On the Spin–Spin Coupling Constants of Trimethylsilylated Iodoacetylene

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Quantum-mechanical calculation of NMR parameters for molecules which include heavy atoms is the challenging task of the present time. The paper by Kaupp et al.[1] published recently in *Chem. Eur. J.* is undoubtedly an important contribution to this field. It concerns the analogy between the iodine–carbon spin–spin coupling constant and the correction of carbon chemical shifts resulting from the spin–orbit coupling of heavy-atom electrons in iodohydrocarbons. It seems that in the case of such a novel theoretical approach it is always desirable to compare the calculated results with the experimental ones. In the paper mentioned, the authors state: "Experimental spin–spin coupling constants are not available for comparison (couplings to iodine are difficult to observe because of the large quadrupole coupling constant of iodine)". In fact, a large quadrupole coupling constant results in the rapid spin relaxation of the iodine nucleus and, moreover, affects relaxation of neighbouring carbon nuclei by the mechanism of scalar relaxation of the second kind.[2] It makes it possible to determine the spin–spin coupling constants from the relaxation data analysis.[3] Actually, we have determined the absolute values of $^1J(^{13}C,^{127}I)$ and $^2J(^{13}C,^{127}I)$ coupling constants of trimethylsilylated iodoacetylene.[4] We are glad that our experimental values, 361 ± 11 Hz and 84 ± 14 Hz, are in reasonable agreement with values calculated for iodoacetylene by Kaupp et al.:[1] -695.5 Hz and -56.2 Hz for ^1J and ^2J, respectively. Moreover, the value of the chemical shift for protonated carbon in iodoacetylene has been reported to be $\delta = 83.5$,[5] showing an excellent agreement with the value $\delta = 81.7$ reported in the paper on which we comment here.[1]

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