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NMR of enaminones

Part 8†—^{1}H, ^{13}C and ^{17}O NMR spectra of primary and secondary 1,2-disubstituted enaminones: configuration, conformation and intramolecular hdydrogen bonding

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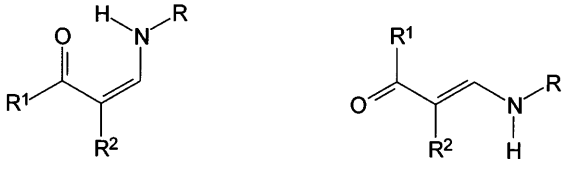
ABSTRACT: The ^{1}H, ^{13}C and ^{17}O NMR spectra for four series of C-2-substituted enaminones are reported: MeCO(Me)C=CHNHR (**1**), EtCO(Me)=CHNHR (**2**), PhCO(Me)C=CHNHR (**3**) and MeCO(Me)C=CHNHR (**4**). The ^{1}H, ^{13}C and ^{17}O NMR data for these enaminones show that **1** and **2** exist as mixtures of *E*- and *Z*-forms, **3** exists mainly in the *E*-form and **4** is in the *Z*-form. The *E*- and *Z*-forms exist in the *E-s-E-s-E* and *Z-s-Z-s-E* conformations, respectively. The ^{17}O shift values of the carbonyl groups in the four series of enaminones show that the influence of N substituents is essentially identical and is additive. The shielding of the carbonyl O atom by intramolecular hydrogen bonding ($\Delta\delta_{HB}$), *ca.* −30 ppm, is dependent on the donor ability of the amino groups and the type of C-1 and C-2 substituents. Correlations of the ^{1}H, ^{13}C and ^{17}O NMR data between the *E*- and *Z*-forms of enaminones are excellent. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{17}O NMR; enaminones; substituent effects; configuration; conformation; intramolecular hydrogen bonding

INTRODUCTION

Enaminones are important organic intermediates[2] and have been reported to have potential biological activity.[3] NMR spectroscopic techniques have been widely applied to enaminones,[2] but so far they have not been systematically applied to C-2-substituted enaminones and only a few ^{1}H,[4] ^{13}C,[5] ^{15}N[5,6] and ^{17}O[1,7,8] NMR spectral data have been reported. Previous NMR spectroscopic and x-ray crystallographic studies[1] have shown that C-2-substituted enaminones exist as either the *E-s-E-s-E* or the *Z-s-Z-s-E* conformations (Scheme 1), or as mixture of both conformations, depending on the C-2 substituent.



Z-s-Z-s-E *E-s-E-s-E*

Scheme 1.

^{17}O NMR spectroscopy is a particularly useful method for studying the bonding state of O atoms and intramolecular hydrogen bonding in molecules.[9,10] Recently, the ^{17}O NMR spectra of enaminones have been investigated.[1,7,8,11–14] These studies showed that the ^{17}O NMR chemical shifts of enaminones correlates well with their vinylic ^{13}C-2 shifts and with the pK_a values of the amines. As the chemical shift of the ^{13}C-2 is a characteristic of its electron density, the shielding of the O atom in enaminones is dependent on the electron density at the O atom and reflects the polarization and degree of n,π-conjugation in the N—C=C—C=O system. In C-2-unsubstituted enaminones, the influence of substitutents on the carbonyl O atom's ^{17}O shift value is additive.[11] The shielding of the carbonyl O atom by intramolecular hydrogen bonding ($\Delta\delta_{HB}$), ranging from −14 to −47 ppm, was sensitive to the nature, number and position of the substitutents on C-1, C-3 and N atoms.[11]

In C-2-substituted enaminones, the C-1 substituent collides either with the C-2 substituent in the *Z-s-Z-s-E* conformation or with H-3 in the *E-s-E-s-E* conformation. In both cases, the conjugation system is reduced owing to twisting of the carbonyl or the amino groups out of the delocalized plane. This change should lead to characteristic differentiation by the shielding of the O atom in the molecule. In order to evaluate the contribution from the C=O···H—N type of intramolecular hydrogen bonding, and to confirm the additive influence of substituents on ^{17}O shift value of the carbonyl O atom in C-2-substituted enaminone systems, and to check the delocalization of the conjugation system, the ^{1}H, ^{13}C and ^{17}O NMR spectra of C-2-substituted

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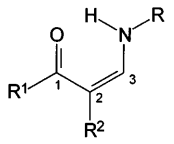
enaminones with primary and secondary groups (**1–4**) were investigated.



	R^1	R^2
1	Me	Me
2	Et	Me
3	Ph	Me
4	Ph	Ph

	R		R
a	H	**e**	i-Bu
b	Me	**f**	CH_2Ph
c	Et	**g**	Ph
d	i-Pr		

Structures 1–4

RESULTS AND DISCUSSION

Structure of C-2-substituted enaminones

Enaminones can theoretically exist in eight configurations and conformations due to restricted rotations around the C=C double and C—C=O and C—N single bonds.[2] The configurational and conformational changes of enaminones depend on the nature, number and position of the substituents. Attaching substituents to the C-2 position of enaminones should be accompanied by significant changes in the observed configurations and conformations and consequently affect the spectral properties.

The configurational *E*- and *Z*-isomers can be easily distinguished by the ^{1}H NMR shifts for the NH protons: the *E*-form at $\delta = 4.1$–6.5 ppm and the hydrogen-bonded *Z*-form at $\delta = 9.5$–12.0 ppm. Enaminones **1–3** exist as mixtures of *E*- and *Z*-isomers and **4** exists predominately as the *Z*-isomer. Population ratios of the *E*- and *Z*-isomers in $CDCl_3$ solution were estimated from the integral intensity of the H-3 and/or 2-Me signals and are presented in Tables 1–3. The *E*:*Z* ratio is dependent on the C-1 and C-2 substituents. *E*:*Z* ratios of *ca.* 1:2.3 were observed for **1b–f** (**1a**, 1.6:1; **1g**, 1:7.5) and of *ca.* 1:3.2 for **2b–f** (**2a**, 1.1:1, **2g**, 1:4.5). A phenyl group at C-1, i.e. **3a–g**, favors the *E*-form and gives *E*:*Z* ratios of *ca.* 5:1. In the C-2 phenyl analogs **4b–g**, the *Z*-isomer predominates ($\geq$95%) with only traces of the *E*-isomer, if not exclusively.

