

NMR of Enaminones Part 3†— ^1H , ^{13}C and ^{17}O NMR Spectroscopic Studies of Acyclic and Cyclic *N*-Aryl Enaminones: Substituent Effects and Intramolecular Hydrogen Bonding

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^{17}O , ^{13}C and ^1H NMR spectra for *para*- and *meta*-substituted 4-arylamino-pent-3-en-2-ones (acyclic enaminones, 1 and 2) and 3-arylamino-cyclohex-2-en-1-ones (cyclic enaminones, 3 and 4) are reported. The ^{17}O , ^{13}C and ^1H shift values of these enaminones correlate well with σ_m^0 and σ_p^- constants in the correlations for *meta* and *para* derivatives, and with $\text{p}K_a$ values of the corresponding anilines. Dual substituent parameters analyses were also performed. Correlations of ^{17}O and ^{13}C chemical shifts of the carbonyl groups with those of the corresponding *N*-acylanilines indicate that the enaminone moiety as a whole has electronic properties similar to those of the RCONH group. The ^{17}O shift values of the carbonyl O atoms of enaminones correlate well with their ^1H and ^{13}C data. Shieldings of 33–45 ppm for O atoms are observed for 1 and 2 compared with 3 and 4, respectively. This is attributed to intramolecular hydrogen bonding. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Enaminones are important organic intermediates² and have been reported to have potential biological activity.³ Recently, the ^{17}O NMR spectra of some enaminones have been reported^{1,4} in which the ^{17}O chemical shifts were shown to be sensitive to the nature, number and position of the substituents and intramolecular hydrogen bonding. The shielding of O by the intramolecular hydrogen bonding components, ranging from 14 to 47 ppm, depends on the nature of the substituents.⁴ The ^{17}O , ^{13}C -2 and ^1H -2 data for enaminones have been shown to correlate with each other and with the $\text{p}K_a$ values of the amines.^{1,4}

NMR substituent-induced chemical shifts (SCS) have been much investigated in aromatic systems.^{5,6} The SCS values of various nuclei have been analyzed by using Hammett substituent constants⁷ [Eqn (1)] and/or dual substituent parameter (DSP)⁸ [Eqn (2)] and DSP-NLR (DSP-nonlinear resonance effect)^{6b} [Eqn (3)]:

$$\delta = \delta^0 + \rho\sigma \quad (1)$$

$$\delta = \delta^0 + \rho_I\sigma_I + \rho_R\sigma_R \quad (2)$$

$$\delta = \delta^0 + \rho_I\sigma_I + \rho_R\sigma_R^0/(1 - \epsilon\sigma_R^0) \quad (3)$$

The transmission of substituent effects in $\text{XC}_6\text{H}_4\text{ZCH}=\text{CH}_2$ ($\text{Z} = \text{O}, \text{S}, \text{Se}$ or Te)⁹ and $\text{XC}_6\text{H}_4\text{ZC(R)}=\text{O}$ ($\text{Z} = \text{O}$ or NH)¹⁰ series have been investigated. However, the SCS for enaminone systems $\text{XC}_6\text{H}_4\text{NHCR}=\text{CHC(R)}=\text{O}$, which can be considered as a combination of the two series mentioned, have not been systematically examined so far.

In order to examine the transmission of *N*-aryl substituent effects to enaminone moiety and to evaluate the sensitivity of the ^{17}O shift values of carbonyl groups on the $\text{C}=\text{O}\cdots\text{H}-\text{N}$ type of hydrogen bonding, the ^{17}O , ^{13}C and ^1H NMR spectra of *para*- and *meta*-substituted 4-(*N*-arylamino)pent-3-en-2-ones (acyclic enaminones 1a–j and 2a–j) and 3-(*N*-arylamino)cyclohex-2-en-1-ones (cyclic enaminones 3a–j and 4a–j) have been investigated.

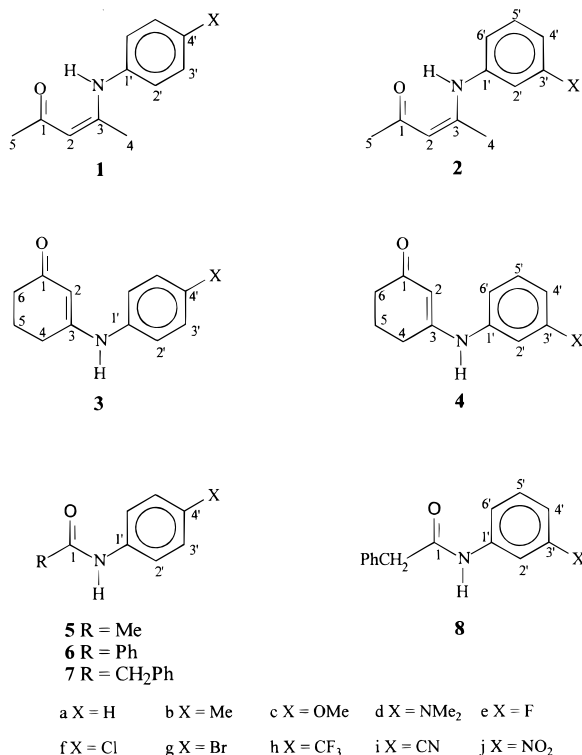
RESULTS AND DISCUSSION

The ^{17}O SCS for acyclic (1 and 2) and cyclic enaminones (3 and 4), recorded in acetonitrile solution at natural abundance are listed in Table 1. The carbonyl ^{17}O signals of enaminones (1–4) appear in the region

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reported for enaminones.⁴ The substituent effects on ¹⁷O chemical shifts of the carbonyl O atoms parallel those reported previously for the corresponding *N*-arylacetamides^{10m} and benzanilides.¹⁰ⁿ Electron-donating groups cause shielding and electron-withdrawing groups cause deshielding. The temperature dependence of the ¹⁷O data is not significant. A slight deshielding at higher temperature (70 °C) was noted only for **1j** (1.1 ppm), **2j** (1.4 ppm) and **3b** (1.0 ppm).

