149. NMR of Enaminones

Part 7[1])

^{1}H-, ^{13}C-, and ^{17}O-NMR and X-Ray Structure Determinations of 1,2-Disubstituted Conjugated 3-[(*tert*-Butyl)amino]enones

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^{1}H-, ^{13}C-, and ^{17}O-NMR spectra for the 2-substituted enaminones MeC(O)C(Me)=CHNH(*t*-Bu) (**1**), EtC(O)C(Me)=CHNH(*t*-Bu) (**2**), PhC(O)C(Me)=CHNH(*t*-Bu) (**3**), and MeC(O)C(Me)=CHNH(*t*-Bu) (**4**) are reported. These data show that **3** exists mainly in the (*E*)-form, **4** in (*Z*)-form, and **1** and **2** as mixtures of both forms. Polar solvents favour the (*E*)-form. The (*Z*)- and (*E*)-forms exist in the 1,2-*syn*,3,*N*-*anti* and 1,2-*anti*,3,*N*-*anti* conformations **A** and **B**, respectively. The structures of the (*E*)- and (*Z*)-form are confirmed by X-ray crystal-structure determinations of **3** and **4**. The shielding of the carbonyl O-atom in the ^{17}O-NMR spectrum by intramolecular H-bonding ($\Delta\delta_{HB}$), ranging from -28 to -41 ppm, depends on the substituents at C(1) and C(2). Crystals of **3** at 90 K are monoclinic, with $a = 9.618(2)$ Å, $b = 15.792(3)$ Å, $c = 16.705(3)$ Å, and $\beta = 94.44(3)°$, and the space group is $P2_1/c$ with $Z = 8$ (refinement to $R = 0.0701$ on 3387 independent reflections). Crystals of **4** at 101 K are monoclinic, with $a = 16.625(8)$ Å, $b = 8.637(6)$ Å, $c = 11.024(7)$ Å, and $\beta = 101.60(5)°$, and the space group is *Cc* with $Z = 4$ (refinement to $R = 0.0595$ on 2106 independent reflections).

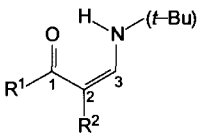
Introduction. – The properties and synthetic applications of enaminones[1]) have been extensively studied [2]. Theoretically, enaminones can exist in eight configurations and conformations owing to restricted rotations around the C=C bond and the C–C=O and C–N single bonds [2]. The configurational and conformational changes of enaminones depend on the nature, number, and position of the substituents. Attaching substituents at the C(2) position of enaminones should be accompanied by significant changes in the observed configurational and conformational properties and consequently affect the spectral parameters.

Various NMR spectroscopies have been widely applied to 2-unsubstituted enaminones [2]. Comparably, only a few ^{1}H- [3], ^{13}C- [4], and ^{15}N-NMR [4] [5] data of 2-substituted enaminones with primary and secondary animo groups have been reported so far. ^{17}O-NMR Spectroscopy has been found to be a particularly useful method for studying the bonding state of O-atoms and intramolecular H-bonding in molecules [6] [7]. The configurational and conformational changes should lead to a characteristic

[1]) Part 6: [1]. The general name enaminone is used for compounds containing the O=C–C=C–N moiety.

differentiation by shielding of O-atoms in a molecule. Recently H-bonded *N*-unsubstituted or *N*-monosubstituted enaminones were studied by ^{17}O-NMR spectroscopy [8] [9], establishing the influence of the nature, number, and position of substituents on the ^{17}O-NMR chemical shift of the carbonyl O-atom. Thus, the shielding of the carbonyl O-atom by intramolecular H-bonding ($\Delta\delta_{HB}$ value) ranged from -14 to -47 ppm, depending on the nature or the substituents.

To get further knowledge of the influence of the substituents on the configuration and conformation of enaminones and on the contribution to the shielding of carbonyl O-atoms from intramolecular H-bonding, ^{1}H-, ^{13}C-, and ^{17}O-NMR spectra of the 2-substituted enaminones **1**–**4** were investigated. Moreover, X-ray crystal-structure analyses of **3** and **4** were performed. The reason for choosing the *N*-(*t*-Bu)-substituted enaminones **1**–**4** was that the ^{1}H-NMR signals of the *t*-Bu group of the (*E*)- and (*Z*)-isomers were expected to be strong enough to detect very small amounts of (*E*)- or (*Z*)-isomers if present. The results show that the enaminones **1**–**4** exist either in mainly the (*E*)- or (*Z*)-form, or as a mixture of the two, depending on the substituents and solvents used.



