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Inter-ring Long-range Spin–Spin Proton Coupling in some 8-Hydroxyquinoline Derivatives

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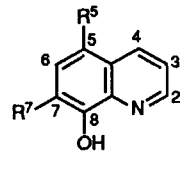
A study of the ^{1}H NMR spectra of a series of 8-hydroxyquinolines has been carried out using the 2D-COSYLR method and inter-ring proton spin–spin coupling constants ^4J, ^5J, ^6J and ^7J have been detected; it has been established that the π-mechanism for transmission of spin–spin coupling predominates and in the case of the planar zig-zag arrangement this results in unexpected annulment of $^6J_{2,7}$ and $^6J_{3,6}$.

Several ^{1}H NMR studies of 8-hydroxyquinolines have been reported.[1–5] In these studies proton chemical shifts and spin–spin coupling constants have been analysed with a first-order approximation, but long-range spin–spin coupling constants of aromatic protons for these substances have never been investigated. In naphthalenes, however, long-range inter-ring proton coupling constants were detected and their correlation with structure was discussed.[6] This prompted us to perform a more precise ^{1}H NMR study of 8-hydroxyquinoline **1** and some of its derivatives **2–4** in order to investigate long-range proton spin–spin coupling.†

† The ^{1}H NMR spectra of 10–20 mg cm^{-3} solutions of **1–4** in [$^2H_6$] acetone were recorded on a Bruker AC-200 NMR spectrometer operating at 200.13 MHz, in 5 mm tubes, with TMS as internal standard, at room temperature. For ^{1}H NMR high resolution spectra the conditions were 45° pulse, 2 s repetition time and digital resolution 0.02 Hz pt^{-1}. To obtain 2D ^{1}H–^{1}H spectra a standard Bruker program COSYLR was used, digital resolution 2.74 Hz pt^{-1}. The calculations of the values of chemical shifts and coupling constants were carried out using the iterative PANIC program (version 850501) on a Bruker ASPECT 3000 computer.

Table 1 Chemical shifts for the aromatic protons of substances **1–4**, δ (ppm)

Compound	H-2	H-3	H-4	H-5	H-6	H-7
1	8.82	7.51	8.28	7.39	7.47	7.17
2	8.88	7.71	8.48	—	7.77	7.09
3	8.92	7.77	8.51	—	7.99	—
4	8.92	7.77	8.58	—	7.73	—



1 $R^5 = R^7 = H$
2 $R^5 = Br$; $R^7 = H$
3 $R^5 = R^7 = Br$
4 $R^5 = R^7 = Cl$

Table 2 Spin–spin proton coupling constants of the aromatic protons of substances 1–4 (Hz)[a]

Compound	$^3J_{23}$	$^3J_{34}$	$^3J_{56}$	$^3J_{67}$	$^4J_{24}$	$^4J_{45}$	$^4J_{57}$	$^5J_{35}$	$^5J_{46}$	$^6J_{47}$	$^7J_{26}$	$^7J_{37}$
1	4.22	8.35	8.28	7.63	1.61	0.28	1.25	0.28	0.16	0.15	0.17	0.27
2	4.22	8.59	—	8.28	1.54	—	—	—	0.16	0.14	0.29	0.29
3	4.26	8.56	—	—	1.48	—	—	—	0.15	—	0.22	—
4	4.25	8.59	—	—	1.53	—	—	—	0.19	—	0.25	—

[a] R.m.s. error estimates are < 0.03.

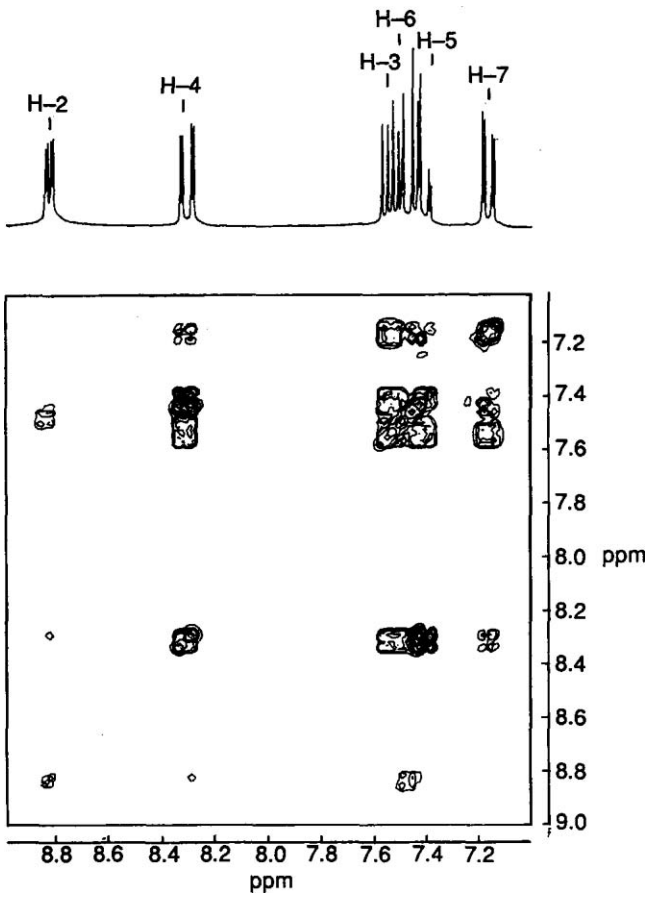


Fig.1 The transformed COSYLR spectrum of **1** with optimization for 0.17 Hz

In respect of inter-ring coupling, **1** and **2** in our conditions became intractable to homonuclear decoupling techniques because of the close proximity and overlapping of the proton resonances of H–3, H–5 and H–6 in the case of **1** and H–3 and H–6 in **2**. Thus, for this purpose, we have used a two-dimensional long-range COSY method COSYLR,[7] with optimization for 0.15–0.30 Hz, because this method of data processing allows a more straightforward identification of long-range constants. We also used Gaussian multiplication for line narrowing and resolution enhancement in one-dimensional spectra and then an iterative PANIC program calculation for the corresponding four-, five- and six-spin systems. The spectral data obtained are given in Tables 1 and 2.

The transformed 2D-COSYLR spectrum of **1** optimized for 0.17 Hz is shown in Fig. 1. We note that H–2 has an off-diagonal response correlating it with H–6. For **1** and **2** a similar coupling pathway is also pertinent for observed interactions between H–3 and H–7 (see Table 2). Importantly, coupling constants $^7J_{2,6}$ have been detected for all the substances **1–4**. In Fig. 1 we also note that H–4 exhibits a long-range coupling to H–7. However a cross-peak correlating H–2 and H–5 has not been detected. Comparatively small deviations in the magnitudes of ^5J, ^6J and ^7J (see Table 2) show that the π-mechanism of transmission of spin–spin coupling predominates over the σ-mechanism. Unfortunately, the signs of the coupling constants were not measured in this study.

It is significant that we did not observe $^6J_{3,6}$ in **1–4** and $^6J_{2,7}$ in **1** and **2**, in spite of the fact that this was expected because of the planar extended zig-zag arrangement. This is contrary to naphthalene,[6] where the magnitude of this constant of 0.2–0.3 Hz was reported. It was shown that an alternation of sign for the π-contribution to the long-range coupling constant is expected for aromatic systems.[8] That allows us to assume that in this case σ- and π-contributions are of opposite signs and their sum results in annulment of the total coupling constant.

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