

SCPT-INDO Calculations of NMR Carbon-Carbon Coupling Constants for Some Alcohols with Different Structures and Their Corresponding Hydrocarbons

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A large number of ^{13}C , ^{13}C -coupling constants have been measured in the last decade, and there is a widespread interest in their interpretation since these values provide information about the electronic structure of organic molecules.¹⁻³

As known from the work of Ramsey,⁴ spin-spin coupling constants $[J(\text{AB})]$ arise from three different coupling mechanisms: the orbital $[J(\text{AB})^{\text{O}}]$, dipolar $[J(\text{AB})^{\text{D}}]$ and Fermi contact $[J(\text{AB})^{\text{FC}}]$ interactions.

$$J(\text{AB}) = J(\text{AB})^{\text{O}} + J(\text{AB})^{\text{D}} + J(\text{AB})^{\text{FC}}$$

If the Fermi contact mechanism is predominant, a linear relationship is valid between $^1J(\text{CC})$ and the percentage *s*-character of the two bonding carbon hybrid orbitals.⁵ This arises because the Fermi contact contribution depends upon the product of the *s*-orbital densities at the coupled nuclei, *i.e.* $S_{\text{C}}^2(\text{O}) \cdot S_{\text{C}}^2(\text{O})$.

For some singly and multiply bound carbon atoms, such a relationship may be less reliable due to significant contributions to the spin-spin coupling interaction by the orbital and dipolar mechanisms.⁶ Both of these non-contact interactions are proportional to the product of the one-centre integrals, $\langle r^{-3} \rangle_{\text{C}}$, for the coupled carbons, where $\langle r^{-3} \rangle_{\text{C}}$ is the expectation value of r^{-3} for the valence shell *p*-orbitals on the carbon atom concerned. The integral products, $S_{\text{C}}^2(\text{O})$ and $\langle r^{-3} \rangle_{\text{C}}$, used in this study, were evaluated by Blizzard and Santry.⁷

Following our previous study⁸ of ^{13}C , ^{13}C -couplings for methylcycloalkanes by the self-consistent perturbation approach, at the INDO level of approximation, we now report the calculated contributions to the carbon-carbon coupling constants $^1J(\text{C-1, C-2})$ of the compounds 1-6, 8-10, 12, 14 and 16-22. The numbering of the atoms in the compounds is different from the rules given by IUPAC. This gives the same symbols for comparable coupling constants. The experimental coupling constants for compounds

1-22 have been published in previous papers.^{2,3,9-12}

In the present paper we evaluate the influence of hydroxyl groups on the magnitude of the coupling constants by comparison of the calculated data for the alcohols with the values obtained for the corresponding hydrocarbons.

Results and discussion. The calculated contributions of the Fermi contact (FC)-, orbital (OT)- and dipolar (DT)-terms to the $^1J(\text{C-1, C-2})$ coupling constants for the compounds 1-22 are summarized in Tables 1 and 2, together with the experimental data.

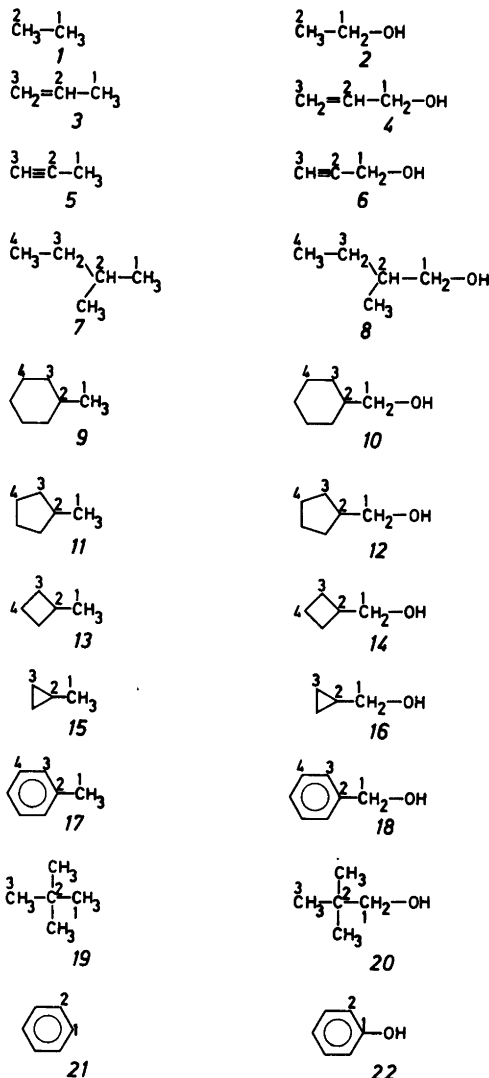


Table 1. Calculated and experimental $^1J(\text{C-1,C-2})$ coupling constants (in Hz) of the hydrocarbons.