The ^{13}C NMR data for the enaminones **1–4** in $CDCl_3$ solution are summarized in Tables 1–4. The peak assignments of the carbon nuclei for the *E*- and *Z*-forms of **1–4** were based on non-equivalent signal intensities and were confirmed by selective ^{13}C–$\{^1H\}$ decoupling experiments. These data are in agreement with those previously reported for corresponding analogs.[1,2,15] The existence of the *E*- and *Z*-isomers for enaminones **1–3** is clearly shown by the chemical shift values for the C-1, C-2, C-3 and 2-Me carbons. The ^{13}C shift differences of these carbon nuclei between the *E*- and *Z*-forms of enaminones have been noted previously.[1] As expected, the signals of the C-3 and 2-Me carbons of the *E*-isomer appear at higher field, and that for the C-2 carbon is found at lower field, compared with those of the *Z*-isomer. The ^{13}C spectra of **4b–g** confirm the existence of only one isomer for each compound.

The ^{17}O NMR chemical shifts for enaminones **1**, **2**, **3** and **4**, obtained in natural abundance in acetonitrile, are listed in Tables 1, 2, 5 and 6, respectively. The existence of the *E*- and *Z*-isomers in enaminones **1a–g** and **2a–g** is clearly shown by their ^{17}O NMR spectra; each compound shows two carbonyl O signals: **1a–g** at *ca.* 450 and 475 ppm (Table 1) and **2a–g** at *ca.* 440 and 465 ppm (Table 2). The identification of the ^{17}O signals for the *E*- and *Z*-isomers was based on non-equivalent signal intensities and the shielding effects of intramolecular hydrogen bonding:[9–14] the low-field signal was assign-

Table 1. ^{1}H, ^{13}C and ^{17}O NMR data for MeCOC(Me)=CHNHR (**1**)

Compound	*E*:*Z*	Isomer	^{1}H-N[a]	^{1}H-3	^1H_3C-2	^{13}C-1	^{13}C-2	^{13}C-3	$^{13}CH_3$-2	$^{17}O^{exp.\,b}$	$^{17}O^{calc.\,c}$	$\Delta\delta^d$	$\Delta\delta_{HB}{}^e$
1a	1.6:1	*E*	4.42	7.38 (tq, 10.6, 1.0)	1.67 (d, 1.0)	196.12	109.38	146.11	7.73	483.7	491.0	−7.3	−17.6
		Z	—	6.67 (tq, 10.9, 0.6)	1.82 (d, 0.6)	199.89	101.37	148.51	17.38	466.1	463.5	2.6	
1b	1:2.2	*E*	4.17	7.21 (dq, 13.4, 0.7)	1.65 (d, 0.7)	194.56	106.92	150.66	8.40	474.2	473.5	0.7	−27.9
		Z	9.56	6.55 (d, 12.4)	1.81 (s)	197.68	99.27	153.63	17.20	446.3	446.0	0.3	
1c	1:2.2	*E*	4.29	7.26 (d, 13.2)	1.66 (s)	194.96	106.70	149.63	8.47	475.6	475.3	0.3	−27.4
		Z	9.72	6.59 (d, 12.5)	1.81 (s)	197.62	98.98	152.48	17.17	448.2	447.8	0.4	
1d	1:2.0	*E*	4.17	7.31 (d, 13.5)	1.65 (s)	194.72	106.77	147.64	8.56	475.3	475.5	−0.2	−28.2
		Z	9.72	6.64 (d, 12.6)	1.82 (s)	197.42	98.81	150.54	17.29	447.2	448.0	−0.8	
1e	1:2.4	*E*	4.38	7.22 (d, 13.5)	1.68 (s)	194.70	106.70	149.62	8.49	473.4	473.0	0.4	−28.1
		Z	9.85	6.55 (d, 12.3)	1.81 (s)	197.61	98.79	152.92	17.21	445.3	445.5	−0.2	
1f	1:2.0	*E*	4.60	7.32 (dq, 13.0, 1.0)	1.70 (d, 1.0)	195.15	107.90	148.88	8.61	478.5	480.7	−2.2	−25.2
		Z	9.98	6.62 (d, 12.3)	1.82 (s)	198.39	100.08	151.99	17.30	453.3	453.2	0.1	
1g	1:7.5	*E*	6.31[f]	7.79 (dq, 13.0, 1.2)	1.84 (d, 1.2)	195.99	111.90	139.45	8.88	504.3	498.1	6.2	−28.6
		Z	11.54[g]	7.14 (dq, 12.0, 0.8)	1.96 (d, 0.8)	199.95	103.51	141.63	17.69	475.7	470.6	5.1	

[a] Singlet unless indicated otherwise.
[b] 0.5 M acetonitrile solution at 40 °C.
[c] *E*-form, $\delta(^{17}O)^{calc.} = 491.0 + \Delta_N$; *Z*-form, $\delta(^{17}O) = 463.5 + \Delta_N$; substituent increment values (Δ_N) taken from Ref. 11.
[d] $\Delta\delta = \delta(^{17}O)^{exp.} - \delta(^{17}O)^{calc.}$.
[e] $\Delta\delta_{HB} = \delta(^{17}O)^{exp.}$ (*Z*-form) $- \delta(^{17}O)^{exp.}$ (*E*-form).
[f] Doublet, $J = 13.0$ Hz.
[g] Doublet, $J = 12.0$ Hz.

Table 2. ^{1}H, ^{13}C and ^{17}O NMR data for EtCOC(Me)=CHNHR (**2**)