1 $R^1 = R^2 = Me$
2 $R^1 = Et$, $R^2 = Me$
3 $R^1 = Ph$, $R^2 = Me$
4 $R^1 = R^2 = Ph$

Results and Discussion. – *^{1}H-NMR Spectra.* Enaminones **1**–**4** exist as mixtures of (*E*)- and (*Z*)-isomers, as shown by their NH signal in the ^{1}H-NMR spectra (*Table 1*). The NH signals of the (*E*)-form (4.35–6.75 ppm) appear at much higher field than those of the H-bonded (*Z*)-form (10.10–11.18 ppm). Populations of the isomers, estimated from the integral intensity of *t*-Bu and/or H–C(3) signals, depend on the substituents at C(1) and C(2) and on the solvent used. The 1-phenyl derivative **3** exists mainly in the (*E*)-form, and the 2-phenyl analogue **4** predominates in the (*Z*)-form with only traces of the (*E*)-form. The amount of the (*E*)-form is increased in highly polar solvents (CD_3CN, (D_6)DMSO, see *Table 1*).

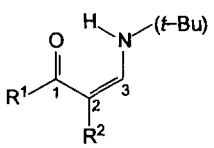
The conformation of enaminones **1**–**4** can be deduced from their ^{1}H-NMR data. In the (*Z*)-form, owing to the influence of strong intramolecular H-bonding, only the 1,2-*syn*,3,*N*-*anti*[2]) conformation **A** is present. In the (*E*)-form of enaminones **1** and **2**, H–C(3) (7.44 ppm) has a large coupling constant ($^3J = 14.0$ Hz) with NH and a small one ($^4J = 1.0$ Hz) with Me–C(2); both *J*'s are slight by enhanced compared to those found in the (*Z*)-form (6.74 ppm, $^3J = 13.0$ and $^4J = 0.6$ Hz). The large coupling constant indicates an *anti*[2]) conformation of the H–C–N–H moiety. Furthermore, the Me–C(2) signal (1.66 ppm) of the (*E*)-form is found at higher field than that of the (*Z*)-form (1.82 ppm). This is due to *van der Waals* effects of the nonbonded carbonyl group on Me–C(2) of the (*E*)-form and indicates that the C=C and C=O bonds are in *anti*[2]) position. Thus, the (*E*)-form of enaminones **1** and **2** exists in solution in the 1,2-*anti*, 3,*N*-*anti* conformation (**B**). This conclusion is further confirmed by NOE exper-

[2]) The descriptors *syn* and *anti* are short forms of *syn*-periplanar and *anti*-periplanar, respectively.

Table 1. *^{1}H-NMR Data of Enaminones* **1–4**. δ in ppm rel. to $SiMe_4$ (= 0 ppm), J in Hz.

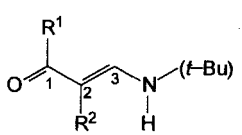
	Solvent	(*E*)/(*Z*)	Isomer	NH	H–C(3)	*t*-BuN	Me–C(2)
1	$CDCl_3$	1:1.9	(*E*)	4.36 (*d*, *J* = 14.0)	7.44 (*dq*, *J* = 14.0, 1.0)	1.33	1.66 (*d*, *J* = 1.0)
			(*Z*)	10.11 (*d*, *J* = 13.0)	6.74 (*dq*, *J* = 13.0, 0.6)	1.27	1.83 (*d*, *J* = 0.6)
2	$CDCl_3$	1:3.1	(*E*)	4.35 (*d*, *J* = 14.0)	7.47 (*dq*, *J* = 14.0, 1.0)	1.32	1.66 (*d*, *J* = 1.0)
			(*Z*)	10.10 (*d*, *J* = 13.0)	6.74 (*dq*, *J* = 13.0, 0.6)	1.27	1.82 (*d*, *J* = 0.6)
3	$CDCl_3$	3.9:1	(*E*)	4.64 (*d*, *J* = 14.0)	7.17 (*dq*, *J* = 14.0, 1.0)	1.21	1.82 (*d*, *J* = 1.0)
			(*Z*)	10.78 (*d*, *J* = 13.0)	7.03 (*d*, *J* = 13.0)	1.34	1.87 (*s*)
3	C_6D_6	4.6:1	(*E*)	4.26 (*d*, *J* = 14.0)	7.21 (*dq*, *J* = 14.0, 1.0)	0.71	1.98 (*d*, *J* = 1.0)
			(*Z*)	11.18 (*d*, *J* = 13.0)	6.98 (*dq*, *J* = 13.0, 0.6)	0.90	1.89 (*d*, *J* = 0.6)
3	CD_3CN	27:1	(*E*)	5.39 (*d*, *J* = 14.0)	7.16 (*dq*, *J* = 14.0, 1.0)	1.16	1.76 (*d*, *J* = 1.0)
			(*Z*)	10.75 (*d*, *J* = 13.0)	7.19 (*dq*, *J* = 13.0, 0.6)	1.32	1.81 (*d*, *J* = 0.6)
3	$(D_6)DMSO$	39:1	(*E*)	6.75 (*d*, *J* = 14.0)	7.11 (*dq*, *J* = 14.0, 1.0)	1.11	1.73 (*d*, *J* = 1.0)
			(*Z*)	10.74 (*d*, *J* = 13.0)	–	1.29	1.79 (*s*)
4	$CDCl_3$	1:11	(*E*)	5.13 (*d*, *J* = 15.0)	7.58 (*d*, *J* = 15.0)	1.38	–
			(*Z*)	11.07 (*d*, *J* = 13.3)	7.26 (*d*, *J* = 13.3)	1.19	–
4	C_6D_6	–	(*Z*)	11.46 (*d*, *J* = 13.0)	7.12 (*d*, *J* = 13.0)	0.86	–
4	CD_3CN	–	(*Z*)	11.02 (*d*, *J* = 13.3)	7.37 (*d*, *J* = 13.3)	1.38	–
4	$(D_6)DMSO$	1:4.0	(*E*)	6.50 (*d*, *J* = 15.0)	7.47 (*d*, *J* = 15.0)	1.20	–
			(*Z*)	11.11 (*d*, *J* = 13.5)	7.48 (*d*, *J* = 13.5)	1.42	–

