Total Range of CC Coupling Constants in Diacetylene Derivatives Calculated by the INDO FPT Method

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Theoretical calculations of spin-spin coupling constants between carbon nuclei (INDO FPT method) for derivatives of diacetylene show that one-bond carbon-carbon coupling constants across the triple, as well as single, CC bonds are strongly dependent on the electronegativity of substituents. The values of $J\,(C_{sp} \equiv C_{sp})$'s cover a range of 43—233 Hz, while those across the $C_{sp} — C_{sp}$ bond are within 104—176 Hz. The calculations predict that the highest value of $J\,(C_{sp} — C_{sp})$ should be found in difluoroacetylene (176 Hz). This is the greatest value which can be attained by $J\,(CC)$ across single bonds.

I. INTRODUCTION

There seems to be little doubt that any reliable piece of information on the magnitudes of spin-spin coupling constants between directly bonded carbon nuclei may be of great value. First of all, they give an insight into the electronic structure of CC bonds.[1] Secondly, relationships between J (CC)'s and other physicochemical parameters, e. g. stretching force constants, allow an estimation of the latter, which are difficult to obtain experimentally[2,3]. For example, such a relationship derived for CC triple bonds[3] allows one to estimate the force constant [K (CC)] of the triple bond. The latter values are assumed by many authors not to depart significantly from that of the K (CC) in acetylene (15.9 mdyn Å⁻¹)[4,5]. Reliability of the relationship which predicts a significant variation in the K (CC)'s in substituted acetylenes has recently been confirmed by force field calculations performed by Belyakov et al.[6] for trimethylstannylacetylene. The K (C≡C) value calculated by these authors equals 14.66 mdyn Å⁻¹ which agrees nicely with that reported in ref.[3] (14.45 mdyn Å⁻¹). Even more spectacular is an agreement in the case of K (C≡C) in sodium acetylide. The K (C≡C) in this compound determined from force field calculations[7] equals 13.1 mdyn Å⁻¹. The experimental J (CC) in NaC≡CH is not known, but it could be estimated by means of the INDO FPT calculation, using geometry reported in ref.[7], as being equal to 73.7 Hz. If the latter is inserted into the equation reported in ref.[3] the value of the K (C≡C) obtained is very close to that given in ref.[7] (13.2 mdyn Å⁻¹).

The two examples demonstrate the usefulness of the knowledge of the reliable magnitude of spin-spin coupling constants.

However, in spite of the progress in NMR techniques,[8] experimental values of J (CC)'s are not always easy to obtain, particularly for symmetrically substituted diacetylenic derivatives, where the determination of the J (CC) across the central, single bond can be performed from ^{13}C enriched samples only. In this group of compounds, only three have been fully analysed, ^{13}C$_4$-diacetylene itself, and bissilyl[9] and bisgermyl[10] derivatives thereof. For diacetylene and bissilyldiacetylene also INDO FPT calculations have been carried out,[11] which accurately reproduced the absolute values of the J (CC)'s across the single $\equiv$C—C$\equiv$ bond. The agreement between the calculated and experimental J (CC)'s across the triple bond has been slightly inferior, but the trends observed experimentally for these J (CC)'s have been well reproduced. Therefore, we decided to compute spin-spin coupling constants in a series of diacetylene derivatives varying substituents systematically along the first row of the Periodic Table. This should provide reliable information on (i) the absolute values of J (CC) across $\equiv$C—C$\equiv$ bond and (ii) the trends in J (CC)'s across triple CC bonds.

II. RESULTS AND DISCUSSION

The calculated J (CC) values are presented in Tables I and II. Table I contains J (CC)'s in symmetrically Li, Li; HBe, HBe; ... F, F substituted diacetylenes. In Table II J (CC)'s in non-symmetrically substituted diacetylenes are presented.

Three general observations follow from the collected data:

(i) J (C_{sp}—C_{sp})'s cover a region 104—176 Hz, while J ($C_{sp}\equiv C_{sp}$)'s lie between 43—233 Hz.