Compound	*E*:*Z*	Isomer	^{1}H-N[a]	^{1}H-3	$^{1}H_3C$-2	^{13}C-1	^{13}C-2	^{13}C-3	$^{13}CH_3$-2	$^{17}O^{exp.\ b}$	$^{17}O^{calc.\ c}$	$\Delta\delta^{d}$	$\Delta\delta_{HB}{}^{e}$
2a	1.1:1	*E*	4.38	7.40 (tq, 10.5, 1.0)	1.68 (d, 1.0)	199.49	108.72	144.38	7.89	473.7	480.8	−7.1	−18.9
		Z	—	6.66 (tq, 10.8, 0.7)	1.81 (d, 0.7)	202.64	101.17	148.00	16.79	454.8	454.3	0.5	
2b	1:3.1	*E*	4.10	7.23 (dq, 13.5, 0.7)	1.66 (d, 0.7)	198.10	105.99	149.36	8.57	463.3	463.3	0.0	−27.0
		Z	9.56	6.54 (dq, 12.5, 0.5)	1.81 (d, 0.5)	200.59	98.84	153.51	16.59	436.3	436.8	−0.5	
2c	1:3.1	*E*	4.19	7.29 (dq, 13.5, 0.6)	1.67 (d, 0.6)	198.13	105.85	147.90	8.67	464.9	465.1	−0.2	−27.1
		Z	9.70	6.58 (dq, 12.5, 0.5)	1.81 (d, 0.5)	200.44	98.58	151.92	16.61	437.8	438.6	−0.8	
2d	1:2.9	*E*	4.09	7.34 (dq, 13.4, 1.0)	1.66 (d, 1.0)	198.34	105.92	146.22	8.68	463.8	465.3	−1.5	−25.6
		Z	9.72	6.63 (dq, 12.5, 0.5)	1.81 (d, 0.5)	200.30	98.39	150.36	16.69	438.2	438.8	−0.6	
2e	1:3.4	*E*	4.30	7.25 (dq, 13.5, 1.0)	1.68 (d, 1.0)	198.42	105.53	148.87	8.62	464.0	462.8	1.2	−27.2
		Z	9.82	6.54 (dq, 12.5, 0.5)	1.80 (d, 0.5)	200.47	98.32	152.93	16.60	436.8	436.3	0.5	
2f	1:2.6	*E*	4.54	7.35 (dq, 13.0, 1.0)	1.70 (d, 1.0)	198.40	106.87	147.63	8.78	469.3	470.5	−1.2	−24.8
		Z	9.96	6.61 (dq, 12.3, 0.6)	1.82 (d, 0.6)	201.50	99.66	151.64	16.67	444.5	444.0	0.5	
2g	1:4.5	*E*	6.27[f]	7.82 (dq, 13.0, 1.0)	1.85 (d, 1.0)	199.59	110.82	138.64	9.02	494.7	487.9	6.8	−28.8
		Z	11.56[g]	7.13 (dq, 12.0, 0.6)	1.95 (d, 0.6)	202.7	103.17	141.56	17.04	465.9	461.4	4.5	

[a] Singlet unless indicated otherwise.
[b] 0.5 M acetonitrile solution at 40 °C.
[c] *E*-form, $\delta(^{17}O)^{calc.} = 480.8 + \Delta_N$; *Z*-form, $\delta(^{17}O) = 454.3 + \Delta_N$.
[d] $\Delta\delta = \delta(^{17}O)^{exp.} - \delta(^{17}O)^{calc.}$.
[e] $\Delta\delta_{HB} = \delta(^{17}O)^{exp.}$ (*Z*-form) − $\delta(^{17}O)^{exp.}$ (*E*-form).
[f] Doublet, J = 13.0 Hz.
[g] Doublet, J = 12.0 Hz.

ed to the *E*-isomer and the high-field signal to the *Z*-isomer. The ^{17}O NMR spectra of enaminones **3a**–**g** show one signal at *ca.* 475 ppm at 40 °C (Table 5). At 70 °C, a small signal corresponding to the *Z*-isomer at *ca.* 440 ppm was also observed. This indicates that these enaminones favor the *E*-form (>95%). Each of the enaminones **4b**–**g** has only one ^{17}O signal at *ca.* 440 ppm at 40 °C, in good agreement with the existence of mainly the *Z*-form. At 70 °C, a large signal attributed to the *Z*-form was observed at *ca.* 445 and a small signal at *ca.* 480 ppm was assigned to the *E*-form (Table 6).

The conformation of enaminones **1**–**4** can be deduced from their ^{1}H and ^{13}C NMR data. The *Z*-form, owing to the influence of strong intramolecular hydrogen

Table 3. ^{1}H and ^{13}C NMR data for PhCOC(Me)=CHNHR (**3**)

Compound	*E*:*Z*	*Isomer*	^{1}H-N[a]	^{1}H-3	$^{1}H_3C$-2	^{13}C-1	^{13}C-2	^{13}C-3	$^{13}CH_3$
3a	—	*E*	4.68	7.04 (tq, 10.9, 1.0)	1.81 (d, 1.0)	196.21	109.06	150.66	8.19
3b	5:1	*E*	4.46	6.92 (dq, 13.6, 0.6)	1.82 (d, 0.6)	194.88	106.61	155.56	8.83
		Z	10.22	6.85 (d, 12.6)	1.84 (s)	194.75	98.46	157.03	17.87
3c	5:1	*E*	4.60	6.98 (dq, 14.0, 0.5)	1.83 (d, 0.5)	194.89	106.55	153.88	8.94
		Z	10.35	6.88 (d, 12.6)	1.84 (s)	194.66	98.19	155.35	17.94
3d	5:1	*E*	4.40	7.03 (dq, 14.0, 0.5)	1.83 (d, 0.5)	194.80	106.59	151.91	8.98
		Z	10.37	6.93 (d, 12.8)	1.85 (s)	194.48	97.97	153.50	18.04
3e	4:1	*E*	4.59	6.93 (dq, 14.0, 0.8)	1.85 (d, 0.8)	194.83	106.27	154.36	8.95
		Z	10.49	6.84 (d, 12.4)	1.84 (s)	194.63	98.03	156.02	17.94
3f	6:1	*E*	4.73	7.06 (dq, 13.6, 1.0)	1.87 (d, 1.0)	195.11	107.33	153.72	9.10
		Z	10.58	6.92 (d, 12.8)	1.86 (s)	195.53	99.19	155.09	18.04
3g	4:1	*E*	6.66[b]	7.54 (dq, 13.0, 1.0)	2.01 (d, 1.0)	196.17	111.22	144.28	9.43
		Z	12.04[c]	7.41 (dq, 12.0, 0.7)	1.99 (d, 0.7)	196.99	102.65	145.01	18.55

[a] Singlet unless indicated otherwise.
[b] Doublet, J = 13.0 Hz.
[c] Doublet, J = 12.0 Hz.

Table 4. ^{1}H and ^{13}C NMR data for (*Z*)-PhCOC(Ph)=CHNHR (**4**)

Compound	^{1}H-N[a]	^{1}H-3	^{13}C-1	^{13}C-2	^{13}C-3
4b	10.52	7.09 (d, 12.4)	192.78	109.03	157.69
4c	10.65	7.14 (d, 12.4)	192.72	108.78	156.07
4d	10.67	7.17 (d, 13.0)	192.53	108.76	154.41
4f	10.87	7.18 (d, 13.0)	193.21	109.57	156.00
4g	12.29[b]	7.63 (d, 12.4)	194.51	112.33	146.41

[a] Singlet unless indicated otherwise.
[b] Doublet, J = 12.4 Hz.