iments: irradiation of the Me–C(2) signal assigned to (*E*)-**1** yields a NOE effect of 19% for the NH signal, and on irradiation of Me–C(1) of (*E*)-**1**, a NOE effect of 15% is observed for the H–C(3) signal.



(*Z*): 1,2-*syn*,3,*N*-*anti*

A



(*E*): 1,2-*anti*,3,*N*-*anti*

B

The ^{1}H-NMR spectrum of enaminone **3** in $CDCl_3$ shows that in the (*E*)-form, the two couplings (^3J = 14.2 and ^4J = 1.0 Hz) for H–C(3) are essentially identical to those found for the (*E*)-form of enaminones **1** and **2**. On irradiation of Me–C(2), a NOE effect of 9% is observed for the NH signal, and irradiation of H–C(3) yields a NOE effect of 5.9% at the *t*-Bu and of 7.3% at the H–C(2′) signal (*i.e.*, H_{ortho} of Ph at 7.45 ppm). These results demonstrate that (*E*)-**3** exists also in the 1,2-*anti*,3,*N*-*anti* conformation **B**.

In the (*E*)-form of enaminone **4**, a large coupling constant (^3J = 15.0 Hz) for H–C(3) (7.58 ppm) and a small chemical-shift difference of H–C(3) between the (*E*)- and (*Z*)-forms (0.32 ppm) suggest that the 1,2-*anti*,3,*N*-*anti* conformation **B** is preferred.

^{13}C-NMR Spectra. The ^{13}C-NMR spectra of the enaminones **1**–**4** were recorded in $CDCl_3$ solution (*Table 2*). The peak assignments to the (*E*)- and (*Z*)-forms of **1**–**4** are achieved on the basis of unequal signal intensities and are confirmed by selective $^{13}C\{^1H\}$ decoupling experiments. They are in agreement with those reported for corresponding analogs [8][10]. The 1,2-*anti*,3,*N*-*anti* conformation **B** of (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** is supported by the δ values of *Me*–C(2), the corresponding signal of the (*E*)-form appearing at higher field (*ca.* 8.5 ppm) than those of the (*Z*)-form (*ca.* 17.5 ppm). This is attributed to repulsive *van der Waals* interactions [11] of the nonbonded carbonyl group with Me–C(2), indicating the *anti* conformation of the C=C and C=O bonds in the (*E*)-form. The shielding due to *van der Waals* effects is also observed for (*E*)-**4**. In enaminone **4**, the signal of C(1′) of Ph–C(2) (*i.e.*, C_{ipso}; 135.61 ppm) of the (*E*)-form is also displaced to higher field than that of the (*Z*)-form (141.17 ppm). This indicates that the C=C and C=O bonds in the (*E*)-form of **4** also exist in the *anti* conformation, *i.e.*, conformation **B**, in agreement with the results inferred from ^1H-NMR data.

Table 2. *^{13}C-NMR Data of Enaminones* **1**–**4** *in $CDCl_3$.* δ in ppm rel. to $SiMe_4$ (= 0 ppm).

	Isomer	C(1)	C(2)	C(3)	*t*-BuN	R^1	R^2
1	(*E*)	194.65	106.02	144.03	51.97, 30.47	24.31	8.42
	(*Z*)	197.27	98.87	147.86	51.41, 30.22	28.13	17.60
2	(*E*)	198.09	106.22	142.97	51.87, 30.47	29.53, 10.30	8.55
	(*Z*)	200.05	98.45	147.71	51.32, 30.22	32.70, 8.34	16.97
3	(*E*)	194.81	106.76	149.13	52.13, 30.24	141.36, 127.83, 128.31, 129.31	8.82
	(*Z*)	194.24	97.99	151.11	51.90, 30.24	142.68, 126.89, 127.83, 128.84	18.30
4	(*E*)	192.91	112.77	148.00	52.35, 30.07	141.31, 127.69, 128.99, 129.54	135.61, 128.61, 130.58, 126.76
	(*Z*)	192.26	108.58	152.11	52.39, 30.12	141.41, 127.34, 128.65, 129.24	141.17, 128.03, 129.84, 125.09

