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INDO CALCULATIONS OF *J*(CC) AND *J*(CSI) IN SILYL DERIVATIVES OF ACETYLENE AND DIACETYLENE

KRYSTYNA KAMIEŃSKA-TRELA *

Institute of Organic Chemistry, Polish Academy of Sciences, PL-00 961 Warsaw (Poland)

and BURKHARD KNIERIEM

Institute of Organic Chemistry, University of Göttingen D-34, Tammannstrasse 2 (B.R.D.)

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Summary

INDO FPT calculations of the carbon—carbon and carbon—silicon spin—spin coupling constants have been performed for silyl substituted acetylenes and diacetylene. The calculated values are compared with available experimental data. The roles of the various contributions to *J*(CC) are discussed.

The NMR spectra of silyl and stannyl substituted acetylenes [1] and diacetylene [2] have been recently measured and analysed by one of us (K.K.T.). The determined spin—spin coupling constants reveal several interesting substituent effects common to both the silyl and stannyl derivatives. In particular, both these substituents cause a large decrease in the CC coupling across the triple bond. A similar observation was made by Wrackmeyer for $(CH_3)_3SiC{\equiv}CCH_3$ and $(CH_3)_3SiC{\equiv}CSn(CH_3)_3$ [3] and for $(CH_3)_3SnC{\equiv}C\text{-}C{\equiv}CSn(CH_3)_3$ [4].

According to the theory of spin—spin coupling between two heavy nuclei (i.e. those other than protons [5]) the coupling constants may involve a considerable contribution of the orbital and spin-dipolar terms. Their relative importance can be revealed by comparing the corresponding experimental and theoretical data. Because of the weakness of the theoretical methods currently in use [5] a study of the substituent effects is expected to give more information than calculation of absolute values of the NMR parameters. On the other hand, theoretical calculations, even approximate ones, may help to rationalize the observed regularities.

In this paper we present the results of INDO calculations of direct and long range CC and CSi coupling constants in silylacetylene, I, bissilylacetylene, II, and bissilyldiacetylene, III. The calculations were carried out by the finite perturbation method in the INDO approximation [6] using the program of Santry

TABLE 1

EXPERIMENTAL AND INDO VALUES OF J(CC)'s ACROSS ONE BOND IN SILYL DERIVATIVES OF ACETYLENE AND DIACETYLENE (IN Hz)

Compound	Coupling constant	Contact	Orbital	Dipolar	Total	Exptl. [a]
$H_3SiC{\equiv}CH$		125.23	7.70	5.68	138.61	130.9 [b]
$H_3SiC{\equiv}CSiH_3$		96.20	7.44	5.53	109.17	101.4 [b]
$HC{\equiv}CH$		163.92	8.24	5.80	177.96	171.5 [c]
1 2 3 4 $H_3SiC{\equiv}C{-}C{\equiv}CSiH_3$	J(C1C2)	126.40	7.28	5.65	139.33	146.4 [d]
1 2 3 4 $HC{\equiv}C{-}C{\equiv}CH$	J(C1C2)	167.57	8.24	5.95	181.77	194.1 [d]
1 2 3 4 $H_3SiC{\equiv}C{-}C{\equiv}CSiH_3$	J(C2C3)	136.92	0.07	0.86	137.92	137.2 [d]
1 2 3 4 $HC{\equiv}C{-}C{\equiv}CH$	J(C2C3)	153.07	0.10	0.81	153.99	154.9 [d]

[a] Experimental ^1J(CC) values correspond to triethylsilyl derivatives. [b] Taken from ref. 1. [c] Taken from ref. 7. [d] Taken from ref. 2.

and Blizzard *. For comparison, we have also included the CC coupling constants in acetylene and diacetylene. The results of our calculations involving the separate contributions to the spin—spin coupling constants are listed in Tables 1—3.

We do not propose to discuss the numerical agreement between the experimental and calculated values. Though in several cases the agreement is striking, e.g. the J(CC) for the central CC bond in III, we focus our attention on the relative values of the spin—spin coupling constants.

First of all we note that the Fermi contact contribution (FC) predominates in the CC coupling across one bond. This contribution reflects both the absolute magnitude of the experimental values of J(CC)'s and general trends observed for them; the magnitude of the FC contribution diminishes drastically upon passing from acetylene and diacetylene to their silyl derivatives (see Table 1). The same feature is observed for experimental J(CC)'s across both triple and single *sp—sp* bonds [1,2].

