

¹⁷O NMR of Enamino-Diesters: Intramolecular Hydrogen Bonding in 5-Alkylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones*

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Abstract: Natural abundance ¹⁷O NMR spectra of a series of 5-alkylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones, recorded in acetonitrile solution, are reported. The (¹⁷O) values correlate well with those of 4-alkylaminobut-3-en-2-ones and with the pK_a values of amines. The effects of the N-alkyl groups on the ¹⁷O shift values is diminished, owing to the resonance effects of the alkoxy groups. The shift difference (Δ_{HB}) between the two carbonyl groups is mainly attributed to the intramolecular hydrogen bonding and depends on the donor property of the amino group.

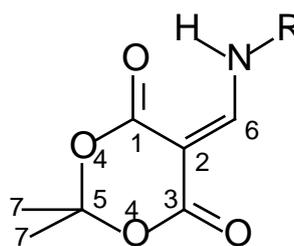
Keywords: NMR, ¹⁷O NMR, enamino-diesters, intramolecular hydrogen bonding.

Introduction

Enamino-diesters [1] are useful starting materials for the synthesis of heterocyclic compounds [1], and antimalarial drug chloroquine and similar products of medicinal interest [2]. The diacylvinyl groups have been used to protect the amino group of amino acids during the synthesis of peptides and penicillin derivatives [3], and amino sugars during Fischer glycosidation [4]. The properties of enamino-diesters have been investigated by UV [5], IR [6], and ¹H [6a, 7], ¹³C [8], ¹⁵N NMR [9], and X-ray crystallography [10]. These studies confirmed the presence of an intramolecular C=O ⋯ HN bond in primary and secondary enamino-diesters.

¹⁷O NMR is a particularly useful tool for the study of intramolecular hydrogen bonding in organic compounds [11, 12]. Recently the ¹⁷O NMR spectra of enamines and enamino-diketones have been investigated [13]. The shielding of the carbonyl O-atom by intramolecular hydrogen-bonding (Δ_{HB}), ranging from −14 to −47 ppm,

was sensitive to the nature, number and position of the substituents. ¹⁷O NMR investigations of enamino-diesters have not been reported.



1 a-1h

- a R = H
- b R = Me
- c R = Et
- d R = i-Pr
- e R = i-Bu
- f R = t-Bu
- g R = CH₂Ph
- h R = Ph

To evaluate the sensitivity of the C=O⋯H-N type of intramolecular hydrogen bonding on the ¹⁷O shift value of the hydrogen bonded carbonyl group, the ¹⁷O NMR

* NMR of Enaminones. Part 5. For part 4, see ref. 13b.

spectra of a series of 5-alkylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones (**1a-1h**) have been investigated.

Results and Discussion

The ^{17}O -NMR data of enamino-diester **1a-1h** are listed in Table 1. The ^{17}O NMR spectra of these types of compounds exhibit three ^{17}O signals: alkoxy O-4 atom appears at 185-189 ppm and two carbonyl O atoms are at

304-314 and 317-326 ppm. The ^1H -N signal appears at 9.2 – 11.2 ppm (Table 1), indicating the existence of strong intramolecular hydrogen bonding in molecules. On the basis of the shielding effects of intramolecular hydrogen bonding upon the ^{17}O shift value [11, 12], the signal at 304-314 ppm is assigned to the hydrogen bonded carbonyl O-1 atom and the signal at 317-326 ppm to the free carbonyl O-3 atom.

Table 1. ^{17}O , ^{13}C and ^1H NMR data (ppm) of **1a-1h**.

Compd	$^{17}\text{O-1}^a$	$^{17}\text{O-3}^a$	$^{17}\text{O-4}^a$	HB^b	$^1\text{H-N}^c$	$^{13}\text{C-2}^c$
1a	307.1 (170)	324.2 (120)	187.7 (350)	17.1	9.18	104.93
1b	304.8 (210)	317.7 (190)	186.0 (300)	12.9	9.46	104.62
1c	304.7 (240)	318.5 (200)	185.9 (330)	13.8	9.54	104.62
1d	305.0 (400)	318.1 (200)	185.5 (340)	13.1	9.52	104.57
1e	304.5 (340)	317.4 (240)	185.8 (390)	12.9	9.58	104.67
1f	305.5 (220)	317.5 (350)	185.4 (430)	12.0	9.84	104.58
1g	305.3 (420)	320.6 (350)	187.2 (8450)	15.3	9.79	104.72
1h	314.0 (360) ^d	325.5 (320)	188.4 (510)	11.5	11.24	105.13

a) 0.5 M Acetonitrile solution at 40°C; linewidth at half-height in parentheses.

b) $\text{HB} = (^{17}\text{O-3}) - (^{17}\text{O-1})$.

c) CDCl_3 solution, relative to internal TMS.

d) Data taken from ref 13b.