The ¹³C NMR data for the acyclic (**1** and **2**) and acyclic enaminones series (**3** and **4**) in CDCl₃ solution are summarized in Tables 2 and 3, respectively. The peak assignments for the enaminone moieties are in agreement with those reported for the corresponding analogs.² The trend of the substituent effects on ¹³C chemical shifts of C-1 and C-2 is similar to that noted for ¹⁷O, but it is reverse for C-3. The assignments of the signals of the aromatic carbon nuclei were achieved by considering peak intensity, peak multiplicity under off-resonance decoupling conditions, SCS for mono-substituted benzenes^{6b} and ⁿJ_{CF} values for fluorine-containing enaminones.

The ¹H NMR spectra of several enaminones have been recorded previously.^{2,11} The present ¹H data for H-2 and H-N (Table 1) are in agreement with available literature values measured under similar conditions.

Table 1. ¹⁷O and ¹H NMR chemical shifts (ppm) for enaminones (1–4)

Compound	X	¹⁷ O ^a	¹ H-2 ^b	¹ H-N ^b	Δδ(O) _{HB} ^c	Compound	¹⁷ O ^a	¹ H-2 ^b	¹ H-N ^b
1a = 2a	H	435.3 ^d	5.19	12.48	−35.9	3a = 2a	471.2 ^d	5.59	6.27
1b	Me	432.7	5.17	12.40	−34.5	3b	467.2 ^e	5.51	6.21
1c	MeO	431.1 ^f	5.16	12.29	−33.2	3c	464.3 ^g	5.37	6.25
1d	NMe ₂	429.1	5.13	12.25	−34.3	3d	463.4	5.36	6.10
1e	F	434.9	5.19	12.35	−36.6	3e	471.5	5.39	6.48
1f	Cl	437.8	5.22	12.44	−39.8	3f	477.6	5.53	6.20
1g	Br	437.5	5.21	12.43	−42.0	3g	479.5	5.54	6.26
1h	CF ₃	444.3	5.26	12.62	−40.0	3h	484.3	5.71	6.23
1i	CN	448.0	5.30	12.69	−45.1	3i	493.1	5.79	6.44
1j	NO ₂	451.4 ^{h,i}	5.34	12.79	−42.1	3j	493.5 ^j	5.87	6.38
2b	Me	433.6	5.17	12.43	−36.6	4b	470.2	5.59	6.25
2c	OMe	435.3 ^k	5.19	12.48	−36.3	4c	471.6 ^l	5.63	6.19
2e	F	440.0	5.22	12.50	−38.0	4e	478.0	5.63	6.51
2f	Cl	440.0	5.22	12.47	−38.7	4f	478.7	5.60	6.27
2h	CF ₃	441.7	5.25	12.57	−38.3	4h	480.0	5.58	6.28
2i	CN	443.5	5.27	12.56	−38.3	4i	481.8	5.57	6.84
2j	NO ₂	444.5 ^{m,n}	5.30	12.66	−41.1	4j	485.6 ^o	5.62	6.83

^a Natural abundance measurements of 0.25–0.5 M CH₃CN solution at 40 °C for series **1** and **2** and 70 °C for series **3** and **4** unless stated otherwise; linewidths at half-height are 190–490 Hz.

^b Relative to internal TMS in CDCl₃ at 20 °C, singlet.

^c Δδ(O)_{HB} = δ(O)(**1** or **2**) − δ(O)(**3** or **4**).

^d Taken from Ref. 1.

^e Measured at 40 °C: δ_O = 466.2 ppm.

^f δ_{OMe} = 50.6 ppm.

^g δ_{OMe} = 46.3 ppm.

^h δ_{NO₂} = 563.6 ppm.

ⁱ Measured at 70 °C: δ_O = 452.5 ppm and δ_{NO₂} = 565.2 ppm.

^j δ_{NO₂} = 565.1 ppm.

^k δ_{OMe} = 48.8 ppm.

^l δ_{OMe} = 49.7 ppm.

^m δ_{NO₂} = 573.9 ppm.

ⁿ Measured at 70 °C: δ_O = 445.9 ppm and δ_{NO₂} = 575.3 ppm.

^o δ_{NO₂} = 574.3 ppm.