(ii) the values of both types of J (CC)'s are governed by changes in the Fermi contact contribution. OD and SD terms are practically negligible in the case of all the J (C_{sp}—C_{sp})'s considered; their sum never exceeds 2% of the total value of the calculated J (CC). In the case of J ($C_{sp}\equiv C_{sp}$)'s both OD and SD terms are more important but their variations upon substituents beared by the diacetylenic fragment are less pronounced than those observed for the Fermi contact contribution. The plot of FC, OD and SD terms for J ($C_{sp}\equiv C_{sp}$)'s taken from Table I vs. atomic numbers of the first atoms of substituents is shown in Figure 1.

(iii) both types of J (CC)'s are strongly dependent upon the electronegativity of the substituent attached to the diacetylene fragment.

The results are not unexpected in view of the data published for derivatives of acetylene[12] and diacetylene itself[9,11], but they allow a very interesting comparison of the behaviour of J ($C_{sp}\equiv C_{sp}$) and J (C_{sp}—C_{sp}) constants.

The influence of substituents is much stronger upon J (CC) across the triple bond than that upon J (CC) across the C_{sp}—C_{sp} single bond. This, however, leads to quite unusual effects. Namely, the coupling constants across triple CC bonds in dilithium (1) and diberyllium (2) diacetylenes are remarkably smaller than the corresponding J (C_{sp}—C_{sp})'s. This, in turn, must lead to the conclusion that s characters of bond forming orbitals in these two

TABLE I

Calculated Spin-Spin-Coupling Constants Between Carbon Nuclei [$^1J(C_{sp}{\equiv}C_{sp})$ and $^1J(C_{sp}{-}C_{sp})$] in Symmetrically Substituted Diacetylenes $X{-}C{\equiv}C{-}C{\equiv}C{-}X$. Experimental J's, if Known, are Given in Parentheses. All Values are in Hz.

Compd. No.	Substituent X	$J(C_{sp}{\equiv}C_{sp})$				$J(C_{sp}{-}C_{sp})$			
		FC	OD	SD	Total	FC	OD	SD	Total
1	Li	36.19	2.98	4.07	43.20	103.36	−0.10	−0.35	103.99
2	HBe	85.59	3.73	4.21	93.53	117.45	0.04	0.14	118.31
3	H$_2$B	126.09	6.37	5.01	137.47	132.84	1.26	1.15	135.26
4	H$_3$C	165.47	7.64	5.74	178.86 (188.3)[a]	152.92	0.16	0.93	154.01
5	H$_2$N[b] H$_2$N[c]	187.37 187.18	8.75 8.75	6.00 6.00	202.12 201.93	163.57 163.36	0.46 0.46	1.06 1.06	165.08 164.88
6	HO[b] HO[c]	201.02 200.84	9.38 9.38	6.14 6.14	216.54 216.36	169.43 169.22	0.34 0.34	1.07 0.99	170.76 170.55
7	F	216.16	10.13	6.30	233.29	174.87	0.30	0.96	176.11
8	H$_3$Si[d]	126.40	7.28	5.65	139.33 (146.4)	136.92	0.07	0.86	137.92 (137.2)
9	H[e]	167.57	8.24	5.95	181.77 (194.1)	153.07	0.10	0.81	153.99 (154.9)

[a] ref. 15; measured for di-t-butyldiacetylene; [b] hydrogens trans arranged; [c] hydrogens cis arranged; [d] ref. 11; measured for bis(triethylsilyl)diacetylene; [e] taken from ref. 11.