^{17}O-NMR Spectra. The ^{17}O-NMR spectra of enaminones **1**–**4** were recorded in MeCN and $CDCl_3$ solutions (*Table 3*). In MeCN, **1** and **2** show two carbonyl O-signals at *ca.* 440 and *ca.* 470 ppm, in accord with the existence of a (*E*)/(*Z*) mixture. The attribution of the O-signals to the (*Z*)- and (*E*)-isomers is achieved by means of the shielding effect due to intramolecular H-bonding [6–9]. The existence of mainly the (*E*)-form of **3** and the (*Z*)-form of **4** in MeCN solution is confirmed by their ^{17}O-NMR spectra. Enaminone **3** shows a large carbonyl O-signal (477.6 ppm) and a small carbonyl O-signal (440.0 ppm) at 70°, and one carbonyl O-signal (474.1 ppm) at 40°. Inverse results are observed for **4**, *i.e.*, a small carbonyl O-signal (480.1 ppm) and a large carbonyl O-signal (443.9 ppm) at 70°, and one carbonyl O-signal (440.8 ppm) at 40°. In $CDCl_3$ solution, the carbonyl O-signals are shifted to higher field relative to those shown in MeCN solution, by *ca.* 8 ppm for the carbonyl O-atoms of the (*E*)-form, and by *ca.* 14 ppm for the carbonyl O-atoms of the Z-form.

The results of *Table 3* show that the $\delta(^{17}O)$ values are influenced by the nature of the substituents. The $\delta(^{17}O)$ of the Ph–C(1) compound (*E*)-**3** is very close to that of the Me–C(1) analogue (*E*)-**1**, indicating no influence of the Ph substituent at C(1). A considerable shielding of *ca.* −34 ppm caused by the Ph–C(1) group has been previously observed for 2-unsubstituted enaminones [8]. The lack of an effect due to Ph–C(1) in (*E*)-**3** suggests that the conjugation between the Ph and C=O groups is absent and

Table 3. *^{17}O-NMR Data of Enaminones* **1**–**4**[a]). δ in ppm rel. to H_2O (= 0 ppm), J in Hz.

	Solvent	(*E*)-isomer	(*Z*)-isomer	$\Delta\delta_{HB}$[b])
1	MeCN	474.8 (190)	446.4 (150)	−28.4
2	MeCN	464.9 (240)	437.1 (190)	−27.8
3	MeCN	474.1 (440)	–	−37.0[c])
3	MeCN	477.6 (300)[d])	440.0 (300)[d])	−37.6
4	MeCN	–	440.8 (540)	−35.8[c])
4	MeCN	480.1 (170)[d])	443.9 (530)[d])	−36.2
1	$CDCl_3$	467.0 (210)	432.7 (270)	−34.3
2	$CDCl_3$	456.0 (120)	424.6 (320)	−31.4
3	$CDCl_3$	465.3 (680)	424.3 (590)	−41.0
4	$CDCl_3$	–	427.8 (1030)	−40.0[c])

[a]) Measurement at 40° unless indicated otherwise, line-width at half-height in parentheses. [b]) $\Delta\delta_{HB} = \delta$((*Z*)-isomer) – δ((*E*)-isomer), unless indicated otherwise. [c]) Estimated value, see text. [d]) Measurement at 70°.

indicates that the Ph group is twisted out of the plane of the C=C–C=O system owing to the steric interaction between H–C(3) and Ph. X-Ray crystallographic studies show that Ph–C(1) is twisted out of the plane of O=C–C=C–N by 117.3 and 74.2° for the two molecules A and B of (*E*)-**3**, respectively (see below, *Fig. 1*).

The Me group at C(2) of enaminone (*E*)-**1** causes a deshielding of *ca.* 16 ppm for the carbonyl O-atom, whereas Me–C(2) of (*Z*)-**1** shows a deshielding of *ca.* 1 ppm, as compared with the (*E*)- and (*Z*)-forms of the corresponding 2-unsubstituted analogs MeC(O)CH=CHNH(*t*-Bu) in MeCN solution [8], respectively. The deshielding effect of Me–C(2) observed for (*E*)-**1** can be attributed to steric interaction between Me–C(2) and the carbonyl group or the amino group, and between Me–C(1) and H–C(3), which reduce the conjugation owing to twisting of the carbonyl or the amino groups out of the plane of the conjugation system. A Ph group at C(2) in enaminone (*Z*)-**4** causes a considerable deshilding, *ca.* 30 ppm, as compared with the (*Z*)-form of the 2-unsubstituted derivative PhC(O)CH=CHNH(*t*-Bu) [8]. The deshilding is attributed to the steric interaction between Ph–C(2) and Ph–C(1), and/or H–C(3) in the 1,2-*syn*,3,*N*-*anti* conformation **A**, and suggests that both Ph groups are twisted out of the plane of C=C–C=O. The X-ray crystal structure of (*Z*)-**4** shows that the enaminone moiety is essentially planar, and the dihedral angles between the aromatic rings of both Ph–C(1) and Ph–C(2) and the plane of O=C–C=C–N are 54.8 and 49.6°, respectively (see below, *Fig. 2*).