Table 5. ^{17}O NMR data for PhCOC(Me)=CHNHR (3)

	E-form at 40 °C			*E*-form at 70 °C			*Z*-form at 70 °C			
Compound	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$\Delta\delta_{HB}{}^d$
3a	477.3	490.1	−12.8	480.3	492.7	−12.4	—	—	—	—
3b	472.7	472.6	0.1	474.1	475.2	−1.1	439.5	440.4	−0.9	−34.6
3c	472.7	474.4	−1.7	476.6	477.0	−0.4	441.2	442.2	−1.0	−35.4
3d	474.2	474.6	−0.4	477.4	477.2	0.2	442.0	442.4	−0.4	−35.4
3e	473.2	472.1	1.1	475.9	474.7	1.2	440.6	439.9	0.7	−35.3
3f	480.3	479.8	0.5	481.8	482.4	−0.6	448.5	447.6	0.9	−33.3
3g	500.0	497.2	2.8	502.8	499.8	3.0	467.1	465.0	2.1	−35.7

[a] 0.5 M acetonitrile solution.
[b] $\delta(^{17}O)^{calc.} = C + \Delta_N$. *E*-form, C = 490.1 (40 °C) and 492.7 ppm (70 °C); *Z*-form, C = 457.9 ppm (70 °C).
[c] $\Delta\delta = \delta(^{17}O)^{exp.} - \delta(^{17}O)^{calc.}$.
[d] $\Delta\delta_{HB}$ (70 °C) = $\delta(^{17}O)^{exp.}$ (*Z*-form) − $\delta(^{17}O)^{exp.}$ (*E*-form).

bonding, exists only as the *Z-s-Z-s-E* conformation (Scheme 1). This is consistent with previous x-ray crystallographic studies of (*Z*)-PhCO(Ph)C=CHN(*t*-Bu).[1]

For the *E*-form of enaminones **1**–**3**, a vicinal coupling constant of *ca.* 13.5 Hz for the =CH—NH moiety of each derivative indicates a dihedral angle of 180°, which is in agreement with the *s-trans* (*s-E*) conformation on this bond.

In enaminones **1** and **2**, the ^{1}H-3 signals for the *E*-form are found at lower field (*ca.* 0.8 ppm) than those of the corresponding *Z*-form. This can be attributed to the deshielding anisotropic effect of the C=O group on the H-3 in this E-form, indicating that the C=C and C=O bonds exist in an *s-trans* conformation in this form. Additionally, the ^{1}H and ^{13}C signals of the 2-Me group (*ca.* 1.65 and 8.7 ppm, respectively) are found at higher field than those of the corresponding *Z*-form (*ca.* 1.82 and 17.0 ppm, respectively) owing to the Van der Waals effect[16] of the non-bonded carbonyl oxygen on the 2-Me group of the *E*-form. This further supports the *s-trans* conformation of the C=C and C=O bonds in the *E*-form, hence enaminones **1** and **2** exist in *E-s-E-s-E* conformation, in agreement with the previous NMR spectroscopic studies of *N*-(*t*-Bu) analogs.[1]

In enaminones **3a**–**g**, the ^{13}C signals of 2-Me of the *E*-form found at *ca.* 9.0 ppm are close to those noted for the *E*-form of enaminones **1** and **2**. This indicates that the C=C and C=C bonds in enaminones **3** also exist in an *s-trans* conformation, and it adopts the *E-s-E-s-E* conformation (Scheme 1). As expected, the ^{1}H signals of the H-3 and 2-Me protons for the *E*-form are found at lower field than those for the corresponding *Z*-form. However, the shift differences of the H-3 and 2-Me between the *E*- and *Z*-forms (*ca.* 0.1 and 0.01 ppm, respectively) are much smaller than those found in enaminones **1** and **2** (*ca.* 0.8 and 0.15 ppm, respectively). This can be explained in terms of the shielding anisotropic effect of the C-1 phenyl ring on the H-3 in the *E*-form and on the 2-Me protons in the *Z*-form, respectively, consistent with the *E-s-E-s-E* conformation and suggesting that the C-1 phenyl ring is twisted out the plane of N—C=C—C=O system. Hence, the *E*-form of enaminones **1**–**3** exists in solution as the *E-s-E-s-E* conformation (Scheme 1), in agreement with previous NMR spectroscopic and x-ray crystallographic studies of (*E*)-PhCO(Me)CH=CHNH(*t*-Bu), which showed that the enaminone system adopting the *E-s-E-s-E* conformation is essentially planar.[1]

Substituent effects

The ^{17}O shift values for enaminones **1**–**4** are influenced by the nature of the substituents at the C-1, C-2 and N

Table 6. ^{17}O NMR data for PhCOC(Ph)=CHNHR (4)

	Z-form at 40 °C			*Z*-form at 70 °C			*E*-form at 70 °C			
Compound	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$^{17}O^{exp.\,a}$	$^{17}O^{calc.\,b}$	$\Delta\delta^c$	$\Delta\delta_{HB}{}^d$
4b	440.1	440.0	0.1	443.5	443.0	0.5	480.1	477.7	2.4	−36.6
4c	441.4	441.8	−0.4	445.1	444.8	0.3	477.5	479.5	−2.0	−32.4
4d	440.9	442.0	−1.1	444.4	445.0	−0.6	481.3	479.7	1.6	−36.9
4f	448.3	447.2	1.1	450.3	450.2	0.1	482.4	484.9	−2.5	−32.1
4g	470.2	464.6	5.6	472.9	467.6	5.3	501.4	502.3	−0.9	−28.5

[a] 0.5 M acetonitrile solution.
[b] $\delta(^{17}O)^{calc.} = C + \Delta_N$. *E*-form, C = 495.2 ppm (70 °C); *Z*-form, C = 457.5 (40 °C) and 457.9 ppm (70 °C).
[c] $\Delta\delta = \delta(^{17}O)^{exp.} - \delta(^{17}O)^{calc.}$.
[d] $\Delta\delta_{HB}$ (70 °C) = $\delta(^{17}O)^{exp.}$ (*Z*-form) − $\delta(^{17}O)^{exp.}$ (*E*-form).