TABLE II

Calculated Spin-Spin Coupling Constants Between Carbon Nuclei. $[^1J\,(C_{sp}{\equiv}C_{sp})$ and $^1J\,(C_{sp}{-}C_{sp})]$ in Non-Symmetrically Substituted Diacetylenes. All Values are Given in Hz.

| Compd. No.	Substituent		$J\,(XC_{sp}{\equiv}C_{sp})$				$J\,(YC_{sp}{\equiv}C_{sp})$				$J\,(C_{sp}{-}C_{sp})$			
	X	Y	FC	OD	SD	Total	FC	OD	SD	Total	FC	OD	SD	Total
10	Li	H	36.56	3.23	4.15	43.95	162.24	7.94	5.84	176.02	123.97	−0.01	0.77	124.73
11	HO	H	197.29	9.14	6.02	212.45	169.43	8.28	5.97	183.68	160.31	0.19	0.88	161.38
12	HO	CH₃	197.50	9.16	6.03	212.69	167.66	7.80	5.80	181.26	160.47	0.24	0.95	161.65
13	F	H	210.52	9.99	6.24	226.74	170.23	8.31	5.98	184.52	162.28	0.19	0.87	163.34
14	Li	OH	36.55	3.28	4.10	43.93	189.77	8.87	5.88	204.51	128.19	0.01	0.81	129.01
15	HBe	OH	86.97	3.66	4.04	94.67	192.42	8.53	5.68	206.63	138.40	−0.07	0.81	139.13
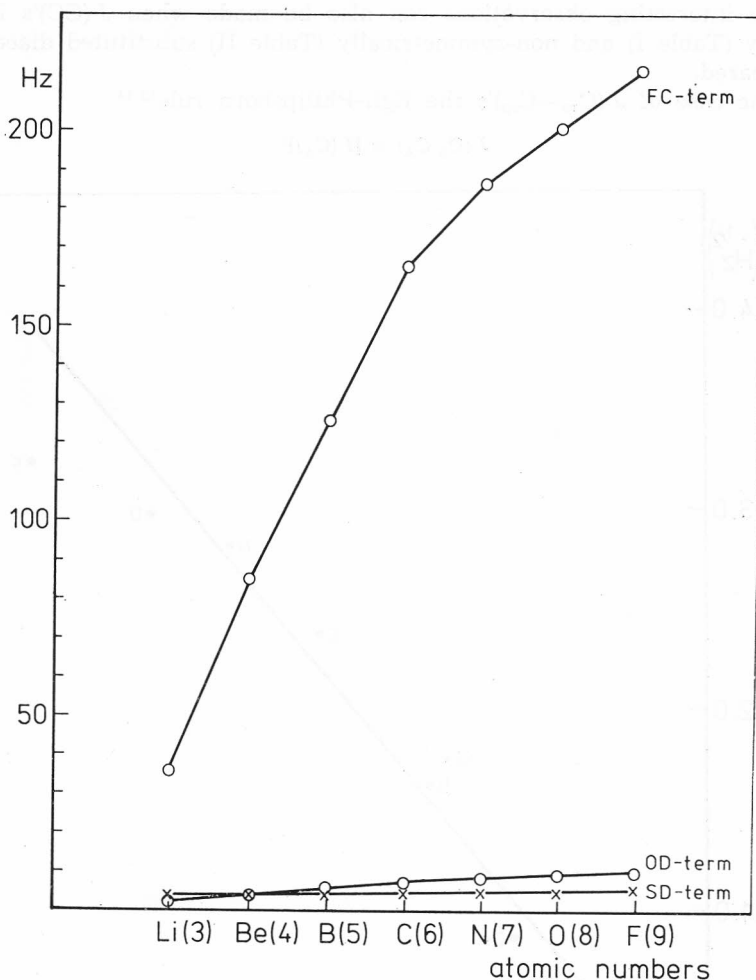
Figure 1. The plot of the Fermi contact, orbital-dipol and spin-dipol terms vs. atomic numbers of the first atom of the substituent for $J\,(C_{sp}{\equiv}C_{sp})$ coupling constants in symmetrically substituted diacetylenes.

compounds are much greater for the single C_{sp}—C_{sp} bond than for the corresponding $C_{sp}{\equiv}C_{sp}$ one (see also Discussion in ref. 12).

