^{13}C–^{13}C Long Range Spin–Spin Coupling Constants in Naphthalene Derivatives

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Summary 1-Hydroxy- and 1-acetoxy-naphthalene with a ^{13}C label at the α-position have been synthesized; the ^{13}C–^{13}C spin coupling constants have been measured by Fourier transform n.m.r. spectroscopy and interpreted in terms of INDO and Hückel calculations.

ALTHOUGH reports of the use of carbon–carbon coupling constants[1] between directly bonded carbon atoms are steadily increasing, very little is known about the long range transmission both in aromatic[2] or olefinic[2] and aliphatic[3] systems. The use of ^{15}N–^{13}C spin coupling constants as a conformational probe in aliphatic systems has been widely discussed recently.[4] ^{15}N–^{13}C long-range spin coupling constants show a directional effect of the nitrogen lone pair in aromatic systems.[5] The only study with a ^{13}C label incorporated in an aromatic ring system, toluene,[2] shows a remarkable alternating effect of the ^{13}C–^{13}C coupling constants, suggesting that π-effects may be the main source of transmission.

To prove whether this coupling constant alternation also holds in more extended aromatic systems, we have synthesized 1-hydroxy- (**1a**) and 1-acetoxy-naphthalene (**1b**) with a ^{13}C label (60%) at the α-position. 1-Hydroxy[1-^{13}C]napthalene was synthesized by catalytic dehydrogenation of [1-^{13}C]-α-tetralone with Pd at 200°. Details will be described later. The ^{13}C-spectra were recorded at least three times with Varian XL-100 and CFT-20 spectrometers at 25·16 and 20 MHz, respectively. The minimum possible

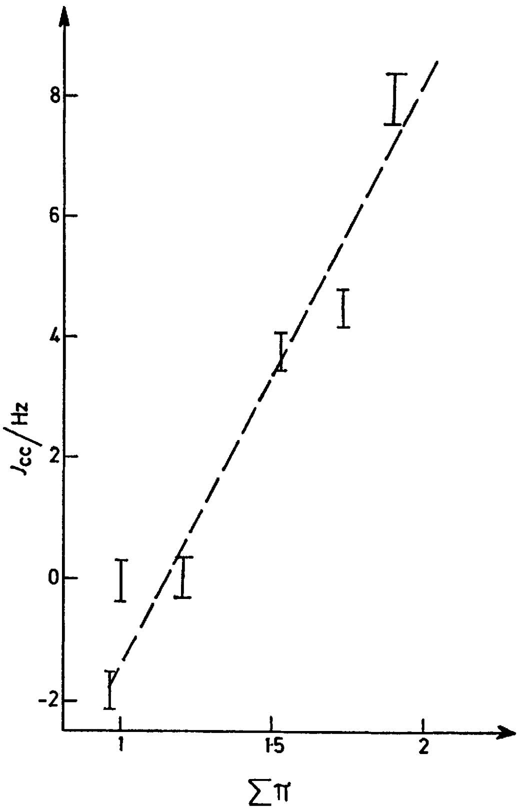


FIGURE. Plot of Hückel bond orders *vs.* $^{13}C-^{13}C$ spin coupling constants in (**1a**). Sum of bond orders for each linkage is computed. $^2J_{CC}$ values taken to be negative, by analogy with C–H coupling constants; $^4J_{CC}$ and $^1J_{CC}$ not given.

sweep-width was chosen to provide a spectral resolution after an 8 k Fourier transform of 0·3 Hz/point. The solutions were *ca.* 10% in $CDCl_3$ and the results from both spectrometers agreed very well within experimental error. Chemical shift assignments were made using the increment system given recently by Wells and his co-workers[6] on naphthalene chemical shifts.

The coupling constants in the Table reveal the well known pattern of second substitution in naphthalene derivatives: positions where simple valence bond theory predicts π-electron excess show a coupling constant, while at the '*meta*' positions the spin coupling constants are beyond spectral resolution.

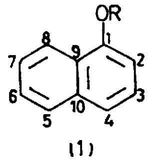
TABLE

$^{13}C-^{13}C$ Spin coupling constants[a] and chemical shifts[b] in (**1a**) and (**1b**)

Carbon atom	(**1a**)		(**1b**)[c]	
1		(151·4)		(146·9)
2	70·0	(108·8)	74·0	(118·2)
3	<0·6	(125·9)	<0·6	(125·4)
4	7·9	(120·9)	8·6	(125·9)
5	3·8	(127·7)	4·2	(128·0)
6	<0·6	(126·3)	<0·6	(126·4)
7	4·5	(125·3)	5·0	(126·4
8	<0·6	(121·6)	<0·6	(121·3)
9	65·4	(124·5)	65·5	(126·9)
10	1·8	(134·9)	2·0	(134·8)

[a] Given in Hz, accuracy ±0·3 Hz. [b] δ, p.p.m. relative to Me_4Si given for the unlabelled compounds. [c] $\delta_{C=O}$ 169·0, *J* 3·7 Hz, δ_{Me} 20·4, *J* 2·1 Hz.

We have calculated the $^{13}C-^{13}C$ spin coupling constants taking only the Fermi contact interaction into account using the INDO-approach given by Pople.[7] Although the results give rather poor agreement with the observed values, they do reveal the experimental trend.



(1)

a; R = H

b; R = COMe

In addition we have taken the bond orders from a simple Hückel calculation[8] and tried to correlate the long-range spin coupling constants with the sum of the π-bond orders for each linkage.† The Figure shows a rough linear relationship for (**1a**). However, $^4J_{CC}$ to C-6 had to be left out from the correlation. We conclude on the basis of these findings that $^{13}C-^{13}C$ spin coupling constants in aromatic systems are mainly transmitted by π-interaction.

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† *Added in proof:* As one referee suggested, two pathways are possible for the three-bond coupling to C-4. The sum of the π-bond orders for the linkage 1,9,10,4 is 0·33 units lower than for the pathway 1,2,3,4. A similar approach has now been published independently by J. L. Marshall, A. M. Ihrig, and D. E. Miiller, *J. Magn. Res.*, 1974, **16**, 439.

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