Intramolecular Hydrogen Bonding. Intramolecular H-bonding in a molecule generally causes shielding of the O-atom [6]. This shielding (−5 to −50 ppm) has been reported for various compounds [1] [6–9] [12–14]. The existence of both (*E*)- and (*Z*)-isomers of the enaminones **1** and **2** is clearly shown by their ^{1}H-, ^{13}C-, and ^{17}O-NMR spectra. The O-signals of the (*Z*)-form appear at higher field than those of the (*E*)-form. The shift differences of *ca.* −30 ppm can be attributed to intramolecular H-bonding ($\Delta\delta_{HB}$ value; see *Table 3*). The NH signals of the (*Z*)-form found at 10.1 ppm (*Table 1*) indicate the presence of strong intramolecular H-bonding. The $\Delta\delta_{HB}$ values of *ca.* −30 ppm are slightly

larger than those of 2-unsubstituted analogs (*ca.* −20 ppm) [8] and close to those of 2-(aminomethylidene)-1,3-diones (2,2-diacetylethenamines; *ca.* −30 ppm) [12].

Similarly, the shielding effect of the intramolecular H-bonding in enaminone **3** was obtained: −41.00 ppm in $CDCl_3$ and −37.6 ppm in MeCN at 70° (*Table 3*). In MeCN at 40°, the carbonyl O-signal of the (*Z*)-form was not observed. Since $\delta(^{17}O)$ of (*Z*)-**3** (424.3 ppm) in $CDCl_3$ solution is close to that of (*Z*)-**2** (424.6 ppm), the contribution of the intramolecular H-bonding ($\Delta\delta_{HB} = -37$ ppm) in MeCN can be inferred from the chemical-shift difference between (*E*)-**3** (474.1 ppm) and (*Z*)-**2** (437.1 ppm). The $\Delta\delta_{HB}$ value estimated for (*E*)-**3** at 40° is in good agreement with that at 70° calculated from the shift difference between the (*Z*)- and (*E*)-form of **3**.

The $\Delta\delta_{HB}$ value for enaminones (*Z*)-**4** in MeCN at 70° is 36.2 ppm (*Table 3*). In MeCN at 40° and in $CDCl_3$, the $\Delta\delta_{HB}$ values can be estimated from the shift differences between (*Z*)-**4** and the corresponding (*E*)-**3**. The contribution of Ph–C(2) to the observed carbonyl $\delta(^{17}O)$ should be taken into account. The effect of Ph–C(2) contributes to the estimated $\Delta\delta_{HB}$ value for (*Z*)-**4** by 2.5 ppm deshielding, based on the chemical shift of (*E*)-**4** and (*E*)-**3**. It has been shown that the torsional effects can considerably influence $\delta(^{17}O)$ [6]. X-Ray analyses of (*Z*)-**4** and (*E*)-**3** show that their C=O, C=C, and C–N bond lengths and relevant bond angles are essentially identical. Therefore, the torsional effects can be reasonably negligible. The $\Delta\delta_{HB}$ value for (*Z*)-**4** in MeCN at 40° (−35.8 ppm), corrected for the effect of Ph–C(2) and estimated from the shift differences between (*Z*)-**4** and the (*E*)-**3**, is very close to that at 70° (−36.2 ppm). This demonstrates that the estimated $\Delta\delta_{HB}$ value is reasonable and acceptable. Similarly, the $\Delta\delta_{HB}$ value in $CDCl_3$ is −40.0 ppm.

Shielding effects ($\Delta\delta_{HB}$) of intramolecular H-bonding of the type of NH ··· C=O, ranging from −4 to −47 ppm, have been previously reported for enaminones [8] [9], 2-(aminomethylidene)-1,3-diones [12], 2-(aminomethylidene)propanedioic diesters [13], 2′-aminoacetophenones [14a], 1-aminoanthraquinones [14b], and 1-amino-9*H*-fluoren-9-ones [14b]. It is generally admitted that $\Delta\delta_{HB}$ values indicate the strength of the H-bond [6]. The high $\Delta\delta_{HB}$ values (−27 to −41 ppm) found in 1,2-disubstituted enaminones **1**–**4** indicate a strong H-bond.

X-Ray Crystallography. The results gathered from the NMR data show that in solution, the (*Z*)-enaminones have the 1,2-*syn*,3,*N*-*anti* structure **A** and the (*E*)-enaminones the 1,2-*anti*,3,*N*-*anti* conformation **B**. Owing to steric interactions between the substituents at C(1) and C(2) in **A** and between the substituent at C(1) and H–C(3) and between the substituent at C(2) and the C=O group in **B**, the substituents at C(1) and C(2) are twisted out of the plane of C=C–C=O. To complete the informations on the conformation of enaminones, X-ray crystal-structure determinations were carried out for **3** at 90 K and for **4** at 101 K (*Table 4*). *Tables 5–8* summarize the bond lengths and bond angles, and ORTEP views of enaminones **3** and **4** are shown in *Figs. 1* and *2*, respectively[3]).