In diboroderivative *3* both couplings are of comparable magnitude and only in the four remaining compounds (carbon, nitrogen, oxygen an fluoro derivatives of diacetylene) $J\,(C_{sp}{\equiv}C_{sp})$'s are greater than $J\,(C_{sp}$—$C_{sp})$'s.

It is interesting to note that $J\,(C_{sp}$—$C_{sp})$ in difluorodiacetylene attains the highest value (176 Hz) which can be expected for $J\,(CC)$ across any single CC bond. The lowest $J\,(CC)$ value (—17.6 Hz) has been found experimentally in a derivative of bicyclobutane.[13] These two figures determine the range covered by $J\,(CC)$'s across single CC bonds.

Some interesting observations can also be made when J (CC)'s in symmetrically (Table I) and non-symmetrically (Table II) substituted diacetylenes are compared.

In the case of J (C_{sp}—C_{sp})'s the Egli-Philipsborn rule[12,14]

$$J (C_A C_A) = [I (C_A)]^2 \tag{1}$$
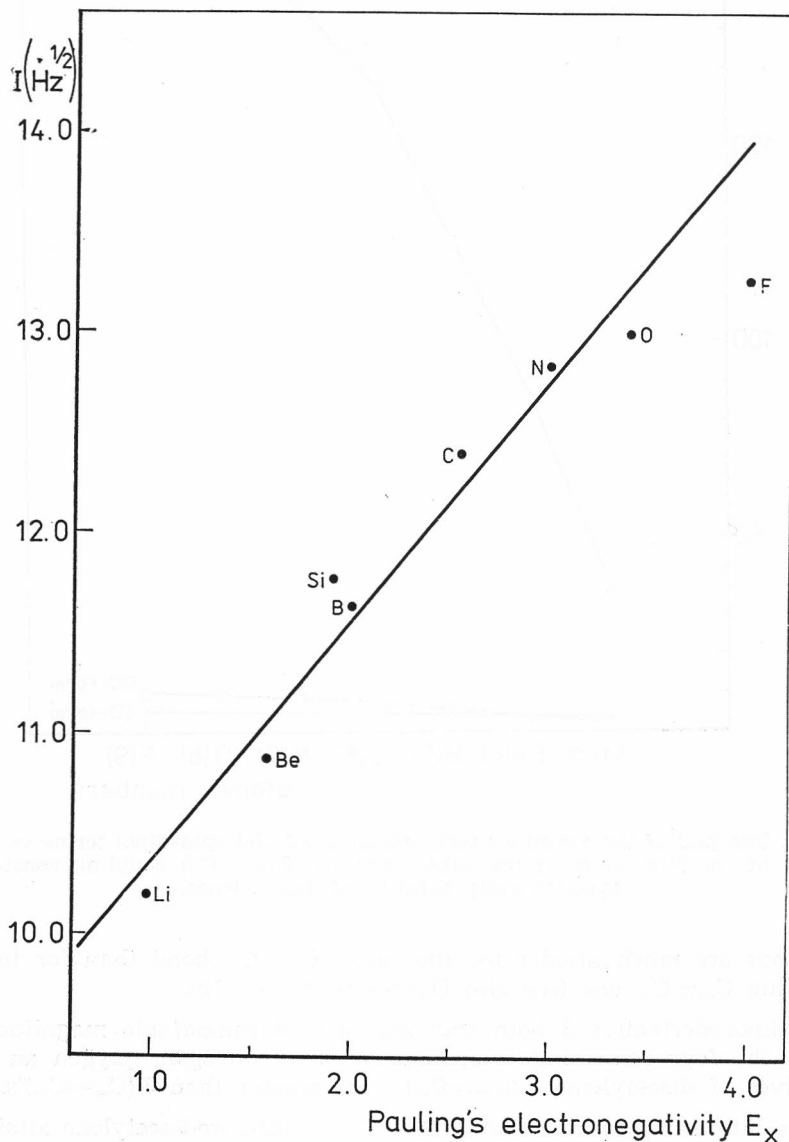
Figure 2. Correlation of I (C_{sp}—C_{sp}) factors calculated as square roots of J (C_{sp}—C_{sp}) coupling constants with the Pauling's electronegativity of the first atom of the substituent in symmetrically substituted diacetylenes. The least-squares line calculated without data for fluorine (see text).

