Equation (2) which correlates the total DFT $^1J_{C\equiv C}$ values with the Pauling electronegativity [22] of the first atoms of the substituents is very similar to that obtained previously by us on the basis of the experimental data (equation 3):

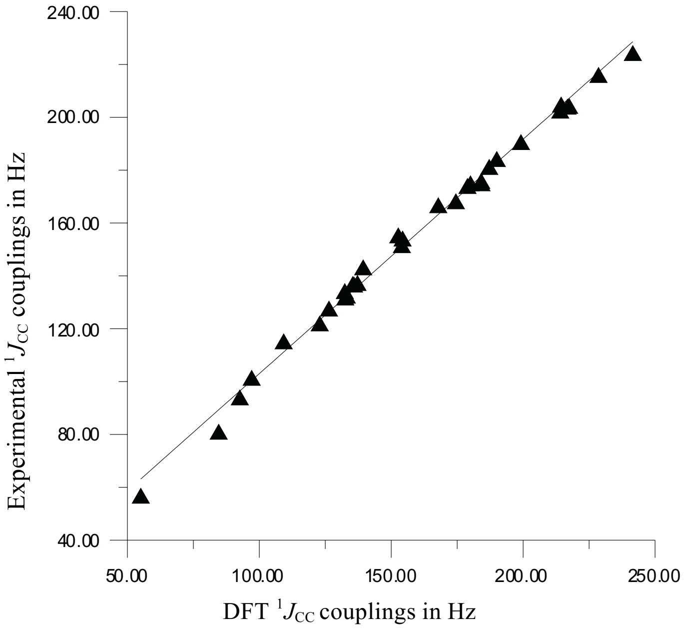

Figure 1. Plot of the DFT calculated $^1J_{C\equiv C}$ couplings against the corresponding experimental $^1J_{CC}$ values.

$$^1J_{XC\equiv CY}\,(\mathrm{TOTAL}) = 25.9\,E_XE_Y + 5.4; \qquad n = 26;\ r = 0.993;\ \mathrm{s.d.} = \pm\,5.7\ \mathrm{Hz} \qquad (2)$$

$$^1J_{XC\equiv CY} = 23.2\,E_X\,E_Y + 15.4;\quad [15] \qquad n = 27;\ r = 0.99;\ \mathrm{s.d.} = \pm 4.2\ \mathrm{Hz} \qquad (3)$$

However, it should be noted at this point that the data obtained for the monosubstituted acetylenes have not been included in the above equations since, according to our earlier observations, the electronegativity of hydrogen, Ex = 2.2, reported in [22] is definitely too low. This problem has been already thoroughly discussed in our previous paper [15].

The $^1J_{C\equiv C}$ couplings for Li_2C_2 (30.3 Hz) and F_2C_2 (415.7 Hz) estimated by the use of the equation (2), are the smallest and the largest coupling values, respectively, predicted for substituted acetylene. These values are in a reasonably good agreement with the coupling values estimated earlier by us by the use of equation (3): 37.7 and 383.0 Hz, respectively. The corresponding DFT values for Li_2C_2 and F_2C_2 molecules, which have not been included in the data used to derive the equation (2), are 31.6 Hz and 420.9, respectively (Table 2).

The PSO term (the DSO contribution is almost negligible) is dramatically smaller than the FC contribution (see Tables 1 and 2, as well as Fig. 2). It varies from –0.83 Hz in the dilithio derivative (**36**) up to *ca*. 10 Hz in the derivatives bearing strongly elec-