In the solid state, enaminone **3** has two independent molecules A and B which have virtually identical structures; corresponding bond lengths involving non-H-atoms agree

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[3]) Supplementary crystallographic data have been deposited with the *Cambridge Crystallographic Data Center* as publication No. CCDC-10/58 and can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 4. *Crystal Data and Structure Refinements for Enaminones* **3** *and* **4**

	3	**4**
Formula	$C_{14}H_{19}NO$	$C_{19}H_{21}NO$
M	217.30	279.37
Temperature	90(2) K	101(2) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	Cc
a[Å]	9.618(2)	16.625(8)
b[Å]	15.792(3)	8.637(6)
c[Å]	16.705(3)	11.024(7)
β[deg]	94.44(3)	101.60(5)
V[Å^3]	2529.5(9)	1551(2)
Z	8	4
d[g/cm]	1.141	1.197
Absorption coefficient [mm^{-1}]	0.553	0.567
$F(000)$	944	600
θ Range for data collection	3.86 to 57.09°	5.43 to 57.13°
Index ranges	$-5 \le h \le 10$ $-17 \le k \le 17$ $-19 \le l \le 18$	$-18 \le h \le 18$ $-9 \le k \le 9$ $-12 \le l \le 12$
Reflections collected	7929	2598
Independent reflections	3387 ($R_{int} = 0.1145$)	2106 ($R_{int} = 0.1343$)
Refinement method	full-matrix least squares on F^2	
Data, restraints, parameters	3387, 0, 340	2106, 2, 218
Goodness-of-fit on F^2	0.811	1.023
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0701$, $wR2 = 0.1788$	$R1 = 0.0595$, $wR2 = 0.1453$
R indices (all data)	$R1 = 0.0727$, $wR2 = 0.1823$	$R1 = 0.0600$, $wR2 = 0.1462$
Extinction coefficient	0.033 (2)	0.0037 (8)
Largest diff. peak and hole	0.658 and -0.540 eÅ^{-3}	0.191 and -0.166 eÅ^{-3}

Table 5. *Selected Bond Lengths* [Å] *for Enaminone* **3**. Arbitrary numbering (s. *Fig. 1*).

Bond	Length	Bond	Length
Molecule A:		Molecule B:	
O(11)–C(11)	1.250(3)	O(21)–C(21)	1.252(3)
C(11)–C(12)	1.432(4)	C(21)–C(22)	1.425(3)
C(12)–C(13)	1.375(3)	C(22)–C(23)	1.366(3)
C(13)–N(11)	1.334(3)	C(23)–N(21)	1.332(3)
N(11)–H(11)	0.89(3)	N(21)–H(21)	0.88(3)
C(13)–H(13)	0.99(3)	C(23)–H(23)	0.95(3)
C(11)–C(18)	1.510(3)	C(21)–C(28)	1.512(3)
C(12)–C(114)	1.502(3)	C(22)–C(214)	1.511(3)
N(11)–C(14)	1.481(3)	N(21)–C(24)	1.480(3)
C(14)–C(15)	1.524(3)	C(24)–C(25)	1.522(3)
C(14)–C(16)	1.528(3)	C(24)–C(26)	1.519(4)
C(14)–C(17)	1.525(3)	C(14)–C(27)	1.521(3)

Table 6. *Selected Bond Angles* [°] *for Enaminone* **3**. Arbitrary numbering (s. *Fig. 1*).

Angle	Value	Angle	Value
Molecule A:		Molecule B:	
O(11)–C(11)–C(12)	122.1(2)	O(21)–C(21)–C(22)	122.8(2)
C(11)–C(12)–C(13)	119.3(2)	C(21)–C(22)–C(23)	119.7(2)
C(12)–C(13)–N(11)	127.7(2)	C(22)–C(23)–N(21)	126.9(2)
C(13)–N(11)–C(14)	122.8(2)	C(23)–N(21)–C(24)	123.8(2)
C(11)–C(12)–C(114)	117.6(2)	C(21)–C(22)–C(214)	119.5(2)
C(13)–C(12)–C(114)	122.7(2)	C(23)–C(22)–C(214)	120.7(2)
O(11)–C(11)–C(18)	116.6(2)	O(21)–C(21)–C(28)	116.6(2)
C(12)–C(11)–C(18)	121.2(2)	C(22)–C(21)–C(28)	120.6(2)
N(11)–C(14)–C(15)	109.5(2)	N(21)–C(24)–C(25)	110.1(2)
N(11)–C(14)–C(16)	110.5(2)	N(21)–C(24)–C(26)	110.2(2)
N(11)–C(14)–C(17)	107.3(2)	N(21)–C(24)–C(27)	107.1(2)

Table 7. *Selected Bond Lengths* [Å] *for Enaminone* **4**. Arbitrary numbering (s. *Fig. 2*).

