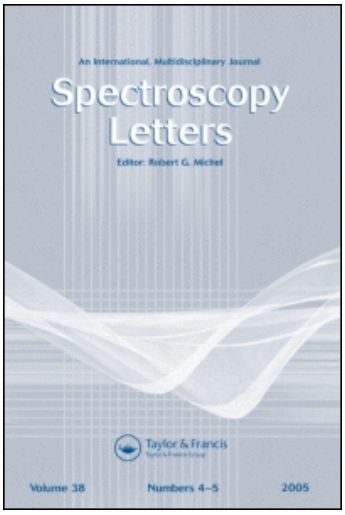

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^{13}C - ^{1}H Coupling Constants. Observation of $^{4}J_{48}$ Long Range Inter - Ring "Zig - Zag" Coupling in the Quinoline System

Alan G. Osborne[a]; Ian R. Herbert[b]
[a] Department of Chemistry and Biological Chemistry, University of Essex, COLCHESTER, Essex, U.K [b] Courtaulds Research PLC, West Midlands, U.K.

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^{13}C - ^{1}H COUPLING CONSTANTS. OBSERVATION OF $^{4}J_{48}$ LONG RANGE INTER - RING "ZIG - ZAG" COUPLING IN THE QUINOLINE SYSTEM

Key Words : long range J_{CH} coupling constants, chloroquinoline, bromoquinoline, NMR

Alan G. Osborne*

Department of Chemistry and Biological Chemistry,
University of Essex,
Wivenhoe Park,
COLCHESTER,
Essex, CO4 3SQ
U.K.

Ian R. Herbert

Courtaulds Research PLC,
Lockhurst Lane,
COVENTRY,
West Midlands, CV6 5RS
U.K.

Abstract Long range inter - ring "zig - zag" coupling between C-4 and H-8 (J_{48} -1.5 to -1.8 Hz) has been observed in some 2,4- and 2,3,4- haloquinolines at 75 MHz. The coupling is influenced by the 4-halo substituent.

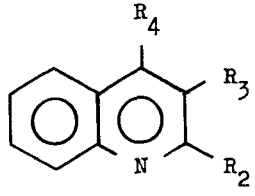
INTRODUCTION

Inter - ring coupling between the H-4 and H-8 quinoline protons through a "zig - zag" pathway was first observed by Anet[1] in 1960. Subsequently this type of coupling has been observed in many systems.[2]

Studies of long range $^{13}C - {}^{1}H$ coupling constants in aromatic systems have already attracted considerable interest.[3,4] In their extensive study of methylquinolines at 20 MHz Johns and Willing[5] noted that " a $^{4}J_{CCCH}$ coupling between C-4 and H-8 or between H-8 and C-4 is not observed in any of the spectra, hence this coupling is assumed to be less than 1 Hz. " In previous studies from these laboratories, performed at 15 MHz,[6] no discernible $^{4}J_{CH}$ coupling between the 4 and 8 positions was detected, and as far as we are aware[3,4] has not been observed in other bicyclic aromatic systems.

RESULTS & DISCUSSION

Recently we have had an opportunity to observe the proton coupled ^{13}C NMR spectra of 3-bromo-2,4-dichloroquinoline (1) at 75 MHz.



	R_2	R_3	R_4
(1)	Cl	Br	Cl
(2)	Cl	Cl	Cl
(3)	Cl	H	Cl
(4)	Br	H	Br

The pertinent results are shown in Table 1, the remainder of the spectral parameters will be reported at a later date.[7] It was immediately evident from the spectra that the C-4 signal was not the anticipated simple doublet (J_{45} = 5.4 Hz) but instead appeared as a doublet of doublets with an additional fine splitting of 1.5 Hz clearly resolved (see Figure 1). That the fine splitting was to H-8 was indicated by a 2D COLOC spectrum[8] which included a connectivity to

Table 1

Long range ^{13}C - ^{1}H coupling constants

at C-4 in some haloquinolines

Compound	Multiplicity of C-4	Coupling constants (Hz) $^{3}J_{45}$	$^{4}J_{48}$ (a)	$^{2}J_{43}$ (b)
(1)	dd	5.4	(-) 1.5	-
(2)	dd	5.5	(-) 1.6	-
(3)	ddd	5.4	(-) 1.6	(-) 4.4
(4)	ddd	5.9	(-) 1.8	(-) 4.2