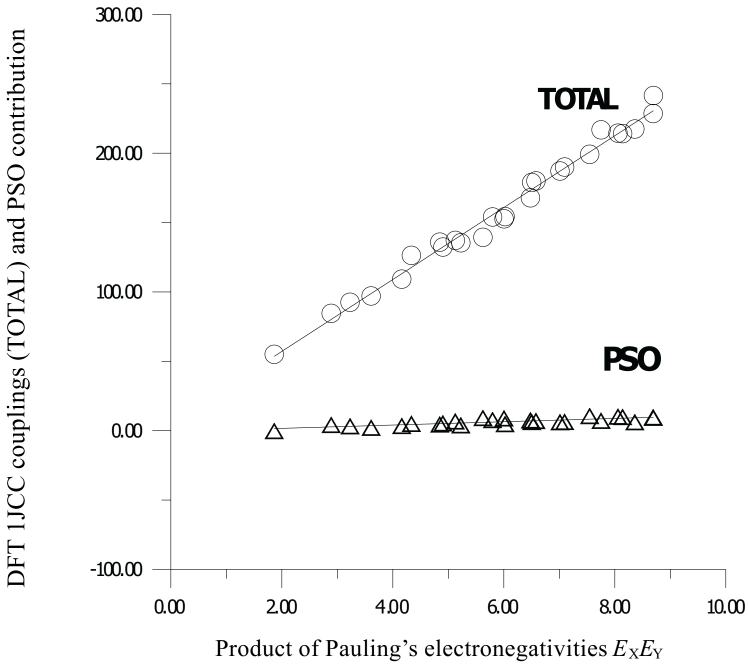

Figure 2. Plot of the DFT calculated $^1J_{CC}$ couplings (TOTAL) against the products of Pauling's electronegativity of the first atoms of the substituents at the CC triple bond; in the Figure also the corresponding plot of the PSO contribution is included for comparison. The data are taken from Table 1 for those compounds only for which also the experimental data are available.

tronegative substituents such as bromine, chlorine, oxygen (compds. **17**, **19**, **26**, **28**, Table 1) and attains 15.8 Hz in difluoroacetylene **37** (Table 2).

The DFT data obtained allowed us to examine the relationship between the $^1J_{C\equiv C(DFT)}$ couplings and the DFT optimized bond length, $r_{C\equiv C}$, over a broad range of ^1J values. The relationship shown in Fig. 3 is poor but reveals some a rough linear correlation of ln ($^1J_{CC}$) as a function of $r_{C\equiv C}$ (eq. 4) and to the best of our knowledge it is the first result of this type obtained as far as $^1J_{CC}$ couplings are concerned:

$$\ln {}^1J_{C\equiv C(DFT)} = -0.429\ r_{C\equiv C(DFT)} + 57.9; \qquad n = 45;\ r = 0.94;\ sd = \pm 0.168 \qquad (4)$$

It is of interest to note that the optimized bond lengths, $r_{C\equiv C}$, vary within a rather narrow range, from 120.5 pm in FC≡CF up to 126.6 pm in LiC≡CLi. In the correlation the data for LiC≡CH and FC≡CH have also been included.

In addition to spin-spin couplings across the triple carbon–carbon bond also the couplings across one Csp^3–Csp and Csp^2(arom)–Csp bonds and the couplings across two **C**sp^3–C≡**C** and **C**sp^2(arom)C≡**C** bonds have been calculated and compared with the corresponding experimental values. Most of the experimental data originate either from our earlier papers [13,17,18] or from Sebald and Wrackmeyer work [19]; some of them have been measured in the present work. Agreement between the calcu-

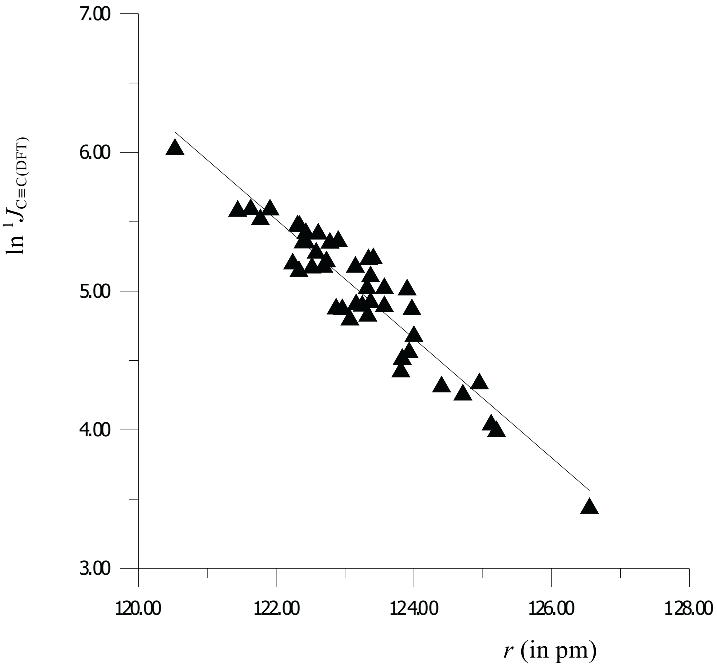

Figure 3. Plot of the ln ($^1J_{C\equiv C(DFT)}$) *vs*. the DFT calculated bond lengths, $r_{C\equiv C(DFT)}$, in pm.

lated and experimental data is generally good, in most cases the difference does not exceed 2 Hz and in a few cases only attains *ca*. 4 Hz.