Bond	Length	Bond	Length
O(1)–C(1)	1.252(3)	C(2)–C(14)	1.486(4)
C(1)–C(2)	1.436(2)	C(1)–C(8)	1.497(4)
C(2)–C(3)	1.398(3)	N(1)–C(4)	1.483(4)
C(3)–N(1)	1.319(1)	C(4)–C(5)	1.504(5)
C(3)–H(3)	0.97(3)	C(4)–C(6)	1.529(4)
N(1)–H(1)	0.99(4)	(C4)–C(7)	1.516(5)

Table 8. *Selected Bond Angles* [°] *for Enaminone* **4**. Arbitrary numbering (s. *Fig. 2*).

Angle	Value	Angle	Value
O(1)–C(1)–C(2)	122.4(2)	C(2)–C(1)–C(8)	120.4(2)
C(1)–C(2)–C(3)	120.0(3)	N(1)–C(4)–C(5)	111.8(2)
C(2)–C(3)–N(1)	125.3(3)	N(1)–C(4)–C(6)	106.8(3)
C(3)–N(1)–C(4)	127.0(2)	N(1)–C(4)–C(7)	107.3(2)
C81)–C(2)–C(14)	122.9(2)	C(5)–C(4)–C(6)	110.7(3)
C(3)–C(2)–C(14)	117.1(3)	C(5)–C(4)–C(7)	110.6(3)
O(1)–C(1)–C(8)	117.1(2)	C(6)–C(4)–C(7)	109.6(3)

within 0.009 Å and bond angles within 2.6°. Both exist in the 1,2-*anti*,3,*N*-*anti* conformation **B** with (*E*)-configuration and exhibit an intermolecular H-bond between the C=O O-atom in one molecule and the NH proton and one proton of Me–C(2) in the other (O ··· *H*N 2.15 Å; O ··· *H*–CH_2–C(2) 2.44 Å). As expected, enaminone **4** exists in the 1,2-*syn*,3,*N*-*anti* conformation **A** with (*Z*)-configuration and exhibits a strong intramolecular H-bond, as evidenced by the lengths of O ··· H (1.80 Å) and O ··· N (2.636 Å). In both **3** and **4** the enaminone moiety O=C–C=C–NH is essentially coplanar except for O, which shows a slight deviation from the least-square plane: a torsion angle O=C–C=C of 170.1 and −171.8° is observed for molecules A and B, respectively, of **3** and of 7.2° for **4**.

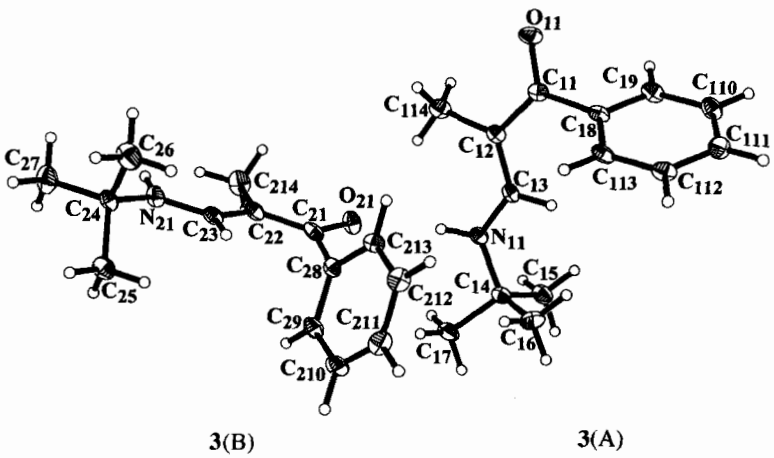

Fig. 1. *ORTEP Views of enaminone* **3**. Arbitrary numbering.

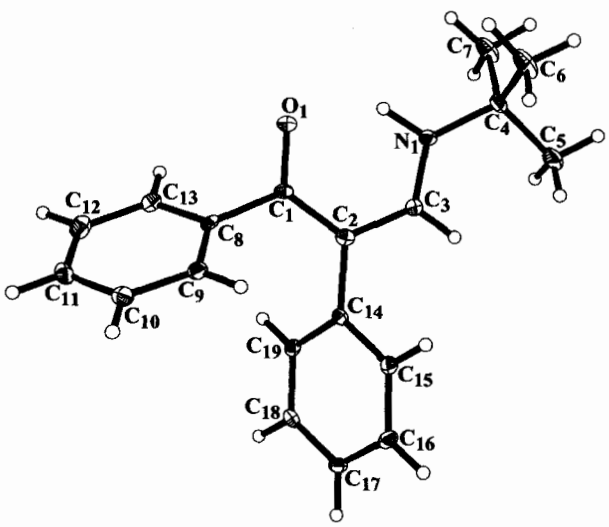

Fig. 2. *ORTEP Views of enaminone* **4**. Arbitrary numbering.