(a) - negative sign allocated after reference 11

(b) - negative sign allocated after reference 9

the other low field component of the ^{1}H ABCD system, viz H-8. This was then confirmed by a series of low power specific proton decoupling experiments (see Figure 1). Careful irradiation of H-5 at 8.102 δ left a narrow doublet, whilst irradiation of H-6 (7.610 δ) and of H-7 (7.746 δ) caused no effect. When H-8 (7.945 δ) was specifically decoupled a clear doublet (J_{45}) remained. That these specific decoupling experiments were effective, and the ^{1}H assignments were correct,[7] was confirmed by the associated collapses of the appropriate meta $^{3}J_{CH}$ couplings. Thus when C-4 collapsed to a narrow doublet the meta-coupling at C-7 was also selectively removed. Moreover, when C-4 appeared as a clear doublet, only the meta-coupling at C-6 was eliminated, whilst J_{57}, J_{75} and J_{86} remained unaltered.

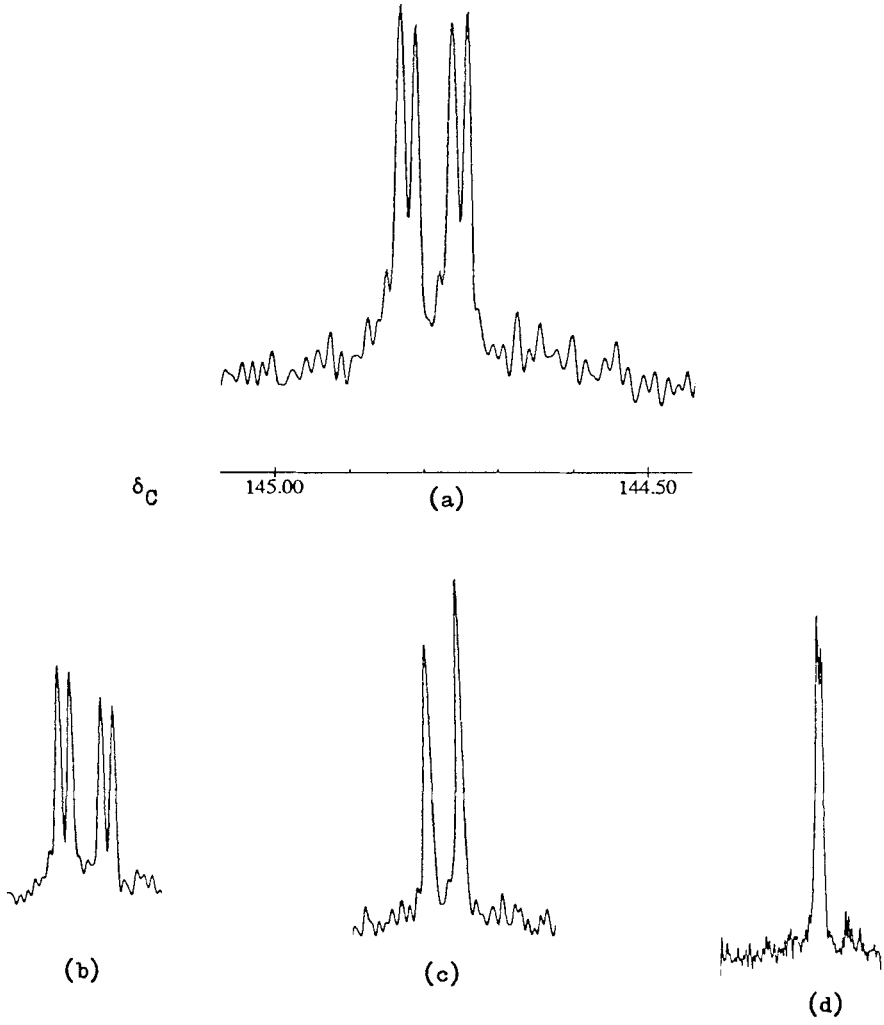


Figure 1

^{13}C proton coupled spectra of C-4 in 3-bromo-2,4-dichloroquinoline

(a) - normal "Gated-1" spectrum

specific proton decoupling experiments :

(b) - at H-6 (similar at H-7)