The results in Table 1 show that the (^{17}O) values are influenced by the nature of the nitrogen substituents. As previously observed for enamines and enamino-diketones [13], the ^{17}O shift values of the carbonyl O atoms of enamino-diester with N-alkyl substituents (**1b-1g**) are very similar. A phenyl group at the N atom (**1h**) causes a deshielding (*ca.* 8 ppm) of the two carbonyl O atoms. Acceptable correlations between the carbonyl O-1 and O-3 in enamino-diester (**1b-1h**) are obtained with those of the *E*- and *Z*-forms of the corresponding MeC(O)CH=CHNHR (**2**) [13a] [Eqns (1) and (2) respectively].

$$(^{17}\text{O-1})(1) = 152.0 + 0.34 (^{17}\text{O}) [(Z)\text{-}2] \quad (1)$$

($r = 0.972$, $n = 7$, $\text{SD} = 0.9$)

$$(^{17}\text{O-3})(1) = 189.7 + 0.28 (^{17}\text{O}) [(E)\text{-}2] \quad (2)$$

($r = 0.988$, $n = 7$, $\text{SD} = 0.5$)

In the correlations, enamino-diester with a primary amino group (**1a**) were excluded because of the influence due to intermolecular hydrogen bonding [13]. The slopes of the correlations show that the substituent effects on the shielding of O-atoms in enamino-diester are much less sensitive than those in enamines and enamino-diketones [13].

The (^{17}O) values of the carbonyl O atoms, as those noted for enaminones and enamino-diketones [13], are dependent on the donor power of the amines. The ^{17}O data of enaminones and enamino-diketones have been shown to correlate with the $\text{p}K_{\text{a}}$ values of the amines [13]. Reasonable correlations between the (^{17}O), (^{13}C -2) and (^1HN) values of enamino-diester (1) and $\text{p}K_{\text{a}}$ values [14] of the corresponding amines were observed [Eqns (3)-(7)]. The small negative slopes (−1.28 to −1.47) of the correlations for (^{17}O) values, compared with those noted for enaminones (*ca.* −4.5) and enamino-diketones (*ca.* −2.9) [13], show that the electron donating alkoxy group at the carbonyl carbon diminishes the shielding effect of the amine group to the carbonyl O-atom, and also indicate that the n , π -conjugation between amino group and C=C double bond is reduced. This can be attributed to the resonance effects between the carbonyl and alkoxy groups. The existence of secondary electron donating groups on the carbonyl carbon diminishes the shielding of the electron donating group to the carbonyl O-atom. This has been previously noted in the series of acetone (569 ppm), N,N-dimethylacetamide (338 ppm) and tetramethylurea (273 ppm) [15] and also in the series of but-3-en-2-one (563 ppm), ethyl acrylate (338 ppm) and ethyl 3-dimethylaminoprop-2-enoate (295 ppm) [15].

$$\begin{aligned} (^{17}\text{O-1}) &= 320.7 - 1.47 \text{ p}K_{\text{a}} \\ (r &= 0.979, N = 8, SD = 0.7) \end{aligned} \quad (3)$$

$$\begin{aligned} (^{17}\text{O-3}) &= 331.6 - 1.28 \text{ p}K_{\text{a}} \\ (r &= 0.977, N = 7, SD = 0.7, \text{ omitting 1a}) \end{aligned} \quad (4)$$

$$\begin{aligned} (^{17}\text{O-4}) &= 199.9 - 1.33 \text{ p}K_{\text{a}} \\ (r &= 0.966, N = 7, SD = 0.2, \text{ omitting 1h}) \end{aligned} \quad (5)$$

$$\begin{aligned} (^1\text{HN}) &= 12.47 - 0.27 \text{ p}K_{\text{a}} \\ (r &= 0.976, N = 7, SD = 0.15, \text{ omitting 1a}) \end{aligned} \quad (6)$$

$$\begin{aligned} (^{13}\text{C-2}) &= 105.53 - 0.087 \text{ p}K_{\text{a}} \\ (r &= 0.991, N = 7, SD = 0.03, \text{ omitting 1a}) \end{aligned} \quad (7)$$