Table 2. ¹³C chemical shifts (ppm) for 4-anilinopent-3-en-2-ones (1 and 2)^a

Compound	C-1	C-2	C-3	C-4	C-5	C-1'	¹³ C-2'	C-3'	C-4'	C-5'	C-6'	X
1a = 2a	196.08	97.62	160.30	19.82	29.13	138.67	124.67	129.09	125.55			—
1b	195.90	97.21	160.80	19.77	29.07	136.02	124.86	129.67	135.51			20.91
1c	195.78	96.84	161.31	19.63	29.04	131.47	126.65	114.25	157.73			55.43
1d	195.34	96.33	161.85	19.65	29.01	127.68	126.43	112.55	148.85			40.65
1e	196.33	97.55	160.55	19.64	29.14	134.73	126.83	115.93	160.64			—
						(3.0) ^b	(8.4)	(22.6)	(246.0)			
1f	196.53	98.13	159.72	19.79	29.23	137.37	125.85	129.22	130.99			—
1g	196.54	98.22	159.62	19.80	29.21	137.83	126.08	132.16	116.68			—
1h	197.15	99.34	158.70	20.13	29.41	142.24	123.59	126.40	126.78			124.07
						(0.7)		(3.7)	(32.8)			(271.7)
1i	197.55	100.49	157.55	20.41	29.54	143.33	122.83	133.30	107.23			118.72
1j	197.90	101.22	157.04	20.62	29.65	145.34	121.86	125.19	143.47			—
2b	195.92	97.47	160.36	19.83	29.11	139.03	125.35	138.61	126.34	128.85	121.70	21.31
2c	196.13	97.76	160.19	19.90	29.14	139.87	110.35	160.16	111.05	129.77	116.89	55.28
2e	196.72	98.47	159.37	19.96	29.29	140.49	111.50	162.90	112.13	130.27	119.99	—
						(9.8)	(23.5)	(246.9)	(21.1)	(9.4)	(2.0)	
2f	196.69	98.48	159.42	19.89	29.25	140.08	124.43	134.62	125.41	130.09	122.57	—
2h	197.01	98.81	159.16	19.88	29.35	139.56	121.07	131.70	121.88	129.78	127.53	123.70
							(3.3)	(32.6)	(3.3)			(272.4)
2i	197.28	99.34	158.50	19.94	29.40	139.96	126.99	113.28	128.48	130.18	128.48	118.15
2j	197.44	99.62	158.36	20.01	29.45	140.33	118.32	148.72	119.56	130.03	129.66	—

^a Relative to internal TMS in CDCl₃ at 20 °C.

^b Values in parentheses are C–F coupling constants (Hz).

The ¹⁹F data for fluorine-containing compounds are listed in Table 4.

Substituent effects on the enaminone moiety

The trends of the ¹⁷O and ¹³C SCS of the carbonyl groups for the *para*-substituted enaminones (1 and 3)

are similar to those previously observed for *N*-acylanilines.¹⁰ Good correlations of ¹⁷O values of the carbonyl groups in series 1 and 3 were observed with those in *N*-(4-substituted phenyl)acetamides (5)^{10m} and *N*-(4-substituted phenyl)benzamides (6)¹⁰ⁿ (Table 5, lines 1–4). The results suggest that the substituent effects on enaminone systems are similar to those in acetamides and benzamides. The slopes of *ca.* 0.9 (Table 5,

Table 3. ¹³C chemical shifts (ppm) for 3-anilinocyclohex-2-en-1-ones (3 and 4)^a

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	X
3a = 4a	198.50	99.15	163.18	29.55	21.84	36.47	138.24	123.93	129.23	125.42			—
3b	198.26	98.96	163.36	29.55	21.87	36.48	135.53	124.08	129.78	135.29			20.95
3c	198.08	98.62	164.06	29.43	21.90	36.46	130.83	126.19	114.43	157.56			55.47
3d	197.81	98.12	164.68	29.34	21.95	36.46	127.16	125.97	112.78	148.80			40.68
3e	198.36	99.02	163.55	29.45	21.83	36.47	134.05	126.30	116.10	160.34			—
							(2.6) ^b	(8.1)	(22.7)	(245.7)			
3f	198.50	99.65	162.60	29.56	21.79	36.48	136.79	125.15	129.38	130.72			—
3g	198.50	99.82	162.32	29.59	21.78	36.48	137.31	125.37	132.36	118.37			—
3h	198.85	100.83	161.55	29.69	21.73	36.53	141.76	122.79	126.51	126.53			123.90
							(0.5)		(3.3)	(32.9)			(271.7)
3i	198.87	102.30	160.14	29.77	21.66	36.55	143.01	122.14	133.47	107.16			118.62
3j	199.14	102.92	160.23	29.75	21.64	36.58	145.04	121.34	125.30	143.25			—
4b	198.47	98.94	163.49	29.53	21.86	36.49	139.12	124.52	138.19	126.21	128.99	120.96	21.33
4c	198.54	99.36	163.26	29.52	21.84	36.51	139.54	109.71	160.26	110.81	129.91	116.11	55.27
4e	198.71	100.15	162.22	29.61	21.78	36.51	139.98	110.79	163.04	112.10	130.48	119.12	—
							(9.9)	(23.9)	(246.7)	(21.1)	(9.3)	(2.0)	
4f	198.68	100.14	162.21	29.62	21.78	36.50	139.54	123.76	134.86	125.44	130.30	121.81	—
4h	198.66	100.28	161.92	29.66	21.76	36.54	138.94	120.37	131.90	121.92	129.92	126.89	123.61
								(3.3)	(32.7)	(3.3)			(272.6)
4i	198.77	100.60	161.64	29.57	21.71	36.51	139.43	126.49	113.42	127.83	130.35	128.51	118.08
4j	198.81	100.94	161.35	29.64	21.70	36.56	139.73	118.01	148.85	119.7	130.21	129.12	—

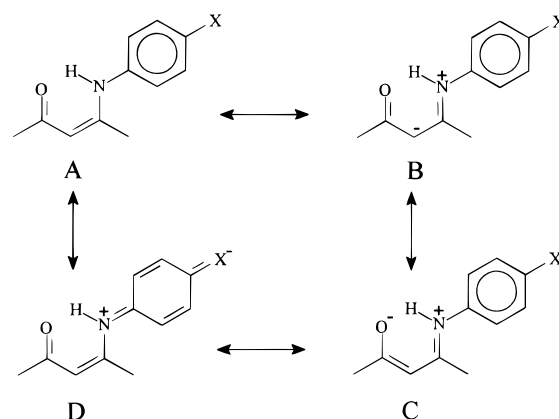
^a Relative to internal TMS in CDCl₃ at 20 °C.