(c) - at H-8

(d) - at H-5

A similar study was then performed with (2), when C-4 was again a doublet of doublets (see Table 1). With the 2,4-dihaloquinolines (3) and (4), the C-4 signal appeared as a doublet of doublets of doublets, showing an additional splitting to H-3. Although such a large $^{2}J_{43}$ coupling has not been detected in quinoline or the methylquinolines,[5] it has been observed in the halopyridine series, affected by an electronegative substituent effect by the halogen. Thus Denisov *et al.*[9] have reported J_{43} = 0.74 Hz in pyridine, but J_{43} = -3.51 Hz in 4-chloropyridine. In accordance with this work[9] it must be assumed that J_{43} in the 2,4-dihaloquinolines should similarly be allocated a negative sign.

It is interesting to note that $^{4}J_{H-4,H-8}$ is very weak (0.8 Hz)[1] whilst $^{4}J_{C-4,H-8}$ is *ca.* 1.6 Hz. Generally it has been found that[3,4] for aromatic *meta*-couplings $^{3}J_{C-H} \sim {}^{3}J_{H-H} \times 0.6$, which might suggest that $^{4}J_{CCCH}$ should be *ca.* 0.48 Hz as originally intimated by Johns and Willing.[5] The larger splittings observed in the present work must therefore similarly be affected by an electronegative substituent effect from the 4-halo substituent. In this respect it should be noted that Tarpley and Goldstein[10] have reported $^{4}J_{14}$ = -1.20 Hz for benzene, but $^{4}J_{14}$ = -2.02 Hz for chlorobenzene. Moreover, Denisov *et al.*[11] have observed $^{4}J_{25}$ = -0.87 Hz in pyridine and $^{4}J_{25}$ = -1.7 Hz in 2-bromopyridine. These observed values of $^{4}J_{CH}$ from *ipso*-halogeno substituted carbons[9-11] are very consistent with the values of $^{4}J_{48}$ found for the quinoline ring system, which should therefore likewise be allocated a negative sign.

Of the two possible ^{4}J couplings which could operate through the favourable "zig - zag" W-pathway, *viz* J_{48} and J_{46}, only the former

has been detected in the present work. This is presumably due to another subtle halogeno substituent effect which may be additionally influenced by the heterocyclic nitrogen.

The technological advances made in the field of NMR instrumentation have facilitated the detection of long range ^{13}C - ^{1}H coupling interactions. Many of the earlier studies performed at lower fields appear to be in need of re-examination to reveal further splittings that could not be originally resolved. We hope to re-examine the proton coupled ^{13}C NMR spectra of quinoline and some methylquinolines at higher field in an attempt to detect any $^{4}J_{48}$ and $^{4}J_{84}$ couplings in these compounds.

EXPERIMENTAL

3-Bromo-2,4-dichloroquinoline (1) (m.p. 94-5°, lit.[12] m.p. 95°) was synthesised by the procedure of Hardman and Partridge.[12]

^{1}H NMR (360 MHz, $CDCl_3$, δ p.p.m. from TMS, coupling constant (Hz)) : 7.610 (1H, ddd, J_{56} 8.5, J_{67} 7.0, J_{68} 1.3, H-6); 7.746 (1H, ddd, J_{78} 8.4, J_{67} 7.0, J_{57} 1.4, H-7); 7.945 (1H, ddd, J_{78} 8.4, J_{68} 1.3, J_{58} 0.6, H-8); 8.102 (1H, ddd, J_{56} 8.5, J_{57} 1.4, J_{58} 0.6, H-5).

Syntheses and spectral data for compounds (2) - (4) will be reported at a later date.[7]

Proton coupled ^{13}C NMR spectra were recorded, for solutions in $CDCl_3$, containing TMS as an internal standard, on a Bruker AC300 spectrometer operating at 75.47 MHz. The "Gated-1" pulse sequence was used, decoupler power (noise) ca. 1.5 watts (setting 20H), pulse width 4.5 μsec. (pulse angle 30°), spectral width 3600 Hz, with 16K data

points, zero-filled to 32K providing 0.22 Hz digital resolution, with no line broadening. For the specific proton decoupling experiments, the decoupler power (CW) was reduced to ca. 0.2 milliwatts (setting 35L).

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