^{17}O NMR data has been shown to be sensitive to intramolecular hydrogen bonding [11]. The shielding in the ^{17}O shift value by the hydrogen bonding components (δ_{HB} value) has been shown to depend on the H-donor and H-acceptor groups. The δ_{HB} values of −50, −30, −19 and −10 ppm have been reported for ketone [12f, g], aldehyde [12h] and amide [12a, j], and ester [12k] carbonyl oxygens, respectively; the difference between these values has been attributed to differences in basicity of the carbonyl groups. For the N–H \cdots O=C type of intramolecular hydrogen bonding in enaminones and enamino-diketones δ_{HB} values range from −14 to −47 ppm [13].

It has been demonstrated that the ^{17}O NMR parameters are sensitive to electronic effects, torsional angles, steric

interactions and intramolecular hydrogen bonding [11, 12]. Therefore, to evaluate the δ_{HB} values these factors should be taken into account. IR [6a] and X-ray [10] analyses show that the conjugated system in hydrogen bonded enamino-diester (1) is essentially planar, and that electron delocalization affects both carbonyl groups almost equally. This demonstrates that the contribution of electronic and torsional effects to observed chemical shifts can be considered negligible. Thus, the ^{17}O chemical shift differences (δ_{HB}) between the carbonyl groups O-1 and O-3 in enamino-diester with primary or secondary amino groups are attributed mainly to the intramolecular hydrogen bonding.

The δ_{HB} values (Tables 1) for enamino-diester 1a–1h, ranging from −11 to −17 ppm, are much smaller than those found for 2,2-diacetyl-enamines (*ca.* −30 ppm) [13b]. It is well known that ester carbonyl groups are less basic than ketone carbonyls [16], and consequently ester carbonyls are expected to be poorer hydrogen bond acceptors than ketone carbonyls. The small δ_{HB} values is consistent with the lower basicity of the ester carbonyl groups. The δ_{HB} values, −4 to −13 ppm have been previously noted for hydroxypyridine carboxy esters and benzoates [12k].

Conclusion

The results of this paper demonstrate that the effects of the N-alkyl substituents on ^{17}O shift values of the carbonyl groups in enamino-diester are diminished, in comparison to those in enaminones and enamino-diketones. This is attributed to the resonance between the carbonyl and alkoxy groups. ^{17}O NMR data show clearly the existence of intramolecular hydrogen bonding in enamino-diester. The shielding effect of intramolecular hydrogen bonding of a NH to an ester carbonyl, ranging from −11 to −17 ppm, is much smaller than that for analogous diacetyl-enamine carbonyl groups (*ca.* −30 ppm). This is because of the lower basicity of the ester carbonyl groups.

Experimental

General

^1H NMR and ^{13}C NMR spectra (δ , in ppm; J , in Hz; relative to internal TMS in CDCl_3 solns. at 20°C) were recorded on Bruker WH-250 and Bruker Advance DPX-400 spectrometers, MS (electron impact mass spectrum; m/z in % of base peak) on a Nermag R-10-10C spectrometer. Melting points (M. p.) were observed under a microscope using a Mettler FP-52 instrument.

^{17}O NMR Spectroscopy

^{17}O NMR spectra were recorded on a Bruker-WH-360 spectrometer, equipped with a 10-mm probe, at 48.8 MHz,

in the Fourier transform (FT) mode without lock. System control, data acquisitions, and data managements were performed by an Aspect-2000 microcomputer. Instrumental settings: spectral width 50 kHz (1025 ppm), 8 K data points, pulse width 33 μ s, acquisition time 20 ms, preacquisition delay 5 μ s, 150000 – 300000 scans, sample spinning 30 Hz. An even number (12-28) left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8 K words and exponentially multiplied with 100-Hz line-broadening factor (LB) before being subjected to the FT. The chemical shifts (^{17}O), measured in 0.5 M acetonitrile solution at 40°C at natural isotopic abundance, are reported relative to (^{17}O)(H_2O) (= 0.0 ppm); dioxane (^{17}O) = 0.0 ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shift values is ca. ± 1 ppm (± 0.2 ppm within the same series).

