

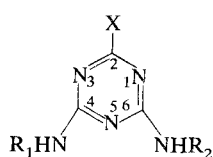
Carbon-13 N.m.r. Studies of Substituted Bisalkylamino-s-Triazines in Acidic Media

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The carbon-13 n.m.r. spectra of six substituted bisalkylamino-s-triazines are reported. The site of protonation of 2-methoxy-s-triazines is shown to be at N-1 or N-3. The effect of trifluoroacetic acid on 2-chloro-s-triazines is also discussed.

Substituted bisalkylamino-s-triazines, **1**, are widely used as herbicides. The proton n.m.r. spectra of **1** were reported by Russell *et al.*¹ and Haque and Lilley.² Protonation of **1** can take place at one of the five



- 1a**: X = Cl, R₁ = R₂ = i-Pr
1b: X = Cl, R₁ = Et, R₂ = i-Pr
1c: X = OCH₃, R₁ = R₂ = Et
1d: X = OCH₃, R₁ = Et, R₂ = i-Pr
1e: X = OH, R₁ = R₂ = i-Pr
1f: X = OH, R₁ = Et, R₂ = i-Pr

nitrogen atoms or on X where X is a hydroxy or methoxy group. Russell *et al.* indicated that protonation occurs at one of the ring nitrogen atoms when X is a hydroxy group. Haque and Lilley observed a doublet for the methoxy protons (X = CH₃O) in their proton n.m.r. studies and concluded that protonation took place at the oxygen atom. We wish, here, to report our studies of the site of protonation of **1** using ¹³C n.m.r.

EXPERIMENTAL

The proton n.m.r. spectra were obtained on a Varian HA-60-IL or a Varian T-60A spectrometer. The carbon n.m.r. spectra were obtained on a Varian CFT-20 n.m.r. spectrometer. All carbon spectra were obtained at concentrations of about 150 mg cc⁻¹ using TMS as an internal reference.

The 2-chlorotriazines **1a** and **1b** were purchased from City Chemical Corporation, New York. They were of high purity and were herbicide reference standard grade. The 2-methoxytriazines **1c** and **1d** were prepared by standard procedures from the corresponding chlorotriazines and sodium methoxide in refluxing methanol. 2-Methoxy-4,6-bis(ethylamino)-s-triazine (**1c**) melted at 91°C (Ref. 3, 93°C). 2-Methoxy-4-ethylamino-6-isopropylamino-s-triazine (**1d**) had a melting point of 94°C (Ref. 3, 95°C). Melting points are uncorrected. The 2-hydroxytriazines **1e** and **1f** were obtained from the 2-methoxytriazines after heating in concentrated hydrochloric acid. The solid hydroxides exhibited no clear

melting point below 360°C and structural proof was based on i.r., proton n.m.r. and mass spectroscopy. The i.r. spectra of **1e** and **1f** are identical to those reported by Chen.⁴

Anal. calc. for C₉H₁₇N₅O (**1e**): C, 51.17; H, 8.11; N, 33.15. Found: C, 50.33; H, 8.18; N, 32.63.

Anal. calc. for C₈H₁₅N₅O (**1f**): C, 48.71; H, 7.66; N, 35.50. Found: C, 48.37; H, 7.69; N, 35.11.

Both **1e** and **1f** can exist in either enol or keto forms. The actual molecular species present appear to depend on the acidity of the surrounding medium.⁵ To simplify presentation, **1e** and **1f** are written here in their enol forms.

RESULTS AND DISCUSSION

Table 1 lists the carbon shifts of substituted bisalkylamino-s-triazines. The assignments were made by off-resonance decoupling and selective proton decoupling techniques. Carbon atoms which are more than three bonds away show little shift change with the variation of X. However, significant changes in shifts were observed when trifluoroacetic acid was used as a solvent.