X-Ray crystallographic analyses [15] have shown that *N,N*-disubstituted enaminones are more delocalized than the corresponding *N,N*-disubstituted enamines [16]. The more extended delocalization also exists in *N*-monosubstituted enaminones **3** and **4**, as reflected in the bond lengths O=C, C=C, and =C–N (*Tables 5* and *7*). The =C–N bond (**3**: 1.334 (A) and 1.332 Å (B); **4**: 1.319 Å) is shorter, and the C=C bond (**3**: 1.375 (A) and 1.366 Å (B); **4**: 1.398 Å) is longer than those found for *N,N*-disubstituted enamines (=C–N 1.38–1.41 Å; C=C 1.33–1.37 Å) [16]. They are close to those reported *N,N*-disubstituted enaminones (=C–N 1.34–1.38 Å; C=C 1.37–1.39 Å) [15] [17], but the O=C bond (**3**: 1.250 (A) and 1.252 Å (B); **4**: 1.252 Å) is slightly longer than those for the latter (1.22–1.24 Å) [15] [17]. The shorter length of the =C–N bond and longer

lengths of the C=C and C=O bonds have been previously noted in several intramolecularly H-bonded 3-methyl-enaminones [18], and suggest that the electron distribution in *N*-monosubstituted enaminones is slightly more delocalized than in *N*,*N*-disubstituted analogs.

It should be noted that the relevant bond angles of the enaminone moiety in compounds **3** and **4** are essentially identical, whereas the C=C bond is slightly shorter and the C–N bond is slightly longer in **3** than in **4**; the O=C bond and C–C single bond in both compounds are very close. The differences between **3** and **4** in bond lengths C=C and C–N may be attributed to the influence of the intramolecular H-bond in the latter and may indicate that the delocalization in the latter is slightly higher than in the former.

The Ph groups in each compound are virtually planar. As expected the aromatic ring of Ph–C(1) is twisted out of the mean plane of the O=C–C=C–NH system; by 117.3 (A) and 74.2° (B) for **3** and by 54.8° for **4**. The dihedral angle for the ring of Ph–C(2) in **4** to the plane is 49.6°. They are in good agreement with the results obtained from NMR data.

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Experimental Part

General. M.p.: *Mettler-FP-52* instrument (microscope). ^{1}H- and ^{13}C-NMR Spectra: *Bruker-DPX-400* spectrometer at 400.13 and 100.62 MHz, resp. $CDCl_3$ solns. at 20°; δ in ppm rel. to $SiMe_4$ (= 0 ppm), J in Hz.

^{17}O-NMR Spectroscopy. 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 50000 Hz (1025 ppm), 2 K data points, pulse width 33 µs, acquisition time 20 ms, preacquisition delay 5 µs, 200000–4200000 scans, sample spinning (28 Hz). An even number (12–28) left-shifts (LS) were applied to 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 $\delta(^{17}O)$, measured in 0.4–0.6M MeCN or $CDCl_3$ soln. at natural isotopic abundance, are reported rel. to H_2O (= 0.0 ppm); dioxane ($\delta(^{17}O)$ = 0 ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shifts values is *ca.* ± 1 ppm.

Structure Determination for **3** *and* **4**. Crystal properties and details of the data collections are given in *Table 4*. Cell dimensions and intensities were measured on a *Syntex-P2$_1$* diffractometer equipped with copper radiation. The data were corrected for the variation of experimental conditions as well as *Lorentz* and polarization effects. For the structure solution, refinement, and representation, the SHELXTL system was used [19]. All non-H-atoms were refined anisotropically. Ideal positions were imposed on the H-atoms, but their isotropic displacement parameters were refined.

4-[(1,1-Dimethylethyl)amino]-3-methylbut-3-en-2-one (**1**) [20] *and 1-[(1,1-Dimethylethyl)amino]-2-methylbut-1-en-3-one* (**2**) were prepared from the sodium salt of 4-hydroxy-3-methylbut-3-en-2-one and 1-hydroxy-2-methylpent-1-en-3-one, resp. and *tert*-butylamine according to [21].

3-[(1,1-Dimethylethyl)amino]-2-methyl-1-phenylprop-2-en-1-one (**3**). *tert*-Butylamine (10 mmol) was added to a soln. of 3-hydroxy-2-methyl-1-phenylprop-2-en-1-one (10 mmol) in MeCN (10 ml). The mixture was left at r.t. for 24 h and then evaporated. The residue was treated with Et_2O and recrystallized from MeCN: 1.95 g (90%) of **3**. M.p. 134.3–134.9°.

3-[(1,1-Dimethylethyl)amino]-1,2-diphenylprop-2-en-1-one (**4**). As described for **3**, from 3-hydroxy-1,2-phenylprop-2-en-1-one and *tert*-butylamine. Yield 93%. M.p. 175.3–176.5° ([22]: 176–178°).

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