General procedure

Compounds **1a-1h** were prepared according to the literature procedure [17, 18]. A solution of 5-methoxymethylene-2,2-dimethyl-1,3-dioxane-4,6-diones [17] (10 mmol) and the appropriate amine (10 mmol) (in cases of gaseous amine, ammonia or methylamine ethanol solution or ethylamine aqueous solution was applied) in acetonitrile (10 ml) was left at room temperature for 30 min. Evaporation of the solvent under reduced pressure gave the product as a crystalline solid, which was filtered and washed with ethyl ether.

5-Aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**1a**)

M.p. 211.3-212.4 °C (lit. [17] 214-215 °C); $^1\text{H-NMR}$ (CDCl_3), 9.18 (br, 1H, NH), 8.27 (dd, $J = 15.8, 8.5$, 1H, H-6), 6.55 (br, 1H, NH), 1.73 (s, 6H, H-7); $^{13}\text{C-NMR}$ (CDCl_3), 165.23 (C-1), 104.93 (C-2), 163.83 (C-3), 87.03 (C-5), 158.82 (C-6), 27.02 (C-7); EI-MS 171 (M^+ , 1), 156 (1), 114 (3), 85 (2), 70 (28), 69 (100), 59 (25), 53 (5).

5-Methylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**1b**)

M.p. 176.4-176.9°C (lit. [6a] 175-176 °C); $^1\text{H-NMR}$ (CDCl_3) 9.46 (br, 1H, NH), 8.11 (d, $J = 15.0$, 1H, H-6), 3.27 (d, $J = 5.0$, 3H, NMe), 1.70 (s, 6H, H-7); $^{13}\text{C-NMR}$ (CDCl_3), 165.71 (C-1), 104.62 (C-2), 163.99 (C-3), 84.44 (C-5), 160.97 (C-6), 26.81 (C-7), 36.71 (NMe); EI-MS 185 (M^+ , 2), 128 (3), 99 (3), 84 (15), 83 (55), 71 (12), 69 (6), 59 (10), 55 (100), 54 (64), 53 (38).

5-Ethylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**1c**)

M.p. 112.9-113.6 °C; $^1\text{H-NMR}$ (CDCl_3) 9.54 (br, 1H, NH), 8.14 (d, $J = 15.0$, 1H, H-6), 3.52 (qd, $J = 7.2, 5.3$, 2H,

NEt), 1.71 (s, 6H, H-7), 1.36 (t, $J = 7.2$, 3H, NEt); $^{13}\text{C-NMR}$ (CDCl_3) 165.70 (C-1), 104.62 (C-2), 164.08 (C-3), 84.26 (C-5), 159.28 (C-6), 26.84 (C-7), 45.22 and 15.57 (NEt); EI-MS 199 (M^+ , 1), 142 (1), 97 (4), 84 (6), 82 (3), 71 (12), 70 (8), 69 (83), 68 (100), 67 (12), 59 (6), 56 (8), 54 (14), 53 (31).

5-(1-Methylethylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1d**)

M.P. 104.4-105.0 °C; $^1\text{H-NMR}$ (CDCl_3) 9.52 (br, 1H, NH), 8.16 (d, $J = 15.0$, 1H, H-6), 3.73 (m, 1H, NCH), 1.70 (s, 6H, H-7), 1.36 (d, $J = 6.7$, 6H, NCHMe₂); $^{13}\text{C-NMR}$ (CDCl_3) 165.65 (C-1), 104.57 (C-2), 164.14 (C-3), 84.02 (C-5), 157.49 (C-6), 26.85 (C-7), 52.18 and 23.09 (NCHMe₂); EI-MS 213 (M^+ , 1), 156 (1), 111 (5), 96 (11), 85 (9), 83 (9), 82 (43), 70 (30), 69 (100), 68 (85), 67 (12), 59 (20), 58 (8), 54 (13), 53 (44).

