

$^{13}\text{C}^{13}\text{C}$ SPIN SPIN COUPLING CONSTANTS IN AZULENES

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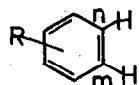
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Abstract—[4- ^{13}C]-Azulene and [4- ^{13}C]-4-methylazulene have been synthesized. The $^{13}\text{C}^{13}\text{C}$ spin coupling constants have been measured and interpreted in terms of π MO theory.

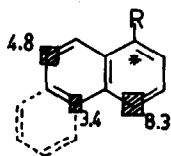
It has been established that vicinal proton proton spin coupling constants in aromatic compounds 1 obey a linear relationship (1) with π bond order from a Hückel MO calculation.^{1,2} These results were "surprising in view of McConnell's prediction"³ that the π electron contribution to the transmission of the spin-spin coupling constant should be only about 10%. As Günther pointed out² the HMO π bond order probably reflects changes in the σ skeleton and therefore the relation (1) still holds.



1

$$^3J_{\text{HH}} = A + B \cdot P_{nm} \quad (1)$$

In order to study the mechanism of spin-spin coupling in aromatic compounds we have chosen ^{13}C as a spin probe being directly a member of the aromatic π system. In our earlier work we demonstrated that vicinal $^{13}\text{C}^{13}\text{C}$ spin coupling constants in naphthalene⁵ and phenanthrene⁶ derivatives 2 can be readily understood in terms of π MO theory giving a linear relationship to the π charge at the various carbon atoms. Others⁷ have found a similar relationship to (1) in different aromatic compounds.



2

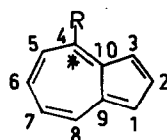
However, recently it has been shown likely^{8,9} that carbon-carbon spin coupling constants are additive for aliphatic systems if two or more pathways between the coupled C atoms are possible. If the $^{13}\text{C}^{13}\text{C}$ spin coupling constants in aromatic systems are transmitted via σ electrons the rather high spin coupling constant to C-4 in 2 can be explained by the double of the typical value for a cisoid linkage with a dihedral angle of 0° and our earlier interpretation in terms of π MO theory is fortuitous.

Clearly the situation called for a decisive experiment. We have therefore synthesized azulenes 3a and 3b labelled at C-4 with 90 at% ^{13}C . The labelling pathway followed the recent azulene synthesis of Leaver¹¹ and Houk¹² starting from [^{13}C]-NN-dimethylformamide and [^{13}C]-NN-dimethylacetamide respectively.

Compounds 3a and 3b provide four independent and unequivocal pathways for vicinal $^{13}\text{C}^{13}\text{C}$ spin coupling constants to C-1, C-2, C-7 and C-8. Furthermore, these compounds are the first examples of non alternant hydrocarbons, where the $^{13}\text{C}^{13}\text{C}$ spin coupling constants are measured. If the π electron relations mentioned above are of any value, they should hold for non alternant hydrocarbons as well.

RESULTS AND DISCUSSION

In Table 1 the $^{13}\text{C}^{13}\text{C}$ spin coupling constants and the ^{13}C chemical shifts of 3a and 3b are given. The ^{13}C chemical shifts assignments follow the detailed study by Braun.¹³ The $^1J_{\text{CC}}$ spin coupling constants are similar to those in 1-Methylphenanthrene⁶ and do not exhibit any peculiarity. Under the vicinal spin coupling constants to C-1, C-2, C-7 and C-8 the high value of 7.5 Hz to C-2 immediately demonstrates that such a magnitude of a vicinal aromatic spin coupling constant is possible without double pathways and is not restricted to a cisoid linkage.



* = 90 at% ^{13}C

3a R = H
3b R = CH₃

In order to correlate the $^{13}\text{C}^{13}\text{C}$ spin coupling constants in the 1-substituted and 1-labelled phenanthrene derivatives⁶ we have calculated the π electron charges in the 1-phenanthrylmethylanion 4a resembling a model for an electron donating substituent. Furthermore, the label at C-1 was computationally fixed in this manner, since the perturbation at C-1 by the charge of the methylanion was thus transmitted to the other C atoms. A similar treatment for azulene, however, fails regardless the degree of sophistication of the MO method as HMO,

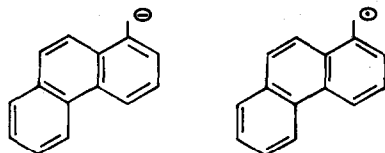
Table 1. $^{13}\text{C}^{13}\text{C}$ spin-spin coupling constants and ^{13}C chemical shifts of the azulenes 3a and 3b^a

		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Me
<u>3a</u>	J	2.0	b)			59.3	1.5	3.7		5.5	61.3	
	δ	118.1	136.9 ^{c)}	118.1	136.4	122.6	137.1 ^{c)}	122.6	136.4	140.2	140.2	
<u>3b</u>	J	2.0	7.5	0.95		60.5	0.8	3.4	2.0	6.0	61.0	41.4
	δ	118.8	135.2	115.8	146.4	126.1	136.0	121.6	136.7	140.1	137.6	24.2

a) Chemical shifts in ppm vs Me_4Si , spin coupling constants in Hz.