^b Values in parentheses are C–F coupling constants (Hz).

Table 4. ^{19}F Chemical shifts (ppm) for fluorine-containing compounds

Compound	$^{19}\text{F}^a$	Compound	$^{19}\text{F}^a$
1e	-3.29	1h	50.87
2e	1.47	2h	50.25
3e	-2.58	3h	50.84
4e	1.99	4h	50.28

^a Relative to internal fluorobenzene which is 113.59 ppm from FCCl_3 in CDCl_3 . Downfield is positive.

**Scheme 1**

lines 1 and 2) for series 1 and *ca.* 1.3 (Table 5, lines 3 and 4) for series 3 indicate that the substituent effects were only slightly diminished in the former case and increased in the latter. This result is not consistent with that the substituent effects are reduced by approximately 50% when a $\text{C}=\text{C}$ double bond is inserted between a substituted aromatic ring and a functional group,¹² indicating that the transmission of substituent effects through $\text{C}=\text{C}$ double bond is efficient. The transmission efficiency of the $\text{C}=\text{C}$ bond can be explained in terms of the resonance structures A–D (Scheme 1) and reflects the extended delocalization in the molecule. The correlations of ^{13}C SCS values of the carbonyl carbons for acyclic series (1 and 2) and cyclic series (3 and 4) with those for *N*-acylanilines (5 and 8) show that the transmission of the substituent effects is enhanced in acyclic enaminones and diminished in cyclic enaminones, as shown by the slopes of more than unity (Table 5, lines 5 and 6) and less than unity (Table 5, lines 7 and 8), respectively.

Correlations of the ^1H , ^{13}C and ^{17}O SCS values between 1 and 3 and between 2 and 4 were also examined (Table 6). Linear relationships of the ^{13}C -2 and

^{13}C -3 data between 1 and 3 were observed with near-unity slopes (Table 6, lines 4 and 5), indicating that the substituent effects in both series are qualitatively identical. The slopes of the correlations between 1 and 3, 0.47 for ^{13}C -1 and 1.47 for ^{17}O , show the difference in substituent effects for the two nuclei. This may be owing to the influence of intramolecular hydrogen bonding and to the enhanced delocalization and n,π interaction in acyclic enaminones (1 and 2).

In previous papers,^{1,4} it has been shown that the ^1H -2, ^{13}C -2 and ^{17}O chemical shifts of enaminones can correlate well with each other, and these data can be used to reflect the polarization and the degree of n,π conjugation. In present study, the ^{17}O data of carbonyl O atoms are correlated with the ^1H -2, ^1H -N, ^{13}C -1, ^{13}C -2 and ^{13}C -3 SCS values (Table 7). These relationships show that ^{17}O , ^{13}C and ^1H shieldings are governed by the same effects. It is obvious that ^{17}O values is very sensitive to reflect the polarization and the degree of n,π conjugation in the $\text{N}-\text{C}=\text{C}-\text{C}=\text{O}$ system.

As has been noted in a previous paper,⁴ excellent correlations of the ^{13}C chemical shifts difference

Table 5. Correlations of ^{13}C and ^{17}O SCS for series 1–4 with those for series 5–8

Line	SCS ^a	Series	Series	Slope	Intercept	r^b	n^c	SD ^d
1	O	1	5 ^e	0.89	0.40	0.991	6 ^f	1.06
2	O	1	6 ^g	0.94	1.95	0.965	9 ^h	1.98
3	O	3	5 ^e	1.29	1.54	0.986	6 ^f	1.96
4	O	3	6 ^g	1.38	3.93	0.940	9 ^h	3.88
5	C-1	1	5 ⁱ	1.28	0.28	0.960	9 ^h	0.22
6	C-1	2	8 ^j	4.01	0.05	0.972	7 ^k	0.13
7	C-1	3	5 ⁱ	0.59	-0.07	0.983	9 ^h	0.07
8	C-1	4	8 ^j	0.84	0.01	0.978	6 ^l	0.03

^a SCS = $\delta(\text{X}) - \delta(\text{H})$.

^b Correlation coefficient.

^c Number of points in the correlation.

^d Standard deviation in ppm.

^e Taken from Ref. 10m.

^f Regression analysis was performed for *p*-H, *p*-Me, *p*-OMe, *p*-Cl, *p*-Br and *p*-NO₂ derivatives.

^g Taken from Ref. 10n.

^h Point for *p*-NMe₂ derivative was not included owing to lack of ^{17}O data for 6d.

ⁱ Taken from Ref. 10e.

^j Taken from Ref. 10d.

^k Point for *m*-NO₂ derivative was excluded.

^l Points for *m*-F and *m*-NO₂ derivatives were excluded.