5-(2-Methylpropylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1e**)

M.p. 151.1-151.8 °C; $^1\text{H-NMR}$ (CDCl_3) 9.58 (br, 1H, NH), 8.09 (d, $J = 14.8$, 1H, H-6), 3.27 (t, $J = 6.5$, 2H, NCH₂), 1.93 (m, 1H, CHMe₂), 1.71 (s, 6H, H-7), 0.99 (d, $J = 6.7$, 6H, CHMe₂); $^{13}\text{C-NMR}$ (CDCl_3), 165.79 (C-1), 104.67 (C-2), 164.06 (C-3), 84.27 (C-5) 160.00 (C-6), 26.87 (C-7), 58.04, 29.30 and 19.60 (NCH₂CHMe₂); EI-MS 227 (M^+ , 2), 170 (3), 145 (1), 126 (10), 125 (6), 96 (3), 85 (2), 84 (6), 83 (32), 82 (26), 70 (100), 69 (48), 68 (27), 67 (5), 59 (12), 58 (15), 57 (15), 56 (23), 55 (30), 54 (33), 53 (80).

5-(Dimethylethylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1f**)

M.p. 148.2-149.1 °C (lit. [18] 151-153 °C); $^1\text{H-NMR}$ (CDCl_3) 9.84 (br, 1H, NH), 8.22 (d, $J = 15.3$, 1H, H-6), 1.71 (s, 6H, H-7), 1.42 (s, 9H, CMe₃); $^{13}\text{C-NMR}$ (CDCl_3) 165.73 (C-1), 104.58 (C-2), 164.24 (C-3), 83.97 (C-5), 155.44 (C-6), 26.86 (C-7), 55.10 and 29.62 (NCMe₃); EI-MS 227 (M^+ , 0.5), 154 (1), 114 (3), 110 (2), 85 (2), 84 (2), 83 (3), 82 (6), 80 (7), 70 (88), 69 (100), 68 (12), 67 (6), 59 (25), 58 (24), 57 (91), 56 (15), 55 (10), 54 (3), 53 (16).

5-(benzylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1g**)

M.p. 164.8-166.5 °C; $^1\text{H-NMR}$ (CDCl_3) 9.79 (br, 1H, NH), 8.22 (d, $J = 14.7$, 1H, H-6), 7.39 (m, 3H), 7.28 (m, 2H), 4.61 (d, $J = 6.0$, 2H, NCH₂), 1.71 (s, 6H, H-7); $^{13}\text{C-NMR}$ (CDCl_3) 165.60 (C-1), 104.72 (C-2), 163.94 (C-3), 84.92 (C-5), 159.63 (C-6), 26.89 (C-7), 134.90 (C, Ph), 129.22 (2 CH, Ph), 127.72 (2 CH, Ph), 128.73 (CH, Ph), 54.04 (NCH₂); EI-MS 262 (M^+ +1, 5), 261 (M^+ , 25), 246 (2), 204 (15), 203 (23), 174 (28), 159 (14), 130 (75), 104

(17), 102 (27), 91 (100), 86 (8), 85 (4), 84 (12), 83 (2), 77 (5), 70 (4), 69 (4), 66 (9), 65 (14), 59 (7), 58 (9), 57 (6), 56 (4), 55 (4), 54 (4), 53 (6), 52 (10), 51 (10).

5-(Anilinomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione
(1h)

M.p. 155.4-156.1°C (lit. [6a] 155-156 °C); ¹H-NMR (CDCl₃) 11.24 (d, J = 14.7, 1H, NH), 8.65 (d, J = 14.7, 1H, H-6), 7.44 (m, 2H), 7.26 (m, 3H), 1.75 (s, 6H, H-7); ¹³C-NMR (CDCl₃) 165.51 (C-1), 105.13 (C-2), 163.52 (C-3), 87.23 (C-5), 152.62 (C-6), 27.03 (C-7), 137.79 (C, Ph), 130.08 (2 CH, Ph), 126.82 (CH, Ph), 118.03 (2 CH, Ph); EI-MS 248 (M⁺+1, 2), 247 (M⁺, 12), 189 (26), 172 (3), 161 (3), 144 (64), 117 (100), 116 (9), 104 (7), 93 (14), 90 (28), 89 (17), 86 (2), 84 (2), 77 (26), 69 (2), 66 (3), 65 (4), 59 (4), 58 (4), 54 (4), 53 (6), 52 (8), 51 (9).

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Sample Availability: Most of the samples published here and in ref. 12a, 13, 15 are available from MDPI.