b) signal to close to signal of labelled carbon atom 4

c) The ^{13}C resonances of C-2 and C-6 are too closely together to be assigned undoubtedly. However, in the spectrum of 4-deuterioazulene the signal at 137.1 ppm is splitted into a triplet whereas the other signal (136.9 ppm) remains unchanged. The splitting is due to a vicinal $^{13}\text{C}^2\text{H}$ spin spin coupling constant between the deuterium atom and C-6 ($J=1.4$ Hz) (K.P.Zeller and E.Katz, unpublished results)

4a4b

PPP,¹⁴ INDO¹⁵ or ab initio¹⁶ calculations. The reason for this is that in 4a all excess charges obtained by the perturbation at C-1 are normalized to unity, since in the neutral compound 4b, as an alternant hydrocarbon all π centers have a π charge of 1.0. This is not true for the analogous 4-azulenylmethylanion 5a and the radical 5b

5a5b

since in non alternant hydrocarbons the π charges are not unity charges even in the neutral species. Therefore, to give an equivalent treatment for the azulenes 3 one has to take the π charge differences between 5a and 5b as given in Table 2 from a PPP calculation.¹⁴ The spin coupling constants in Table 2 are from 3b, they are equivalent to those in 3a showing that they are a function of the π system and not determined by the substituent. We have shown earlier that the vicinal $^{13}\text{C}^{13}\text{C}$ spin coupling constants in aromatic compounds are not largely influenced by the substituent.^{5,6} In Fig. 1 a plot between the charge differences and the geminal and vicinal spin coupling constants shows that both kind of spin couplings obey the same straight line. This is the first time that aromatic geminal and vicinal spin coupling constants are reproduced by the same model. The plot suggests that the spin coupling constant to C-8 may be negative.

It has been shown that vicinal carbon hydrogen spin coupling constants in azulene and similar compounds also depend on bond lengths and bond angles.¹⁷ Possibly similar effects are operative to some extent for $^{13}\text{C}^{13}\text{C}$ spin coupling and responsible for the scatter of the points in Fig. 1.

Table 2. π Electron densities in 5a and 5b, their differences and $^{13}\text{C}^{13}\text{C}$ spin-spin coupling constants in 3b

C-Atom	<u>5a</u>	<u>5b</u>	<u>5a-5b</u>	<u>3b</u> (Hz)
1	1.154	1.07	0.084	2.0
2	1.136	0.9793	0.1567	7.5
3	1.137	1.068	0.069	0.95
6	1.017	0.9773	0.04	0.8
7	1.130	1.003	0.127	3.4
8	0.9534	0.9567	-0.003	(-) 2.0
9	1.115	0.9894	0.126	6.0

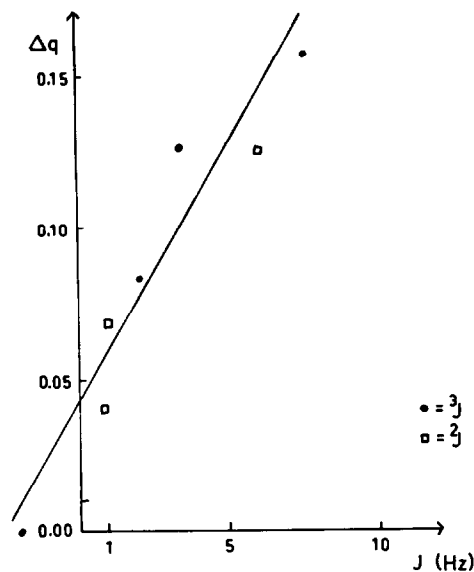


Fig. 1. Plot of the charge density differences in 5a-5b vs the ^{13}C spin-spin coupling constants in 3b.

CONCLUSIONS

We are now able to correlate geminal and vicinal $^{13}\text{C}^{13}\text{C}$ spin coupling constants in naphthalene, phenanthrene and azulene derivatives with the same model, a simple application of π MO theory. This is of course no scientific proof that the mechanism of the transmission of spin coupling constants is really dominated by π electrons, but as a working hypothesis of predictable value it may be sufficient. We believe therefore that $^{13}\text{C}^{13}\text{C}$ spin coupling constants, when we are ever able to measure all of them within an aromatic ring system perhaps on a natural abundance level using 2D nmr spectroscopy,¹⁸ would give a very detailed experimental description of the π electron system.

EXPERIMENTAL

The ^{13}C spectra were obtained on a Varian XL-100-15 spectrometer equipped with a 16 K 620 L computer and a Varian disc

system. Thus, 32 K FT spectra were obtained with a digital resolution of less than 0.2 Hz/point. Where no coupling constants are given, the values are lower than 0.4 Hz. Spectra were taken in dilute solns of CDCl_3 , the coupling constants in Table 1 are the average out of three measurements.

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