

LONG-RANGE PROTON COUPLING IN REISSERT COMPOUNDS

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Long-range coupling between protons separated by four or more bonds has recently been observed for a number of compounds¹ and it appears that a near planar zig-zag arrangement of the atoms concerned is required.^{2,3} We report here observation of coupling between the C-1 and C-3 protons in isoquinoline Reissert compounds, and offer some deductions regarding the stereochemistry of these compounds. The Reissert compounds (I) were prepared from the parent isoquinoline by the method of Popp and Blount.^{4,5} The N.M.R. information obtained is summarised in the table.

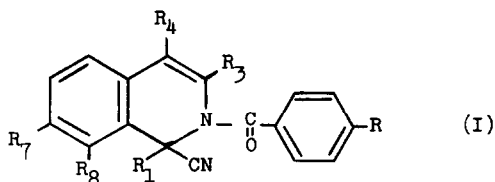


TABLE: N.M.R. Spectral data**

	R ₁	R ₂	R ₄	R ₇	R ₈	R	C-1 Proton	C-3 Proton	J _{1,3} , c./sec.
Ia	H	H	H	H	H	H	3.42τ Doublet	3.36τ Quartet	0.8
Ib	D	H	H	H	H	H	-	3.36τ Doublet	-
Ic	H	H	Br	H	H	H	3.44τ Doublet	3.00τ Doublet	0.9
Ic**	H	H	Br	H	H	H	3.44τ Singlet	Saturated	-
Id	H	H	H	OMe	OMe	H	3.06τ Doublet	3.39τ Quartet	0.9
Ie	H	Me	H	H	H	H	3.50τ Singlet	-	-
If	H	Me	H	H	H	Me	3.50τ Singlet	-	-
Ig	H	H	H	H	H	Me	3.46τ Doublet	3.33τ Quartet	0.8
Ih	H	H	H	H	OCOPh	Me	3.33τ Doublet	3.27τ Quartet	0.8

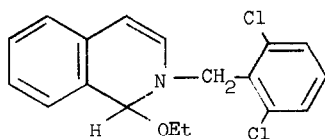
** Recorded with CDCl₃ as solvent at 60 Mc./sec, except for Id at 40 Mc./sec.

** C-1 Proton spin-decoupled by saturation at 3.00 τ .

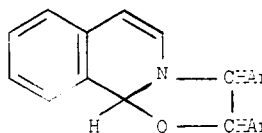
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In each case the coupling between the C-1 and C-3 protons was slightly less than 1 c.p.s. On exchange of the C-1 proton for deuterium, which was effected by addition of deuterium oxide to the Reissert compound carbanion⁶ followed by neutralisation with carbon dioxide,⁷ the deuterio compound (Ib) showed only a doublet for the C-3 proton in place of the quartet in (Ia). A spin-decoupling experiment provided further evidence of long-range coupling in that the C-1 proton doublet of (Ic) collapsed to a singlet on saturation of the C-3 proton signal. Furthermore, in (Ie) and (If) where the 3-position was substituted the C-1 hydrogen absorption was unsplit.

The value of the coupling constant suggests the five atoms involved are adopting a conformation near planar but not completely so.³ This requires that the hydrogen atom at C-1 adopts a quasi-equatorial conformation and the nitrile substituent a quasi-axial one. This conformation, with a quasi-equatorial C-1 hydrogen, is similar to that suggested for another 1,2-dihydroisoquinoline, viz. 1,2-dihydro-N-methylpapaverine⁸ and it would also appear to be the case for (II).⁹



(II)



(III)

It is interesting to note, however, that the C-1 hydrogen must be adopting the quasi-axial position when carbon atom-1 is part of the five-membered ring in (III) since here its signal is reported⁹ to be unsplit.

In furtherance of these conformational studies we are currently carrying out some variable temperature N.M.R. measurements on appropriate compounds.

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