An inspection of the data presented in Tables 3 and 4 shows that the $^1J_{CC}$ couplings across the single bonds are governed almost entirely by the Fermi contact contribution, the paramagnetic spin orbital contribution being dramatically smaller and in almost all cases negative. The diamagnetic spin orbital term is almost negligible. The influence of the electronegativity of substituent X at carbon β on these couplings is similar to that observed for the couplings across the triple bond; it is reflected in an increase from 56.51 Hz in 1-lithiopropyne-1 (**39**) up to 76.03 in 1-fluoropropyne-1 (**40**) and from 78.72 in lithiophenylacetylene (**43**) up to 101.22 Hz in fluorophenylacetylene (**44**). However, some other factors such as the presence of the lone pair also have to be taken into account since, for example, the $^1J_{CC}$ coupling in 1-dimethylaminophenylacetylene (**27b**) is slightly larger than that in 1-chlorophenylaceylene (**28**), whereas $E_N < E_{Cl}$; the corresponding DFT $^1J_{CC}$ couplings are 98.9 and 96.1, respectively (see Table 4).

The number of the published carbon-carbon coupling data across two bonds, $^2J_{CC}$, is relatively small. These couplings (presented in Tables 5 and 6) are entirely determined by the FC term. The DSO and PSO contributions are negative and their absolute values are of *ca*. 0.1–0.2 Hz only. The smallest couplings are, as in the case of the couplings across one bond, found in the lithio derivatives and the largest ones in the corresponding fluoro derivatives. The total range covered by these couplings varies from

1.94 Hz in 1-lithiopropyne-1 (**39**) up to 18.82 Hz in 1-fluoropropyne-1 (**40**) and from 4.35 Hz in lithiophenylacetylene (**43**) up to 20.74 Hz in fluorophenylacetylene (**44**) (see Tables 5 and 6, respectively).

CONCLUSIONS

The total range covered by $^1J_{C\equiv C}$ couplings in substituted acetylenes is of *ca.* 380 Hz. The sensitivity of $^1J_{C\equiv C}$ towards substitution is its most fascinating feature. It makes the one-bond C≡C coupling one of the most sensitive parameters, which reflects changes occurring within the triple carbon–carbon bond upon substitution. The obtained data allowed us to draw the following conclusions: (i) the magnitude of the coupling is strongly dependent on the electronegativity of the first atom of the substituent attached to the triple bond; (ii) the mesomeric effects are much less important, almost negligible, in this case; (iii) the influence of β-substitutents, though not very substantial, cannot be neglected especially in such cases when several substituents are introduced. The DFT method can be applied in order to obtain reliable information on the magnitude of the coupling between two carbon atoms and on the mechanism governing it.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Full density functional theory geometry optimizations were carried out using the TURBOMOLE program (BIOSYM/MSI) [23,24]. The gradient-corrected exchange-correlation energy functional employed consists of the exchange functional of Becke [25,26] and the correlation energy functional of Perdew [27]. Standard double ξ quality basis with polarization functions (DZVP) and a fine grid with 32 radial points for the numerical integrations were selected.

The DFT calculations were performed using the recent approach proposed by Malkin, Malkina and Salahub and the deMon program developed by this group [12]. The spin-spin couplings were calculated using the correlation functional of Perdew [28,29] and the semilocal exchange of Perdew and Wang [30]. The basis set employed was the IGLO-III of Kutzelnigg *et al.* [31] and a fine grid with 64 radial points was used. The value of 0.001 was used for the perturbation parameter.

In most cases NMR spectra were measured in 5 mm tubes in $CDCl_3$ solutions; only the spectrum of compound **23** was recorded in DMSO-d_6. 1D INADEQUATE ^{13}C NMR spectra were measured on a Bruker DRX "Avance" spectrometer using the standard B microprogram (32-phase Freeman cycle with automatic data storage). Typical conditions were: acquisition time 2.4–6.2 s, digital resolution 0.16–0.25 Hz per point and 215 cycles within 12 h.

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