Table 7. ^{17}O chemical shifts of enaminones **1g**, **2a** and **3g** at various concentrations

Concentration (M)	(*E*)-**1g**	(*Z*)-**1g**	(*E*)-**2a**	(*Z*)-**2a**	(*E*)-**3g**	(*Z*)-**3g**
0.1	506.1	478.1	476.9	462.2	—	—
0.2	505.3	478.4	475.5	459.1	502.0	—
0.5	504.3	475.7	473.7	454.8	502.8[b]	467.1[b]
1.0	503.6	476.0	471.7	453.8	502.9[b]	468.3[b]

[a] Measurement at 40 °C in acetonitrile solution, unless indicated otherwise.
[b] Measurement at 70 °C.

atoms. The ethyl group at C-1, as in the enaminones (*E*)-**2** and (*Z*)-**2**, causes a shielding of *ca.* −10 ppm compared with the corresponding C-1 methyl analogs (*E*) − **1** and (*Z*)-**1**, respectively. The ^{17}O chemical shifts of C-1 phenyl compounds (*E*)-**3** and (*Z*)-**3** are very close to those of the corresponding C-1 methyl analogs (*E*)-**1** and (*Z*)-**1**, indicating that the influence of C-1 phenyl group is very weak. That the C-1 phenyl group gave considerable shielding of *ca.* −34 ppm has been observed previously for C-2-unsubstituted enaminones.[11] The lack of the significant shielding effects of the C-1 phenyl group in enaminones (*E*)-**3** and (*Z*)-**3** reflects that the conjugation between the phenyl and C=O groups is absent owing to the steric interaction between H-3 and the phenyl in the *E-s-E-s-E* conformation or between Me-2 and the phenyl in the *Z-s-Z-s-E* conformation. In fact, previous x-ray crystallographic studies of (*E*)-PhCO(Me)CH=CHNH(*t*-Bu) show that the C-1 phenyl ring is twisted out the plane of O=C—C=C—N by 74.2°.[1]

The C-2 methyl group in enaminones (*E*)-**1** causes a deshielding of *ca.* 14 ppm for the carbonyls, whereas the C-2 methyl in (*Z*)-**1** shows no influence, as compared with the *E*- and *Z*-forms of the corresponding C-2-unsubstituted analogs MeCOCH=CHNHR,[11] respectively. The deshielding effect of the C-2 methyl observed for (*E*)-**1** can be attributed to the steric interaction between the C-2 methyl and the carbonyl group or the amino group, and also between the C-1 methyl and H-3, which reduces the conjugation by twisting the carbonyl or the amino groups out of the conjugation plane. A phenyl group at C-2 in enaminones (*Z*)-**4** causes a considerable deshielding, *ca.* 29 ppm, compared with the *Z*-form of the corresponding C-2-unsubstituted derivatives PhCOCH=CHNHR.[11] The deshielding is attributed to the steric interaction between the C-2 phenyl and the C-1 phenyl groups, and/or H-3. The x-ray crystal structure of (*Z*)-PhCO(Ph)CH=CHNH(*t*-Bu) shows that the enaminone moiety is essentially planar and both the C-1 and C-2 phenyl rings are twisted out the plane of O=C—C=C—N by 54.8° and 49.6°, respectively.[1]

The effects of N substituents in these compounds are similar to those previously noted for the corresponding 2-unsubstituted enaminones.[11] The enaminones with an alkyl group at the N atom has very similar chemical shifts. A marked deshielding (*ca.* 7 ppm) was noted for the enaminones with a benzyl group at the N atom. The NPh enaminones showed strong deshielding. This can be interpreted as a result of delocalization of the nitrogen electron lone pair to the phenyl ring.

It has been demonstrated that the influence of the substituents on the ^{17}O chemical shifts of the carbonyl groups in various enaminone systems is additive:[11]

$$\delta(^{17}O) = 462.2 + \sum \Delta_i(R_i) \quad (1)$$

where the Δ_i is the increment value of substituent R at the *i*-position. Since the torsion angle and Van der Waals repulsions caused by steric interactions can have a considerable influence on the ^{17}O chemical shift,[9] this additivity relationship is represented by

$$\delta(^{17}O) = C + \Delta_N(R_N) \quad (2)$$

where Δ_N is the increment value of substituent R at the N atom and C is a constant that can be deduced from the experimental $\delta(^{17}O)$ values and the known increment values Δ_N.[11] The constant *C* is dependent on the enaminone system, inter- and intramolecular hydrogen bonding, steric interactions and temperature.

The calculated ^{17}O chemical shifts for the carbonyl O atoms are included in Tables 1, 2, 5 and 6. The differences between the calculated and the experimental data, $\Delta\delta = \delta(^{17}O) - \delta(^{17}O)^{calc.}$, are also given in these tables. The $\Delta\delta$ values are in agreement generally within ±2 ppm. Considerable deviations of the $\Delta\delta$ values are observed for NH_2 and NHPh derivatives. The former may arise from the formation of intermolecular hydrogen bonding and the latter is attributed to steric repulsion between NPh and H-3.[11] The additivity relationship demonstrates that the C-2 substituent does not influence the shielding effect of the amino group to the carbonyl O atom and the n,π-conjugation between amino group and C=C double bond, suggesting that the N—C=C—C=O system is essentially planar. This is consistent with previous x-ray analyses of (*E*)-PhCO(Me)CH=CHNH(*t*-Bu) and (*Z*)-PhCO(Ph)CH=CHNH(*t*-Bu).[1]

Intramolecular hydrogen bonding

Intramolecular hydrogen bonding in a molecule generally causes shielding of O atoms.[9] The shielding of the O atom (−5 to −50 ppm) has been reported for various compounds.[1,9–14] The ^{17}O NMR data have

been shown to be sensitive to electronic effects, torsional angles, steric interactions and intramolecular hydrogen bonding.[9] Therefore, these factors should be taken into account for evaluating the contribution of intramolecular hydrogen bonding ($\Delta\delta_{HB}$ value).