Table 6. Correlations of ¹H, ¹³C and ¹⁷O SCS for series 3 or 4 with those for series 1 or 2

Line	SCS	Series	Series	Slope	Intercept	<i>r</i>	<i>n</i>	SD
1	O	3	1	1.47	1.09	0.983	10	2.14
2	H-2	3	1	2.55	−0.09	0.944	10	0.06
3	C-1	3	1	0.47	−0.22	0.968	10	0.10
4	C-2	3	1	1.00	0.11	0.996	10	0.14
5	C-3	3	1	0.97	−0.07	0.993	10	0.19
6	C-1'	3	1	1.02	−0.05	1.000	10	0.09
7	C-2'	3	1	1.02	−0.09	0.997	10	0.13
8	C-3'	3	1	1.00	0.01	1.000	10	0.04
9	C-4'	3	1	0.99	0.27	0.999	10	0.58
10	O	4	2	1.35	0.51	0.987	8	0.99
11	C-1	4	2	0.21	0.02	0.964	8	0.04
12	C-2	4	2	0.89	0.06	0.985	8	0.13
13	C-3	4	2	1.01	1.08	0.982	8	0.16
14	C-1'	4	2	0.95	−0.02	0.986	7 ^a	0.10
15	C-2'	4	2	1.00	0.09	1.000	8	0.17
16	C-3'	4	2	1.00	−0.05	1.000	8	0.22
17	C-4'	4	2	0.99	−0.04	0.999	8	0.25
18	C-5'	4	2	1.04	0.00	0.999	8	0.02
19	C-6'	4	2	1.04	0.14	0.999	8	0.23

^a Point for Me derivatives was excluded.

between the two olefinic carbons, $\delta(\text{C-3-C-2}) = \delta(\text{C-3}) - \delta(\text{C-2})$, with the ¹⁷O data were observed (Table 7, lines 17–20). This further supports that the shielding of the carbonyl O atoms depends on the polarization and the degree of n, π conjugation. The ¹³C-1 SCS values also correlate well with $\delta(\text{C-3-C-2})$ (Table 7, lines 21–24).

Hammett-type correlations

The results of Hammett correlations [Eqn (1)] of the ¹⁷O, ¹³C and ¹H SCS data for the four series of enaminones are listed in Table 8. The ¹⁷O SCS of a variety of substituted benzoyl compounds and α, β -unsaturated

Table 7. Correlations of ¹⁷O with ¹H and with ¹³C SCS for series 1–4

Line	Series	SCS	SCS	Slope	Intercept	<i>r</i>	<i>n</i>	SD
1	1	O	C-1	9.03	−0.97	0.992	10	1.01
2		O	C-2	4.64	−0.22	0.997	10	0.56
3		O	C-3	−4.68	0.31	0.995	10	0.80
4		O	H-2	112.61	−0.13	0.996	10	0.69
5		O	H-N	41.17	3.20	0.979	10	1.61
6	2	O	C-1	7.10	−0.17	0.997	8	0.35
7		O	C-2	5.07	−0.25	0.989	8	0.64
8		O	C-3	−5.13	−0.39	0.987	8	0.71
9		O	H-2	88.93	0.71	0.970	8	1.07
10	3	O	C-1	26.38	5.70	0.942	10	3.93
11		O	C-2	6.74	0.04	0.973	10	2.68
12		O	C-3	−7.11	1.00	0.987	10	1.89
13		O	H-2	57.88	6.75	0.928	10	4.40
14	4	O	C-1	43.09	−0.20	0.971	8	1.44
15		O	C-2	7.44	−0.22	0.993	8	0.72
16		O	C-3	−6.91	0.61	0.993	8	0.71
17	1	O	C-3-C-2 ^a	−2.33	146.37	0.997	10	0.60
18	2	O	C-3-C-2	−2.55	159.77	0.989	8	0.66
19	3	O	C-3-C-2	−3.49	224.08	0.984	10	2.06
20	4	O	C-3-C-2	−3.67	235.04	0.995	8	0.60
21	1	C-1	C-3-C-2	−0.25	16.08	0.991	10	0.11
22	2	C-1	C-3-C-2	−0.36	22.60	0.995	8	0.06
23	3	C-1	C-3-C-2	−0.12	7.49	0.946	10	0.14
24	4	C-1	C-3-C-2	−0.08	5.23	0.980	8	0.03

^a $\delta(\text{C-3-C-2}) = \delta(\text{C-3}) - \delta(\text{C-2})$.

Table 8. Correlations for ^1H , ^{13}C and ^{17}O SCS for series 1–4 with Hammett constants