Table 2 presents the effect of addition of trifluoroacetic acid to substituted s-triazines **1c** and **1d**. In s-triazine **1c**, addition of 20% by volume of trifluoroacetic acid causes C-2 to undergo -9.2 ppm shift; C-4 and C-6, -6.4 ppm; methoxy, +2.8 ppm; methylene, +1.4 ppm; methyl, -0.7 ppm. This indicates that the site of protonation is at N-1 or N-3. The shift change of -6.4 ppm for C-4 and C-6 is due to the tautomeric averaging of protonation of N-1 and N-3.

Table 1. Carbon-13 chemical shifts for substituted s-triazines

Compound	1a	1b	1c	1d	1e	1f
Solvent	CDCl ₃	CDCl ₃	CDCl ₃	CDCl ₃	CF ₃ CO ₂ D	CF ₃ CO ₂ D
CH ₃ CH ₂		14.5	14.9	15.5		13.9
(CH ₃) ₂ CH	22.2	22.2		22.8	22.1	21.9
CH ₃ CH ₂		35.4	35.7	35.6		38.9
(CH ₃) ₂ CH	42.3	42.3		42.4	47.8	47.4
CH ₃ O			53.6	53.6		
C-2	167.9	167.8	171.0	171.1	151.6	151.3
C-4	164.7	165.5	167.2	167.2	155.7	156.3
C-6	164.7	164.7	167.2	166.6	155.7	155.5

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Table 2. Effects of acid on carbon-13 shifts of *s*-triazines

	1c			1d		
	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆ + 20% CF ₃ CO ₂ H	Δδ ^a	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆ + 20% CF ₃ CO ₂ H	Δδ ^a
CH ₃ CH ₂	14.8	14.1	-0.7	14.8	14.2	-0.6
(CH ₃) ₂ CH				22.4	21.9	-0.5
CH ₃ CH ₂	34.9	36.3	+1.4	34.9	36.2	+1.3
(CH ₃) ₂ CH				41.6	43.3	+1.7
CH ₃ O	53.1	55.9	+2.8	53.0	55.9	+2.9
C-2	170.6	161.4	-9.2	170.5	161.5	-9.0
C-4	166.6	160.2	-6.4	166.7	160.2	-6.5
C-6	166.6	160.2	-6.4	166.1	159.5	-6.6

$$^a \Delta\delta = \delta_{(\text{DMSO-}d_6 + \text{CF}_3\text{CO}_2\text{H})} - \delta_{(\text{DMSO-}d_6)}$$

Had protonation occurred at the methoxy oxygen as proposed by Haque and Lilley, both the methoxy carbon and C-2 would have significant shift changes. The observed shift change of +2.8 ppm for the methoxy carbon is consistent with the effect observed by Pugmire and Grant⁶ on benzimidazole and purine. Therefore, the site of protonation of **1c** and **1d** is N-1 or N-3.

In our proton n.m.r. studies of **1c** and **1d**, we were unable to reproduce the doublets observed by Haque and Lilley for the methoxy protons, observing only a singlet. Protonation of ethers has been studied by

Olah *et al.*^{7,8} The ranges of H—H coupling constants of the type, H—O⁺—CH₃ are 3.4–4.1 Hz which differ significantly from the values of 12 Hz reported by Haque and Lilley.

It is interesting to note that the carbon spectrum of **1a** exhibited two sets of peaks immediately after being dissolved in deuterated trifluoroacetic acid. Two hours later, the spectrum gave only one set of peaks which are identical to those of **1e**. Similarly, the carbon spectrum of **1b** in deuterated trifluoroacetic acid is identical to that of **1f**. The i.r. spectra of the residues of **1b** and **1f** after evaporation to dryness, are identical. Apparently, the chlorine atom in **1a** and **1b** has been replaced by a hydroxy group but we are not certain how this reaction occurs. One possible explanation may be the presence of water in trifluoroacetic acid which hydrolyzes **1a** and **1b**. The hydrolysis of chloro-*s*-triazines under acidic conditions is known to be fast.^{5,9}

When **1a** was heated to reflux in glacial acetic acid and the solvent evaporated, only **1e** in its salt form remained. This suggests a solvolytic displacement mechanism not dependent on water. In this scheme, chloride is first displaced by carboxylate and the resulting ester is then deacylated by a second molecule of acetic acid to give **1e** and acetic anhydride.

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