The existences of both the *E*- and *Z*-isomers of the enaminones **1a**–**g** and **2a**–**g** are clearly shown by their ^{1}H, ^{13}C and ^{17}O NMR spectra. The ^{17}O signals of the *Z*-form appear at higher field than those of the *E*-form. The shift differences of between the *Z*- and *E*-forms, *ca.* −30 ppm, can be attributed to intramolecular hydrogen bonding ($\Delta\delta_{HB}$ value). The NH signals of the *Z*-form found at 9.5–12.3 ppm (Tables 1 and 2) indicate the presence of strong intramolecular hydrogen bonding. The ^{17}O shift values of (*E*)-**1g** and (*Z*)-**1g** alter only slightly upon dilution (Table 7), showing that the shielding of the ^{17}O shift value in the (*Z*)-form of the enaminones is not attributable to intermolecular hydrogen bonding. However, the electronic and torsional effects in the *E*- and *Z*-forms of the enaminones should be also considered. The additive influences of the N substituents on the ^{17}O chemical shifts of the carbonyl groups of the *E*- and *Z*-forms of enaminones **1** and **2** and the excellent linear relationships between the ^{1}H, ^{13}C and ^{17}O shift values of the *E*- and *Z*-forms with a near unity value of the slope (Table 8) demonstrate that the contributions of the electronic and torsional effects to the observed chemical shifts are essentially identical in the two forms. Therefore, the ^{17}O chemical shift differences between the *E*- and *Z*-forms of enaminones are mainly attributable to intramolecular hydrogen bonding. The $\Delta\delta_{HB}$ values for the amino compounds **1a** and **2a**, *ca.* 18 ppm, are smaller than those for their derivatives, *ca.* 28 ppm, suggesting the influence coming from intermolecular hydrogen bonding. The $\Delta\delta_{HB}$ values for enaminones **3** and **4** are obtained in a similar fashion. The $\Delta\delta_{HB}$ values of *ca.* −30 ppm are larger than those of the C-2-unsubstituted analogs (*ca.* −20 ppm),[11] but close to those of the 2-acetylenaminones (2, 2-diacetylethenamines) (*ca.* −30 ppm).[13]

The shielding effects ($\Delta\delta_{HB}$) of intramolecular hydrogen bonding of the type of NH···C=O, ranging from −4 to −47 ppm, have been reported previously for 2-aminoacetophenones,[18a] 1-aminoanthraquinones,[18b] 1-aminofluorenones,[18b], enaminones,[1,11,12] enamino diketones[13] and enamino diesters.[14] It is generally accepted that $\Delta\delta_{HB}$ values are an indication of the strength of hydrogen bonding.[9] The large values of $\Delta\delta_{HB}$ of *ca.* −30 ppm found in 1,2-disubstituted enaminones **1**–**4** indicate strong hydrogen bonds.

CONCLUSION

The present results demonstrate that the configuration and conformation of enaminones are influenced by the type of substituents at the C-1 and C-2 positions. The ^{1}H, ^{13}C and ^{17}O NMR data together with the previous x-ray analyses indicate that enaminones **1** and **2** exist in both the *E-s-E-s-E* and *Z-s-Z-s-E* conformations, enaminones **3** favor the *E-s-E-s-E* conformation and enaminones **4** dominate in the *Z-s-Z-s-E* conformation either in the solid state or in solution. The additive influences of N substituents on the ^{17}O shift values of enaminones

Table 8. Correlations of ^{17}O, ^{13}C and ^{1}H data between the *E*- and *Z*-forms of enaminones **1–4**

Correlation	Atom	Slope	Intercept	*n*	*r*	S.D.
(*E*)-**1** *vs.* (*Z*)-**1**	O	1.02	18.12	6[a]	0.995	1.33
	C-1	0.56	84.09	7	0.975	0.15
	C-2	1.11	−3.56	7	0.998	0.15
	C-3	0.92	9.66	7	0.999	0.21
	H-3	0.96	0.94	7	0.995	0.02
(*E*)-**2** *vs.* (*Z*)-**2**	O	1.07	−2.31	6[a]	0.995	1.31
	C-1	0.56	86.73	7	0.934	0.25
	C-2	1.08	−0.46	7	0.997	0.16
	C-3	0.90	11.75	7	0.9995	0.13
	H-3	0.97	0.94	7	0.995	0.02
(*E*)-**3** *vs.* (*Z*)-**3**	O[b]	1.01	32.85	6[a]	0.995	1.19
	C-1	0.55	87.42	6[a]	0.994	0.07
	C-2	1.04	4.12	6[a]	0.995	0.22
	C-3	0.93	9.25	6[a]	0.999	0.16
	H-3	1.07	−0.37	6[a]	0.996	0.02
(*E*)-**4** *vs.* (*Z*)-**4**	O[b]	0.76	141.6	5	0.981	2.14
(*E*)-**3** *vs.* (*Z*)-**4**	O	0.91	71.85	5	0.998	0.82
	C-1	0.71	58.31	5	0.993	0.08
	C-2	1.33	−38.43	5	0.997	0.18
	C-3	0.99	−1.26	5	0.999	0.18
	H-3	1.13	−1.06	5	0.998	0.02

[a] Point for NH_2 group was excluded.
[b] Data measured at 70 °C were taken.

1–4 demonstrate that the C-1 and C-2 substituents do not affect the conjugation of the amino group to the C=C—C=O moiety, and suggest that the N—C=C—C=O system is essentially planar. The existence of strong intramolecular hydrogen bonding in the *Z*-form of enaminones is evidenced by the shielding of the chelated carbonyl O atoms: $\Delta\delta_{HB}$ values of *ca.* −30 ppm, depending on the character, number and position of the substituents in the N—C=C—C=O system.

Experimental

Materials

Enaminones **1a–g** were prepared from the sodium salt of 3-hydroxymethylenebutan-2-one and **2a–g** from 2-hydroxymethylenepentan-3-one and the appropriate amine according to the literature method.[19]

General procedure for the preparation of 3a–g and 4b–g. To a solution of the corresponding β-diketone (10 mmol) in acetonitrile (10 ml) were added ammonia (aqueous solution, 33%, 2 ml), methylamine (ethanol solution, 33%, 2 ml), ethylamine (aqueous solution, 70%, 2 ml) or the appropriate amine (10 mmol). After 24 h at room temperature, the volatiles were removed under vacuum. The residue was triturated with hexane or diethyl ether and filtered to give the desired product (by ^{1}H NMR).

Compounds **1a**,[20] **1b–d**,[21] **1g**,[22] **2a**,[20] **2b**,[21] **2c**,[21] **3b**,[4a] **3d**,[23] **3f**,[23] **3g**,[4b] **4b**,[24] **4f**[23] and **4g**[4b] are known. Characterization of the remaining compounds is described below (chemical shifts in ppm; *J* in Hz). Melting points were observed under a microscope using a Mettler-FP-52 instrument.