It was interesting to find that for the ^1J(CC) across a single *sp—sp* bond the orbital-dipolar (OD) and spin-dipolar (SD) terms can practically be neglected. The terms become more important for ^1J(CC)'s across triple bonds in I—III. Nonetheless, they still account for less than about 10% of the total computed value of J(CC). Inclusion of the OD and SD terms in general improved the agreement with experimental data. This is exemplified by the values of ^1J(CC) across triple bonds in III and in diacetylene. However, the absolute magnitude of these terms depends only slightly on the structures of the compounds examined.

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* Adapted by V. Wray.

TABLE 2

EXPERIMENTAL AND INDO VALUES OF LONG-RANGE J(CC) COUPLINGS IN BISSILYLDIACETYLENE (IN Hz). FOR A COMPARISON DATA FOR DIACETYLENE TAKEN FROM REF. 2 ARE INCLUDED

Compound	Coupling constant	Contact	Orbital	Dipolar	Total	Exptl. [a]
$\mathrm{H_3SiC{\equiv}C{-}C{\equiv}CSiH_3}$	^2J(CC)	−12.65	−2.17	−1.33	−16.15	13.0
$\mathrm{HC{\equiv}C{-}C{\equiv}CH}$	^2J(CC)	−6.46	−2.28	−1.33	−10.10	18.9
$\mathrm{H_3SiC{\equiv}C{-}C{\equiv}CSiH_3}$	^3J(CC)	10.61	5.08	2.58	18.27	14.1
$\mathrm{HC{\equiv}C{-}C{\equiv}CH}$	^3J(CC)	8.55	5.21	2.68	16.45	16.0

[a] Experimental values taken from ref. 2 correspond to the triethylsilyl derivative of diacetylene.

TABLE 3

EXPERIMENTAL AND INDO VALUES OF J(CSi)'s IN SILYL DERIVATIVES OF ACETYLENE AND DIACETYLENE (IN Hz)

Compound	Coupling constant	Contact	Orbital	Dipolar	Total	Exptl.
$\mathrm{H_3SiC{\equiv}CH}$	^1J(CSi)	−39.10	0.43	0.15	−38.52	75.0 [a]
$\mathrm{H_3SiC{\equiv}CH}$	^2J(CSi)	2.20	0.11	−0.34	1.97	18.6 [a]
$\mathrm{H_3SiC{\equiv}CSiH_3}$	^1J(CSi)	−36.48	0.47	−0.34	−36.59	74.8 [a]
$\mathrm{H_3SiC{\equiv}CSiH_3}$	^2J(CSi)	4.40	0.04	0.13	4.57	11.5 [a]
$\mathrm{H_3SiC{\equiv}C{-}C{\equiv}CSiH_3}$	^1J(CSi)	−39.44	0.51	−0.35	−39.28	80.1 [b]
$\mathrm{H_3SiC{\equiv}C{-}C{\equiv}CSiH_3}$	^2J(CSi)	1.72	0.11	0.14	1.97	14.3 [b]

[a] Experimental J(CSi) values taken from ref. 1 correspond to triethylsilyl derivatives of acetylene. [b] Trimethylsilyl derivative, ref. 4.

It can be expected that absolute values of the OD and SD contributions will not properly be taken into account by the INDO method. Thus the method gives reasonable results for ^1J(CC) since these contributions are not too large. On the other hand, this is most probably the reason that the INDO method fails when J(CC)'s across more than one bond are considered. For long range couplings the OD and SD terms become important and for J(CC) across three bonds they account for almost a half of the total values (see Table 2).

The importance of the OD and SD contributions is also responsible for unacceptable theoretical results for ^2J(CC). As can be seen from the data in Table 2, even the changes of ^2J(CC) and ^3J(CC) upon silyl substitution are not properly accounted for.

Both the computed direct and long-range J's between carbon and silicon nuclei are much too low when compared with experiment. It is interesting to note, however, that the computed J(CSi)'s across one bond are almost identical in I and II. This is in accordance with experimental results, which show that the sharp changes occurring in J(CC)'s upon passing from I to II are not reproduced in the corresponding J(CSi)'s, which remain practically constant for I and II.

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References

1 K. Kamieńska-Trela, J. Organometal. Chem., 159 (1978) 15.
2 K. Kamieńska-Trela, Org. Magn. Resonance, accepted for publication.
3 B. Wrackmeyer, J. Organometal. Chem., 166 (1979) 353.
4 F. Hölzl and B. Wrackmeyer, J. Organometal. Chem., 179 (1979) 397.
5 J. Kowalewski, Prog. Nucl. Magn. Reson. Spectrosc., 11 (1977) 1.
6 A.C. Blizzard and P.P. Santry, J. Chem. Phys., 55 (1971) 950.
7 R.M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. London Ser. A, 269 (1962) 385.