Line	Series	δ^a	σ^b	ρ	δ^0	r	n	SD
1	1	O	σ_p^-	13.145	434.99	0.998	9	0.51
2		H-2	σ_p^-	0.114	5.19	0.996	9	0.006
3		H-N	σ_p^-	0.30	12.40	0.968	9	0.04
4		C-1	σ_p^-	1.373	196.20	0.993	9	0.09
5		C-2	σ_p^-	2.826	97.60	0.999	9	0.07
6		C-3	σ_p^-	-2.73	160.39	0.996	9	0.13
7	1	O	σ_p^-	12.90	435.14	0.998	10	0.55
8		H-2	σ_p^-	0.114	5.19	0.997	10	0.005
9		H-N	σ_p^-	0.30	12.40	0.975	10	0.04
10		C-1	σ_p^-	1.41	196.17	0.993	10	0.10
11		C-2	σ_p^-	2.78	97.63	0.999	10	0.09
12		C-3	σ_p^-	-2.74	160.40	0.997	10	0.12
13		C-4	σ_p^-	0.58	19.79	0.956	10	0.11
14		C-5	σ_p^-	0.38	29.15	0.993	10	0.03
15	2	O	σ_m^0	14.18	434.88	0.995	8	0.43
16		H-2	σ_m^0	0.15	5.18	0.972	8	0.01
17		C-1	σ_m^0	1.99	196.05	0.995	8	0.06
18		C-2	σ_m^0	2.77	97.59	0.995	8	0.08
19		C-3	σ_m^0	-2.72	160.29	0.994	8	0.09
20		C-5	σ_m^0	0.45	29.13	0.986	8	0.02
21	3	O	σ_p^-	19.01	472.04	0.984	10	2.10
22		H-2	σ_p^-	0.29	5.50	0.951	10	0.06
23		C-1	σ_p^-	0.67	198.33	0.965	10	0.11 ^c
24		C-2	σ_p^-	2.77	97.28	0.993	10	0.21
25		C-3	σ_p^-	-2.64	163.20	0.986	10	0.27
26		C-4	σ_p^-	0.23	29.51	0.945	10	0.05
27		C-5	σ_p^0	-0.25	21.85	0.992	10	0.01
28		C-6	σ_p^-	0.071	36.48	0.961	10	0.01
29	4	O	σ_m^0	21.08	472.65	0.989	8	0.95
30		C-1	σ_m^0	0.43	198.51	0.982	8	0.03
31		C-2	σ_m^0	2.50	99.18	0.995	8	0.08
32		C-3	σ_m^0	-2.79	163.27	0.992	8	0.11 ^d
33		C-5	σ_m^0	-0.21	21.85	0.994	8	0.01

^a $\delta = \delta^0 + \sigma\rho$.^b σ_p^- , σ_p^- and σ_m were taken from Ref. 16a and σ_m^0 from Ref. 16b. A σ_p^- value of -0.52 was used for *p*-NMe₂, estimated from lines 1–6 in which the point for **1d** was excluded.^c Correlation with σ_p gives $\rho = 0.80$; $r = 0.977$; SD = 0.09.^d Correlation with σ_m gives $\rho = 2.62$; $r = 0.996$; SD = 0.07.

carbonyl compounds have been obtained the best correlation with Hammett σ^+ values,¹³ and acetanilides^{10m} and benzanilides¹⁰ⁿ with Hammett σ values. The ^{13}C SCS of the carbonyl carbons of chalcones have been correlated with Hammett σ values.¹⁴ In α,β -unsaturated carbonyl compounds, the ^1H chemical shifts of the ethylenic protons H- α and H- β were found to correlate with σ^+ and σ^0 values,¹⁵ respectively. The ^1H chemical shifts of the H- β protons in aryl vinyl ethers and sulfides were previously correlated with the σ value.^{9a} In enaminone cases, the best correlations of the ^1H -2, $^{13}\text{C}=\text{O}$, ^{13}C -2, ^{13}C -3 and ^{17}O NMR SCS values of *para*-substituted enaminones (**1** and **3**) are obtained with σ_p^- constants (Table 8, lines 7–14 and 21–28, respectively) by using the σ_p^- constant for the NMe₂ group (-0.52) instead of -0.12,^{16a} whereas those of *meta*-substituted enaminones (**2** and **4**) with constants σ_m^0 (Table 8, lines 15–20 and 29–33, respectively). The correlations of the ^{13}C chemical shifts of carbons at side chain in the *para* series, i.e. C-4 and C-5 in **1** and C-4, C-5 and C-6 in **3**,

were observed with σ_p^- . In the *meta* series **2** and **4**, the correlations were observed only for C-5. The σ_p^- constant (-0.52) for the NMe₂ group was statistically estimated from the ^1H , ^{13}C and ^{17}O NMR data for **1d** and the corresponding correlation equations (Table 8, lines 1–6) in which the point for the -NMe₂ group (**1d**) was excluded.

The magnitude of the ρ values for these correlations illustrates their relative sensitivity to the substituents. In the four series of enaminones, the slopes of the correlations of σ 's with the δ values of ^{13}C -2 and ^{13}C -3 show similar absolute values, but with opposite signs. The opposite sign has been previously observed for aryl vinyl ethers and sulfides,^{9b} it probably reflects the polarization of the C-2=C-3 double bond, as described in the resonance structures **B** and **C** (Scheme 1). The ρ value for ^{17}O shows that the SCS values of acyclic enaminones (**1** and **2**) are less sensitive to the substituents than those of cyclic derivatives (**3** and **4**), but it is reverse for ^{13}C -1. The sensitivity of the ^1H -2 in cyclic

derivatives (3 and 4) may come from the anisotropic effects of the aryl ring. The chemical shift differences of ¹H-2 between acyclic enaminones (1 and 2) and cyclic derivatives (3 and 4) for an *N*-aryl substituent, *ca.* 0.5 ppm, are much larger than that for an *N*-alkyl group, *ca.* 0.2 ppm.¹ The deshielding of the ¹H-2 in 3 and 4 can be attributed to the anisotropic effects of the *N*-aryl rings and suggests that the aryl rings are located at the H-2 side. This is consistent with the previous analysis of cyclic enaminones.¹⁷