(*E*)-1e. ^{1}H NMR, 7.22 (1H, d, J = 13.5, H-3), 4.38 (1H, br, HN), 3.05 (2H, t, J = 6.7, CH_2), 2.18 (3H, s, 1-Me), 1.78 (1H, m, C*H*Me$_2$), 1.68 (3H, s, 2-Me), 0.95 (6H, d, J = 6.7, CH*Me*$_2$); ^{13}C NMR, 194.70 (C-1), 106.70 (C-2), 149.62 (C-3), 56.30, 30.19 and 19.72 (NCH$_2$CHMe$_2$), 24.20 (1-Me), 8.49 (2-Me).

(*Z*)-1e. ^{1}H NMR, 9.85 (1H, br, HN), 6.55 (1H, d, J = 12.3, H-3), 2.96 (2H, t, J = 6.5, CH_2), 2.09 (3H, s, 1-Me), 1.81 (3H, s, 2-Me), 1.75 (1H, m, C*H*Me$_2$), 0.91 (6H, d, J = 6.7, CH*Me*$_2$); ^{13}C NMR, 197.61 (C-1), 98.79 (C-2), 152.92 (C-3), 56.83, 29.97 and 19.79 (NCH$_2$CHMe$_2$), 27.92 (1-Me), 17.21 (2-Me).

(*E*)-1f. ^{1}H NMR, 7.22–7.40 (5H, m), 7.32 (1H, dq, J = 13.0, 1.0, H-3), 4.60 (1H, br, HN), 4.43 (2H, d, J = 6.0, CH_2), 2.18 (3H, s, 1-Me), 1.70 (3H, s, 2-Me); ^{13}C NMR, 195.15 (C-1), 107.90 (C-2), 148.88 (C-3), 138.43, 128.90, 127.13, 127.85 and 52.12 (PhCH$_2$N), 24.27 (1-Me), 8.61 (2-Me).

(*Z*)-1f. ^{1}H NMR, 9.98 (1H, br, HN), 7.22–7.40 (5H, m), 6.62 (1H, d, J = 12.3, H-3), 4.34 (2H, d, J = 6.0, CH_2), 2.10 (3H, s, 1-Me), 1.82 (3H, s, 2-Me); ^{13}C NMR, 198.39 (C-1), 100.08 (C-2), 151.99 (C-3), 138.61, 128.85, 127.04, 127.50 and 52.28 (PhCH$_2$N), 28.04 (1-Me), 17.30 (2-Me).

(*E*)-2d. ^{1}H NMR, 7.34 (1H, dq, J = 13.4, 1.0, H-3), 4.09 (1H, br, HN), 3.50 (1H, m, C*H*Me$_2$), 2.52 (2H, t, J = 7.5, CH_2Me), 1.66 (3H, d, J = 1.0, 2-Me), 1.25 (6H, d, J = 6.3, CH*Me*$_2$), 1.12 (3H, t, J = 7.5, CH$_2$CH_3).

(*Z*)-2d. ^{1}H NMR, 9.72 (1H, br, HN), 6.63 (1H, dq, J = 12.5, 0.5, H-3), 3.37 (1H, m, C*H*Me$_2$), 2.39 (2H, t, J = 7.4, CH_2Me), 1.81 (3H, d, J = 0.5, 2-Me), 1.21 (6H, d, J = 6.3, CH*Me*$_2$), 1.09 (3H, t, J = 7.4, CH$_2$CH_3).

(*E*)-2e. ^{1}H NMR, 7.25 (1H, dq, J = 13.5, 1.0, H-3), 4.30 (1H, br, HN), 3.04 (2H, t, J = 6.5, NCH$_2$), 2.51 (2H, t, J = 7.5, CH_2Me), 1.74 (1H, m, C*H*Me$_2$), 1.68 (3H, d, J = 1.0, 2-Me), 1.12 (3H, t, J = 7.5, CH$_2$CH_3), 0.94 (6H, d, J = 6.7, CH*Me*$_2$).

(*Z*)-2e. ^{1}H NMR, 9.82 (1H, br, HN), 6.54 (1H, dq, J = 12.5, 0.5, H-3), 2.95 (2H, t, J = 6.5, NCH$_2$), 2.39 (2H, t, J = 7.4, CH_2Me), 1.80 (3H, d, J = 0.5, 2-Me), 1.74 (1H, m, C*H*Me$_2$), 1.09 (3H, t, J = 7.4, CH$_2$CH_3), 0.91 (6H, d, J = 6.7, CH*Me*$_2$).

(*E*)-2f. ^{1}H NMR, 7.23–7.38 (5H, m), 7.35 (1H, dq, J = 13.0, 1.0, H-3), 4.54 (1H, br, HN), 4.42 (2H, d, J = 6.0, NCH$_2$), 2.52 (2H, t, J = 7.5, CH_2Me), 1.70 (3H, d, J = 1.0, 2-Me), 1.11 (3H, t, J = 7.5, CH$_2$CH_3); ^{13}C NMR, 198.40 (C-1), 106.87 (C-2), 147.63 (C-3), 138.64, 128.85, 127.11, 127.76 and 52.05 (PhCH$_2$N), 29.40 and 10.19 (1-Et), 8.78 (2-Me).

(*Z*)-2f. ^{1}H NMR, 9.96 (1H, br, HN), 7.23–7.38 (5H, m), 6.61 (1H, dq, J = 12.3, 0.6, H-3), 4.33 (2H, d, J = 6.0, NCH$_2$), 2.40 (2H, t, J = 7.4, CH_2Me), 1.82 (3H, d, J = 0.6, 2-Me), 1.09 (3H, t, J = 7.4, CH$_2$CH_3); ^{13}C NMR, 201.05 (C-1), 99.66 (C-2), 151.64 (C-3), 138.64, 128.68, 127.11, 127.45 and 52.29 (PhCH$_2$N), 32.80 and 8.35 (1-Et), 16.67 (2-Me).

(*E*)-2g. ^{1}H NMR, 7.82 (1H, dq, J = 13.0, 1.0, H-3), 7.30–7.36 (2H, m), 6.95–7.05 (3H, m), 6.27 (1H, d, J = 13.0, HN), 2.66 (2H, t, J = 7.5, CH_2Me), 1.85 (3H, d, J = 1.0, 2-Me), 1.17 (3H, t, J = 7.5, CH$_2$CH_3); ^{13}C NMR, 199.59 (C-1), 112.77 (C-2), 138.64 (C-3), 141.02, 115.54, 129.73 and 119.99 (NPh), 29.85 and 9.92 (Et), 9.02 (2-Me).

