Determination of the Sign of Electron-Nuclear ^{13}C Hyperfine Coupling Constants by CIDNP Techniques

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Summary The combined analyses of ^{13}C and ^{1}H CIDNP spectra can yield absolute signs of ^{13}C hyperfine coupling constants in radical intermediates.

THE radical-pair theory of CIDNP is now well established.[1] In principle the parity rules formulated by Kaptein[2] for net polarisation [equation (1)] should provide a useful method

TABLE 1

CIDNP effects in products (II) and (III).

	Product				
	(II)			(III)	
Nucleus	^{1}H[a]	^{13}C[b]	^{13}C[b]	^{1}H[a]	^{13}C[b]
Shift[c]	3·30	175·8	166·6	2·97	168·3
Assignment[d] ..	$-\mathrm{CO}-\overset{-\mathrm{S}}{\overset{\mid}{\mathrm{N}}}-\mathrm{C}H_3$	$-\overset{\mid}{\mathrm{N}}-\overset{\mathrm{Ar}}{\overset{\mid}{C}}=\mathrm{O}$	$\mathrm{R_2N}-\overset{-\mathrm{S}}{\overset{\mid}{C}}=\mathrm{O}$	$-\mathrm{CO}-\overset{\mathrm{H}}{\overset{\mid}{\mathrm{N}}}-\mathrm{C}H_3$	$-\overset{\mid}{\mathrm{N}}-\overset{\mathrm{Ar}}{\overset{\mid}{C}}=\mathrm{O}$
Polarisation ..	A	E	A	E	A

[a] Ref. 3. [b] This work. [c] p.p.m. downfield from $\mathrm{Me_4Si}$. [d] By comparison with authentic material.

for sign-determination of isotropic electron–nuclear hyperfine coupling constants in unstable radical intermediates. This should be particularly valuable in the case of less abundant nuclei such as ^{13}C, where sensitivity problems make conventional methods very unattractive.

$$\Gamma_{\mathrm{ne}} = \mu\cdot\epsilon\cdot\Delta g\cdot a \tag{1}$$

The requirements are (a) a good understanding of the mechanism of the reaction leading to polarised products† and (b) a knowledge of the relative magnitudes of the *g*-values of the components of radical-pair intermediates. The latter data are often readily available from e.s.r. studies but the difficulty attending the unambiguous establishment of reaction mechanism is an obvious hindrance. However, we point out that *both* these requirements can be waived when CIDNP effects in the n.m.r. spectra of two or more nuclei in at least one of the products of a given radical can be observed, provided that: (a) only relative signs of hyperfine coupling constant values for the nuclei concerned are required or, (b) where absolute signs are required, that the sign of the hyperfine coupling constant for one of the nuclei is known.

TABLE 2

Signs of hyperfine splitting in radicals (IV) and (V)

	(IV)		(V)
Nucleus (x)	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\dot{\mathrm{N}}-\mathrm{C}H_3$	$-\overset{\mathrm{O}}{\overset{\|}{C}}-\dot{\mathrm{N}}-\mathrm{CH_3}$	$\dot{\mathrm{S}}-\overset{\mathrm{O}}{\overset{\|}{C}}-\mathrm{N(CH_3)_2}$
Sign of a_{x}	+[a]	—[a]	—[b]

[a] Determined from polarisation in both (II) and (III). [b] Determined from polarisation in (III) only.

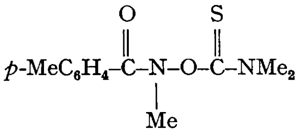
Then from a consideration of equation (1), for any one radical carrying two nuclei i and j, (hyperfine coupling constants a_{i} and a_{j}), $\Gamma_{\mathrm{ne}}{}^{\mathrm{i}}$ and $\Gamma_{\mathrm{ne}}{}^{\mathrm{j}}$ in any one reaction product are related by the sign equation (2). Conversely,

$$\Gamma_{\mathrm{ne}}{}^{\mathrm{i}}\cdot\Gamma_{\mathrm{ne}}{}^{\mathrm{j}} = a_{\mathrm{i}}\cdot a_{\mathrm{j}} \tag{2}$$

for nuclei i and j sited on separate components of the pair, equation (3) applies.

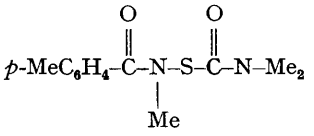
$$\Gamma_{\mathrm{ne}}{}^{\mathrm{i}}\cdot\Gamma_{\mathrm{ne}}{}^{\mathrm{j}} = -a_{\mathrm{i}}\cdot a_{\mathrm{j}} \tag{3}$$

We now report one such study where the sign of one (^{1}H) hyperfine coupling constant involved can be assigned with considerable confidence, thus allowing the determination of the absolute sign of ^{13}C hyperfine coupling constants. The thermolysis of (I) in $\mathrm{CDCl_3}$ at 110° results in the formation of (II) and (III) in good yield, with strong polarisation of certain lines in the ^{1}H n.m.r. spectra[3] and in the ^{13}C n.m.r. spectra of products (II) and (III) (Table 1), resulting from geminate recombination and separation respectively, of the components of the radical pair (IV + V).



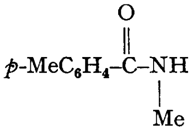
$$p\text{-MeC}_6\text{H}_4\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Me}}{\underset{|}{\mathrm{N}}}\text{-O-}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\text{-NMe}_2$$

(I)



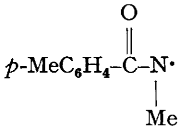
$$p\text{-MeC}_6\text{H}_4\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Me}}{\underset{|}{\mathrm{N}}}\text{-S-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-N-Me}_2$$

(II)



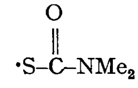
$$p\text{-MeC}_6\text{H}_4\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Me}}{\underset{|}{\mathrm{NH}}}$$

(III)



$$p\text{-MeC}_6\text{H}_4\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Me}}{\underset{|}{\mathrm{N}}}\cdot$$

(IV)



$$\cdot\mathrm{S}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-NMe}_2$$

(V)

Use of equations (2) and (3) in conjunction with the data in Table 1 now gives the absolute signs of the carbonyl group ^{13}C hyperfine coupling constants in the acylamino radical (IV) and the thiocarbamoyl radical (V) when $a_{\mathrm{H}}(\cdot\mathrm{N{-}CH_3})$ is taken to be positive‡ (Table 2).

These preliminary results indicate the potential usefulness of CIDNP in the determination of the sign of hyperfine coupling constants in unstable radicals such as (IV) and (V).

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† The difficult problem of assessing to what extent radical processes contribute to the conversion of reactant into product does not arise here, since we are interested solely in the radical component.

‡ In particular, the experimental results and calculations of Danen *et al.* (W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, 1972, **94**, 6853; W. C. Danen and T. T. Kensler, *ibid.*, 1970, **92**, 5235) on acylamino and dialkylamino radicals leave no doubt as to the validity of this.

[1] For a recent review see 'Chemically Induced Magnetic Polarisation,' eds. A. R. Lepley and G. L. Closs, Wiley-Interscience, New York, 1973.
[2] R. Kaptein, *Chem. Comm.*, 1971, 732.
[3] W. B. Ankers, C. Brown, R. F. Hudson, and A. J. Lawson, *J.C.S. Chem. Comm.*, 1972, 935.