

Journal of The Chemical Society, Chemical Communications

NUMBER 9/1974

8 MAY

Protonation of Some 3-Arylsydnes: a Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Study

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Summary Evidence for a proposed structure for the conjugate acid of sydnes has been obtained from n.m.r. spectra of 3-phenyl- and 3,4-diphenyl-sydne in strong acid media.

THE first step in the acid-catalysed hydrolysis of sydnes (I) involves the formation of the conjugate acid (II) (Scheme).¹

The nature of the products requires eventual protonation on N-2, but apart from this consideration, the only evidence for N-protonation is the observation² of a low-intensity band assigned to an N-H stretching mode in the i.r. spectrum of 3-methylsydne (Ic) in acidic media. Protonation at the carbonyl oxygen atom of 3-phenylsydne (Ia) has been observed in FSO₃H-SbF₅.³ Molecular orbital calculations suggest that protonation is most likely to occur at either N-2 or the carbonyl oxygen.^{2,4}

The ¹³C chemical shifts of 3-phenylsydne (Ia) and the ¹⁵N chemical shifts of 3,4-diphenylsydne (Ib) have been measured in neutral media, aqueous sulphuric acid, and trifluoroacetic acid in an attempt to shed light on the electronic structure and the site of protonation of (II). It is known⁵ that (Ib) is substantially protonated in the media concerned, but (Ia) may be only partially protonated; it is assumed that the degree of protonation will affect the magnitude and not the direction of the chemical shift.⁶

The ¹³C data (Table 1) show a downfield shift in the sydne C-4 resonance (as well as small shifts for the carbonyl and phenyl carbon resonances) when the solvent is changed from CDCl₃ to aqueous acids. Although part of this shift must arise from solvent effects other than ionisation, it is likely that the major part of the shift in the sydne C-4 resonance results from partial protonation of the sydne. This suggests that C-4 carries a significant

TABLE I

¹³C Chemical shifts of 3-phenylsydne^a (Ia) in neutral and acidic media^b

	δ^c (p.p.m.)	CDCl ₃ ^d	60% H ₂ SO ₄ -D ₂ O	D ₂ SO ₄	$\Delta\delta^e$ (p.p.m.)
Phenyl carbons	C(4)	93.0	102.5	104	+11
	2,6	121.3	123.1	124	+2.5
	3,5	130.3	132.1	132	+2.0
	4	132.5	133.9	134	+1.5
	1	134.5 ^f	136.2	137	+2.5
	C=O	169.0	173	174	+5

^a Cf. (Ic) δ 39.9 (Me), 97.6 (C-4), and 170.1 (C=O) p.p.m. (neat liquid relative to external Me₄Si). ^b Measured on a Varian XL100 FT spectrometer operating at 25.2 MHz; ²H lock. ^c ± 0.5 p.p.m., relative to external Me₄Si (capillary). ^d Low solubility prevented measurement of chemical shifts in dil. H₂SO₄. ^e $\Delta\delta = \delta$ (D₂SO₄) - δ (CDCl₃). ^f Low peak height.

increase in positive charge on protonation, although it is unlikely that all the charge is located on this site. Support for structure (II) comes from the ^1H n.m.r. spectrum of (Ia); the chemical shift of the sydnone ring proton is dependent upon acid concentration, it is experiencing a downfield shift in strong acid.^{3,5}

TABLE 2

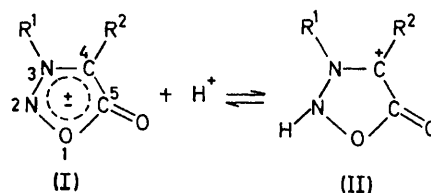
^{15}N Chemical shifts of 3,4-diphenyl[2- ^{15}N]sydnone (Ib) in neutral and acidic media^a

δ^d (p.p.m.)	$(\text{CD}_3)_2\text{CO}^b$	20% H_2SO_4 - $(\text{CD}_3)_2\text{CO}^b$	$\text{CF}_3\text{CO}_2\text{H}$	60% H_2SO_4 - D_2O^c
		37.8	26.1	23.2

^a Measured on a Bruker HFX13 FT spectrometer operating at 9.12 MHz; ^2H lock. (Ib) 96% ^{15}N enriched at N(2) was prepared from $\text{Na}^{15}\text{NO}_2$ and the appropriate glycine by a standard method (cf. ref. 1). ^b With added $\text{Cr}(\text{acac})_3$ (0.03M). ^c Low solubility prevented measurement of chemical shifts in dil. H_2SO_4 . ^d Upfield from external $^{15}\text{NO}_3^-$ in NH_4NO_3 .

The ^{15}N data show similar downfield shifts in the N-2 resonance in (Ib) on changing the solvent from $(\text{CD}_3)_2\text{CO}$ to aqueous acid (Table 2). These shifts are accompanied by increases in sensitivity. A possible explanation for this is reduction of an otherwise large T_1 value for the N-2 nucleus, upon protonation. However, T_1 for this nucleus may be short owing to nuclear quadrupole relaxation; protonation could then reduce the electric field gradients and T_1 could increase. Similar shifts have been observed for the protonation of alkylamines,⁷ though generally N-protonation

can cause (large or small) upfield or downfield shift in nitrogen resonances.⁸



a; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$
 b; $\text{R}^1 = \text{R}^2 = \text{Ph}$
 c; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$

SCHEME

The present n.m.r. data do not provide unequivocal evidence for protonation at nitrogen although this may be inferred from the absence of large downfield shifts in $\delta(\text{C}=\text{O})$ and upfield shifts in the resonance of carbons α to the carbonyl function which have been observed in the protonation of the carbonyl oxygen in ketones.⁶

Available evidence suggests that, site of protonation aside, the structure (II) is an important contributor to the actual electronic structure of the conjugate acid of sydnones.

Thanks are due to Drs. M. Kinns (Imperial College) and L. F. Farnell (Queen Mary College) for running the spectra. A grant from the Chemical Society Research Fund for part of the work is acknowledged.

(Received, 22nd February 1974; Com. 228.)

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