(*Z*)-2g. ^{1}H NMR, 11.56 (1H, d, J = 12.0, HN), 7.26–7.30 (2H, m), 7.13 (1H, dq, J = 12.0, 0.6, H-3), 6.95–7.05 (3H, m), 2.50 (2H, t, J = 7.4, CH_2Me), 1.95 (3H, d, J = 0.6, 2-Me), 1.13 (3H, t, J = 7.4, CH$_2$CH_3); ^{13}C NMR, 202.70 (C-1), 103.17 (C-2), 141.56 (C-3), 140.88, 115.57, 129.59 and 122.47 (NPh), 33.33 and 8.14 (Et), 17.04 (2-Me).

(*E*)-3a. ^{1}H NMR, 7.30–7.43 (5H, m, Ph), 7.04 (1H, tq, J = 10.9, 1.0, H-3), 4.68 (1H, d,J = 10.9, HN), 1.81 (3H, d, J = 1.0, Me); ^{13}C NMR, 196.21 (C-1), 109.06 (C-2), 150.66 (C-3), 140.87, 128.19, 127.90 and 129.50 (1-Ph), 8.19 (2-Me).

(*E*)-3c. M.p. 105.6–106.6 °C; ^{1}H NMR, 7.42–7.47 (2H, m), 7.36–7.41 (3H, m), 6.98 (1H, dq, J = 14.0, 0.5, H-3), 4.60 (1H, br, HN), 3.19 (2H, qd, J = 7.3, 5.8, CH_2), 1.83 (3H, d, J = 0.5, 2-Me), 1.17 (3H, t, J = 7.3, Me); ^{13}C NMR, 194.89 (C-1), 106.55 (C-2), 153.88 (C-3), 141.30, 127.89, 128.26 and 129.25 (1-Ph), 8.94 (2-Me), 43.19 and 16.53 (EtN).

(*Z*)-3c. ^{1}H NMR, 7.42–7.47 (2H, m), 7.36–7.41 (3H, m), 6.88 (1H, d, J = 12.6, H-3), 10.35 (1H, br, HN), 3.31 (2H, qd, J = 7.3, 6.0, CH_2), 1.84 (3H, s, 2-Me), 1.27 (3H, t, J = 7.3, Me); ^{13}C NMR, 194.66 (C-1), 98.19 (C-2), 153.35 (C-3), 142.52, 126.82, 128.13 and 128.93 (1-Ph), 17.94 (2-Me), 43.73 and 14.67 (EtN).

(*E*)-3e. M.p. 125.2–125.9 °C; ^{1}H NMR, 7.42–7.46 (2H, m), 7.34–7.41 (3H, m), 6.93 (1H, dq, J = 14.0, 0.8, H-3), 4.59 (1H, br, HN), 2.95 (2H, t, J = 6.5, CH_2), 1.85 (3H, d, J = 0.8, 2-Me), 1.70 (1H, m, C*H*Me$_2$), 0.90 (6H, d, J = 6.7, CH*Me*$_2$); ^{13}C NMR, 194.83 (C-1), 106.27 (C-2), 154.36 (C-3), 141.36, 127.87, 128.28 and 129.23 (1-Ph), 8.95 (2-Me), 56.22, 30.07 and 19.62 (*i*-PrCH$_2$N).

(*Z*)-3e. ^{1}H NMR, 7.42–7.46 (2H, m), 7.34–7.41 (3H, m), 6.84 (1H, d, J = 12.4, H-3), 10.49 (1H, br, HN), 3.07 (2H, t, J = 6.5, CH_2), 1.84 (3H, d, J = 0.8, 2-Me), 1.77 (1H, m, C*H*Me$_2$), 0.97 (6H, d, J = 6.7, CH*Me*$_2$); ^{13}C NMR, 194.63 (C-1), 98.03 (C-2), 156.02 (C-3), 142.56, 126.88, 127.87 and 128.90 (1-Ph), 17.94 (2-Me), 57.10, 29.89 and 19.84 (*i*-PrCH$_2$N).

(*Z*)-4c. M.p. 136.4–137.2 °C; ^{1}H NMR, 10.65 (1H, br, HN), 7.21–7.29 (3H, m), 7.06–7.18 (5H, m), 7.14 (1H, d, J = 12.4, H-3), 6.98–7.02 (2H, m), 3.40 (2H, qd, J = 7.2, 6.0, CH_2), 1.32 (3H, t, J = 7.2, Me); ^{13}C NMR, 192.72 (C-1), 108.78 (C-2), 156.07 (C-3), 141.35, 127.40, 128.64 and 129.32 (1-Ph), 140.77, 128.02, 129.83 and 125.15 (2-Ph), 43.96 and 16.37 (Et).

(*Z*)-4d. M.p. 180.0–180.7 °C; ^{1}H NMR, 10.67 (1H, br, HN), 7.21–7.30 (3H, m), 7.07–7.19 (5H, m), 7.17 (1H, d, J = 13.0, H-3), 6.99–7.03 (2H, m), 3.57 (1H, m, C*H*Me$_2$), 1.34 (6H, d, J = 6.3, CH*Me*$_2$); ^{13}C NMR, 192.53 (C-1), 108.76 (C-2), 154.41 (C-3), 141.35, 127.38, 128.67 and 129.32 (1-Ph), 140.91, 128.03, 129.82 and 125.12 (2-Ph), 50.52 and 23.84 (*i*-Pr).

NMR spectra

The ^{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 acquisition and data management

were performed by an Aspect-2000 microcomputer. The instrumental settings were as follows: spectral width 50 kHz (1025 ppm), 2K data points, pulse width 33 μs, acquisition time 20 ms, preacquisition delay 5 μs, 150 000–300 000 scans, sample spinning (28 Hz). An even number (12–28) of left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8K words and exponentially multiplied with a 100 Hz line-broadening factor (LB) before being subjected to the FT. The chemical shifts δ_0, measured in 0.5 M acetonitrile solution at 40 °C at natural isotopic abundance, are reported relative to $\delta_0(H_2O)(= 0.0$ ppm); dioxane ($\delta_0 = 0$ ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shifts values is *ca.* ± 1 ppm.

The ^1H and ^{13}C NMR spectra (δ, in ppm relative to internal TMS in $CDCl_3$ solns. at 20 °C) were recorded on a Bruker DPX-400 spectrometer.

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