DSP correlations

The results of the DSP treatment [Eqn (2)] for the ¹H-2, ¹³C-1, ¹³C-2, ¹³C-3 and ¹⁷O NMR SCS are listed in Table 9. In order to achieve the best fit, σ_R^0 , σ_R , σ_R^- and σ_R^+ were used along with σ_I . In series 1, for ¹H-2, ¹H-N, ¹³C-2 and ¹⁷O SCS values the best correlations are with σ_R^- parameters,^{7b} whereas for ¹³C-1 and ¹³C-3 with σ_R^0 parameters.^{7b} In series 3, for ¹H-2 and ¹³C-2 SCS values the best correlations are with σ_R^- param-

eters, whereas for ¹³C-1, ¹³C-3 and ¹⁷O with σ_R^0 parameters. These results suggest that the contribution of resonance structure C is more important in series 1 and the resonance structure B is more important in series 3. An electron donor substituent decreases the ability of the nitrogen lone pair delocalization with the aromatic ring and increases the contribution of the resonance structures B and C, whereas an electron acceptor substituent leads to increased contribution of resonance structure D (Scheme 1), and to enhanced the π - π -interaction between the nitrogen lone pair and the aromatic ring, resulting in decreased electron densities at the O, H-2 and C-2 atoms with concomitant deshielding. This result is consistent with that previously noted for acetanilides.^{10e,k} DSP analysis for *meta*-substituted enaminones (2 and 4) shows that the correlations of ¹H-N in series 2, and ¹H-2 in series 4 are poor (Table 9, lines 11 and 26, respectively).

The results of DSP treatment also show that the inductive effects are greater in series 2 and 4, and the resonance effects are greater in series 3, whereas both effects (inductive and resonance effects) are similar in series 1 except for ¹H-N (Table 9, line 3), which shows

Table 9. DSP analysis of ¹H, ¹³C and ¹⁷O SCS for series 1–4

Line	Series	δ^a	Scale ^b	ρ_I	ρ_R	δ^0	SD	<i>r</i>	<i>n</i>	<i>f</i> ^c
1	1	O	σ_R^-	15.47	15.89	435.14	0.61	0.996	10	0.08
2		H-2	σ_R^-	0.14	0.14	5.19	0.01	0.996	10	0.08
3		H-N	σ_R^-	0.22	0.44	12.46	0.02	0.995	10	0.10
4		C-1	σ_R^0	2.55	2.29	196.14	0.04	0.998	10	0.05
5		C-2	σ_R^-	3.34	3.42	97.63	0.08	0.999	10	0.05
6		C-3	σ_R^0	-4.52	-4.83	160.22	0.15	0.995	10	0.09
7		C-4	σ_R^-	0.49	0.84	19.88	0.06	0.984	10	0.18
8		C-5	σ_R^-	0.48	0.46	29.14	0.02	0.997	10	0.07
9	2	O	σ_R	13.88	6.28	435.06	0.32	0.996	8	0.06
10		H-2	σ_R^-	0.13	0.07	5.19	0.004	0.995	8	0.07
11		H-N	σ_R^-	0.17	0.13	12.47	0.02	0.933	8	0.30
12		C-1	σ_R	1.92	0.93	196.09	0.04	0.998	8	0.05
13		C-2	σ_R^0	2.95	1.50	97.65	0.03	0.999	8	0.02 ^d
14		C-3	σ_R^0	-2.89	-1.44	160.25	0.08	0.994	8	0.07
15		C-4	σ_R	0.23	-0.016	19.82	0.02	0.923	8	0.22
16		C-5	σ_R	0.43	0.22	29.14	0.02	0.990	8	0.10
17	3	O	σ_R^0	33.98	31.53	471.80	1.60	0.988	10	0.14
18		H-2	σ_R^-	0.16	0.47	5.58	0.02	0.991	10	0.14
19		C-1	σ_R	0.69	0.96	198.46	0.06	0.988	10	0.15
20		C-2	σ_R^-	3.24	3.47	99.32	0.13	0.996	10	0.08
21		C-3	σ_R^0	-4.18	-4.85	162.92	0.23	0.987	10	0.16
22		C-4	σ_R^0	0.29	0.50	29.58	0.03	0.981	10	0.20
23		C-5	σ_R^-	-0.30	-0.29	21.84	0.01	0.996	10	0.08
24		C-6	σ_R^-	0.071	0.13	36.48	0.03	0.857	10	0.60
25	4	O	σ_R	19.16	8.37	471.33	0.56	0.994	8	0.07
26		H-2	σ_R	0.03	-0.06	5.58	0.01	0.784	8	0.52
27		C-1	σ_R	0.47	0.11	198.49	0.02	0.991	8	0.08
28		C-2	σ_R	2.58	0.86	99.12	0.04	0.999	8	0.03 ^e
29		C-3	σ_R	-2.73	-1.25	163.23	0.08	0.994	8	0.08
30		C-4	σ_R	0.13	0.071	29.55	0.03	0.756	8	0.61
31		C-5	σ_R^0	-0.22	-0.12	21.84	0.005	0.996	8	0.06
32		C-6	σ_R^-	0.075	0.024	36.49	0.02	0.802	8	0.48

^a $\delta = \delta^0 + \rho_I \sigma_I + \rho_R \sigma_R$.

^b σ_I and σ_R were taken from Ref. 18 and σ_R^0 and σ_R^- from Ref. 7b.

^c $f = SD/rms$.

