

The Methyl-methyl Long Range Spin Coupling in Aromatic Compounds

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Our recent work on dimethylsubstituted aromatic compounds^{1,2} has made it desirable to determine the magnitude of methyl-methyl (interbenzylic) spin coupling constants for different substitution patterns.

In the preceding paper,¹ the constitution of a naturally occurring methoxydimethylbenzofuran was determined partly by means of a detailed examination of long range coupling constants. The magnitude of the methyl-methyl coupling (0.5 Hz) excludes a *meta* relationship, as this coupling has invariably been reported to be less than 0.35 Hz,^{3,4} but is intermediate between the values of the *ortho* and *para* couplings in substituted xylenes:⁴ 4,6-dibromo-2,3-dimethylaniline (+0.40 Hz) and 4,6-dibromo-2,5-dimethylaniline (+0.62 Hz). However, in the case of the natural product, an *ortho* relationship could be deduced from other evidence.

Both smaller (2-carbomethoxy-5,6-dimethylbenzofuran:⁵ 0.37 Hz) and larger (2,3-dimethylbenzothiophene:⁶ 0.7 Hz; 2,3-dimethylthiophenes and 2,3-dimethylfuran:⁷ 0.55–0.8 Hz) values are known for the *ortho* interbenzylic coupling. In the case of the *para* coupling, two further examples can be quoted:⁸ 7,12-dimethylbenz[*a*]anthracene (0.55 Hz) and *p*-methylbenzylbromide (0.4 Hz).

Theoretical calculations for the xylenes indicate that the π -electron contributions to all the interbenzylic couplings are of the same magnitude, *i.e.* 0.6–0.7 Hz.⁹ However, a smaller value (–0.32 Hz) has also been calculated for the *meta* coupling.³ In order to clarify the structural problem and to permit comparisons with the theoretical values, we have determined the interbenzylic coupling constants of the isomeric xylenes and, in addition, some dimethylphenols and one dimethylaniline.

The interbenzylic coupling constants were determined from (assumed) first order splittings of the methyl signals, when these

were totally or partially decoupled from the aromatic protons. In the case of the xylenes, the ¹³C-satellites¹⁰ of the equivalent methyl signals were examined.

Irradiation exactly at the sharp signal due to the aromatic protons of neat *p*-xylene caused saturation of the spectrometer receiver. Dilution of the sample with carbon tetrachloride removed this effect.

In *m*-xylene, the ¹³C-satellites were single but slightly broadened peaks. This might be due to imperfect decoupling of the aromatic protons or to the existence of a finite methyl-methyl coupling of less than 0.3 Hz. The first possibility seems less probable as irradiation with different frequencies and amplitudes failed to produce a sharper line.

As seen from Table 1, the value of the *para* interbenzylic coupling is only slightly smaller than calculated. The magnitude of the observed *meta* coupling is consistent only with the smallest of the calculated values.³ The signs of these couplings were not determined, but are here assumed to be the same as those reported for the substituted xylenes.⁴

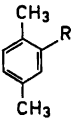
The substituent effects appear to be small, but a meaningful discussion must await a larger number of examples. However, the *ortho* interbenzylic coupling appears to be very dependent on the bond order. The values for 2,3-dimethylthiophene (0.7 Hz) illustrate this point. Also, the *ortho* interbenzylic coupling in 5-methoxy-6,7-dimethylbenzofuran¹ (0.5 Hz) is larger than that found between the 5 and 6 methyl groups in 2-carbomethoxy-5,6-dimethylbenzofuran.⁵ This is in agreement with the prediction that the π -bond order between C₆ and C₇ should be larger than that between C₅ and C₆.⁵

The determination of the magnitude of an interbenzylic coupling can be of great help in elucidating the substitution patterns of aromatic compounds. Although, as in the case of benzylic coupling,¹¹ it is not always possible to distinguish unequivocally between an *ortho* and a *para* relationship of the substituents, the interbenzylic couplings can provide decisive evidence when taken together with other information, *e.g.* results obtained by nuclear Overhauser effects (NOE).¹²

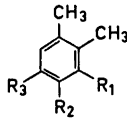
Experimental. The PMR spectra were recorded at 31° on a Varian HA-100D spectrometer, operated at 100 MHz in the frequency sweep mode. The audio frequencies were measured with a Hewlett-Packard 5512 A

Table 1.

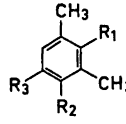
Compound	R ₁	R ₂	R ₃	$J_{\text{CH}_3-\text{CH}_3}$ (calc)	$ J_{\text{CH}_3-\text{CH}_3} $ (exptl.)
I	H			0.63 ⁹	0.55
II	OH				0.6
III	NH ₂				0.6
IV	H	H	H	0.74 ⁹	0.4
V	OH	H	H		0.4
VI	H	O=C-CH ₃	OH		0.4
VII	H	H	H	-0.60 ⁹	<0.3
VIII	H	O=C-CH ₃	OH	-0.32 ³	<0.3



I-III



IV-VI



VII, VIII

frequency counter. In the double resonance experiments, the modulation frequency was produced by a Muirhead D-890-B decade oscillator. Immediately before use the sample solutions (carbon tetrachloride or deuteriochloroform with ca. 3 % TMS added), were de-aerated with argon for 5 min.

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- Aasen, A. J., Kimland, B., Almqvist, S.-O. and Enzell, C. R. *Acta Chem. Scand.* **25** (1971) 3182.
- Almqvist, S.-O. and Olsson, K. *Nordiska Kemistmötet*, Umeå 1971.
- Acrivos, J. V. *Mol. Phys.* **5** (1962) 1.
- MacDonald, C. J. and Reynolds, W. F. *Can. J. Chem.* **48** (1970) 1002.
- Cohen, A. D. and McLauchlan, K. A. *Mol. Phys.* **9** (1965) 49.
- Takahashi, K., Kanda, T. and Matsuki, Y. *Bull. Chem. Soc. Japan* **38** (1965) 1799.
- Gronowitz, S., Gestblom, B. and Hoffman, R. A. *Acta Chem. Scand.* **15** (1961) 1201; Rodmar, S., Rodmar, B., Ali Khan, A., Gronowitz, S. and Pavulans, V. *Acta Chem. Scand.* **20** (1966) 2515.
- Bartle, K. D., Jones, D. W. and Matthews, R. S. *Rev. Pure Appl. Chem.* **19** (1969) 191.
- Barfield, M. and Chakrabarti, B. *J. Am. Chem. Soc.* **91** (1969) 4346.
- Jackman, L. M. and Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, London, New York 1969, p. 140.
- Barfield, M. and Chakrabarti, B. *Chem. Rev.* **69** (1969) 757.
- Hart, P. A. and Davis, J. P. *J. Am. Chem. Soc.* **91** (1969) 512.

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