Compound	Calculated				Exp. ^a
	FCT	OT	DT	Total	
1	35.64	-2.91	0.82	33.55	34.6
3	47.58	-3.12	0.71	45.17	41.9
5	66.54	-2.65	0.53	64.42	67.4
7 ^b	37.50	-2.47	0.82	35.85	35.4
9	34.66	-2.51	0.84	32.99	35.7
11 ^b	35.22	-2.49	0.83	33.56	36.2
13 ^b	39.07	-2.58	0.76	37.25	36.1
15 ^b	49.19	-2.59	0.68	47.28	43.4
17	42.97	-2.88	1.22	41.31	44.2
19	35.23	-2.29	0.82	33.76	33.7
21	65.44	-12.83	2.70	55.31	57.0

^a Data taken from Ref. 12 (and references therein). ^b Calculated data taken from Ref. 8.

Table 2. Calculated and experimental $^1J(\text{C-1,C-2})$ coupling constants (in Hz) of the alcohols.

Compound	Calculated				Exp. ^a
	FCT	OT	DT	Total	
2	42.61	-2.75	1.32	41.18	37.7
4	55.39	-3.06	1.17	53.50	45.4
6	78.08	-2.38	0.86	76.56	72.3
8	44.28	-2.51	1.28	43.05	37.7
10	40.79	-2.56	1.33	39.56	38.3
12	41.62	-2.56	1.33	40.39	38.8
14	45.76	-2.64	0.73	43.85	39.3
16	56.52	-2.61	1.09	55.00	47.8
18	50.31	-2.90	1.14	48.55	47.7
20	41.38	-2.42	1.27	40.23	37.5
22	73.76	-11.93	2.71	64.54	65.6

^a Data taken from Ref. 12 (and references therein).

As shown in the tables the $^1J(\text{C-1,C-2})$ coupling constants are dominated by the Fermi contact terms. The two non-contact terms add up to -1.8 Hz (± 0.6 Hz), thus being almost negligible, except for compounds 21 and 22. In these compounds (benzene and phenol) the carbon atoms are multiply bound. This is the reason why the orbital and dipolar terms are much larger than the non-contact terms for the compounds with common single carbon-carbon bonds¹³ and, therefore, cannot be neglected.⁷

Changes in the size of the $^{13}\text{C},^{13}\text{C}$ -coupling constants caused by structural variations were

observed both for the calculated and the experimental values. The calculated data agree mostly with the experimental findings. The largest deviations were found for the cyclopropane derivatives and the compounds with multiply bonded carbons.

Comparisons of the calculated coupling constants for the alcohols with the data obtained for the corresponding hydrocarbons show that an introduction of a hydroxyl group in an organic molecule leads to an average increase of the $^1J(\text{C-1,C-2})$ values of about 7 Hz. Exceptions were observed for the alcohols 4, 6 and 22, with

Δ^1J values [$\Delta^1J=^1J$ (alcohol)– 1J (hydrocarbon)] of 8.33 Hz, 12.14 Hz and 9.23 Hz, respectively. The value for the propyne system (5 and 6) is very large, presumably due to the fact that one of the carbons concerned is *sp*-hybridized.

Finally, it should be emphasized that the calculations confirm the experimental findings, although the calculated Δ^1J -values are larger than the experimental ones.

Experimental. The calculations were based on the self-consistent perturbation theory (SCPT) approach, within the INDO (intermediate neglect of differential overlap) framework, as developed by Blizzard and Santry.⁷

They were performed with the SCPT-INDO program of Blizzard and Santry⁷ on the IBM 3032 computer system of the University of Münster, Germany. We used a modified version of the program with values of 3.7387 and 2.8793 a.u. for $S_C^2(O)$ and $\langle r^{-3} \rangle_C$, respectively. Bond distances and bond angles were based on the standard geometrical model.¹⁴

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