can be applied. By means of this approach any unknown J (CC) in a non-
-symmetrically substituted diacetylene can be estimated with a very good
approximation if the corresponding I (C_A), I (C_B) factors (which are square
roots of J (CC)'s in symmetrically substituted diacetylenes) are known.

To check the reliability of this approach, INDO values of J (C_{sp}—C_{sp})'s
in various, randomly selected, non-symmetrically substituted diacetylenes have
been calculated (Table II). The I factors, in turn, could be easily derived
from the INDO data collected for symmetrically substituted compounds in
Table I. Indeed, in all cases, J (C_{sp}—C_{sp})'s calculated for non-symmetrical
diacetylenes are of magnitudes very close to those obtained from multipli-
cation of the corresponding I factors.

A plot of the I factors against Pauling's electronegativity E_x[16] (Figure 2)
shows that there is a linear relationship between the two parameters except
for fluorine.* The corresponding equation in which the data for bissilyldiace-
tylene are included has a good correlation coefficient $r = 0.981$.

$$I (C_A) = 1.20 \ E_x + 9.16 \qquad (2)$$

Inclusion of the data for difluorodiacetylene changes somewhat the a
and b parameters and lowers r to 0.970.

A combination of the Egli-Philipsborn rule and equation (2) allows one to
estimate J (C_{sp}—C_{sp}) in any bisubstituted diacetylene.

A comparison of the J (C≡C)'s collected in Tables I and II shows that the
decisive influence upon J (C≡C) in exerted by the substituent directly attached
to C≡C bond. The influence of the second substituent, attached to the other
end of diacetylenic fragment, is negligible or at least by several orders weaker.

III. CALCULATIONS

The calculations of the coupling constants were based on the self-con-
sistent perturbation approach within the INDO framework. A modified version
of the Blizzard-Santry program[17] with values of 4.0318 and 1.6920 a. u. for
S_C^2 (O) and $\langle r^{-3} \rangle_{C'}$ respectively, was used.

Standard geometries of C≡C and C—C bonds 1.217 Å, and 1.3837 Å,[18]
respectively, have been used throughout the whole series of the compounds
studied. The XC≡ (X = Be, B, ..., F) distances, as quoted in ref.[12], have been
applied. The LiC≡ distance equal to 1.836 Å has been taken from ref.[19].

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* The Santry program generally seems to underestimate the magnitudes of
J (CC) in the case of strongly electronegative substituents. This, however, can be
definitely proved and eventually corrected only when experimental data are
available for fluoroacetylene compounds and these are difficult to obtain.

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SAŽETAK

Raspon konstanti sprezanja spin-spin direktno vezanih C-atoma u derivata diacetilena, predviđen primjenom semiempirijske INDO FPT metode

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Teorijski računi konstanti sprezanja spinova jezgri direktno vezanih atoma ugljika s pomoću INDO FPT metode pokazuju u nizu derivata diacetilena da numeričke vrijednosti jako ovise o elektronegativnosti supstituenata. Vrijednosti za J (C(sp) C(sp)) konstante imaju raspon od 43—233 Hz, dok se J (C(sp)—C(sp)) konstante nalaze u granicama između 104 i 176 Hz. Vrijednost J (C(sp)—C(sp)) od 176 Hz odnose se na difluoroacetilen i predstavlja najveću do sada nađenu konstantu sprezanja za jednostruku vezu C—C.