^d Correlation with σ_R^- : $\rho_I = 2.49$; $\rho_R = 1.00$; $SD = 0.06$; $r = 0.997$; $f = 0.05$.

^e Correlation with σ_R^- : $\rho_I = 2.47$; $\rho_R = 0.61$; $SD = 0.10$; $r = 0.990$; $f = 0.09$.

that the contribution of the resonance effect is more important.

The ρ_I and ρ_R values for ^{13}C -3 have the opposite sign to those for ^1H -2, ^{13}C -2 and ^{17}O . The negative sign reflects the reverse nature of the ^{13}C -3 shifts. The fact that the σ_R^0 or σ_R scale is preferred for the C-3 and C-1, and the σ_R^- scale for O, C-2 and H-2 indicates the contribution of the resonance structure C.

Correlations with the $\text{p}K_a$ values of anilines

The ^1H -2, ^{13}C -2 and ^{17}O NMR data of enaminones have been found to depend on the donor quality of the amino group and previously correlate with the $\text{p}K_a$ values of the corresponding amines.^{1,4} In present paper, the correlations of the ^1H -2, ^1H -N, ^{13}C -1, ^{13}C -2, ^{13}C -3 and ^{17}O NMR SCS values with the $\text{p}K_a$ values of anilines¹⁹ are good to excellent (Table 10). This indicates that the effects of substituents on the chemical shifts for enaminone moiety are parallel to those on the basic strength of the amines. The slope of the correlation of ^{17}O data is *ca.* -6.7 for the cyclic enaminones and -4.7 for acyclic enaminones. The results are in good agreement with those previously noted for the corresponding enaminone systems.¹ These data can be compared with the slopes of -4.92 ($r = 0.963$, $n = 10$,

Table 10. Correlations of ^1H , ^{13}C and ^{17}O SCS for series 1–4 with $\text{p}K_a$ ^a

Line	Series	δ^b	a	δ^0	r	n	SD
1	1	O	-4.58	456.03	0.998	10	0.46
2		H-2	-0.040	5.374	0.995	10	0.007
3		H-N	-0.106	12.89	0.972	10	0.04
4		C-1	-0.50	198.46	0.995	10	0.08
5		C-2	-0.98	102.12	0.996	10	0.15
6		C-3	0.97	155.96	0.996	10	0.15
7		C-4	-0.20	20.72	0.948	10	0.12
8		C-5	-0.14	29.77	0.993	10	0.03
9	2	O	-4.90	457.20	0.977	8	0.93
10		H-2	-0.053	5.42	0.965	8	0.01
11		C-1	-0.69	199.19	0.980	8	0.12
12		C-2	-0.97	102.00	0.989	8	0.12
13		C-3	0.95	155.97	0.988	8	0.13
14		C-5	-0.16	29.84	0.970	8	0.03
15	3	O	-6.77	502.88	0.987	10	1.90
16		H-2	-0.10	5.97	0.947	10	0.06
17		C-1	-0.24	199.41	0.967	10	0.11
18		C-2	-0.98	103.74	0.988	10	0.27
19		C-3	0.94	158.92	0.986	10	0.28
20		C-4	-0.082	29.89	0.946	10	0.05
21		C-5	0.062	21.56	0.991	10	0.01
22		C-6	0.071	36.48	0.961	10	0.01
23	4	O	-6.75	501.87	0.979	8	1.22
24		C-1	-0.15	199.20	0.984	8	0.02
25		C-2	-0.87	103.14	0.989	8	0.12
26		C-3	0.96	158.89	0.971	8	0.21
27		C-5	0.073	21.52	0.986	8	0.01

^a Taken from Ref. 19. A $\text{p}K_a$ value of 6.05 was used for *p*-NMe₂, estimated from the correlation of the $\text{p}K_a$ values of *para*-substituted anilines with σ_p^- values ($\text{p}K_a = 4.56 - 2.81 \sigma_p^-$, $r = 0.998$, $\text{SD} = 0.10$) by using a σ_p^- value of -0.52 for *p*-NMe₂.

^b $\delta = \delta^0 + a \text{p}K_a$.

$\text{SD} = 2.3$) for benzaniles 6 and -5.77 ($r = 0.989$, $n = 8$, $\text{SD} = 1.7$) for intramolecular hydrogen-bonded salicylanilides (calculated from the published data).¹⁰ⁿ The slopes of the correlations of ^{13}C data of the carbonyl carbons, -0.50 for 1, -0.24 for 3 and -0.36 for acetamides 5 (calculated from the published data),^{10e} are slightly diminished in cyclic enaminone systems relative to those in acyclic system and the acetamides.

Intramolecular hydrogen bonding

The ^{17}O chemical shifts for the carbonyl O atoms in 1 appear at higher field than those in 3. The shielding effects in acyclic enaminones can be attributed to the intramolecular hydrogen-bonding. The ^1H NMR spectra show that the N-H signals appear at *ca.* 6.5 ppm for 3 and *ca.* 12.5 ppm for 1, indicating the presence of intramolecular hydrogen bonding in 1. Comparison of the ^{17}O chemical shifts for the cyclic with acyclic systems allows calculation of the chemical shift change coming from the intramolecular hydrogen bonding $[\Delta\delta(\text{O})_{\text{HB}}]$. The values of $\Delta\delta(\text{O})_{\text{HB}}$ range from -33 to -45 ppm, which are slightly larger than those in *N*-alkylenaminones¹ [$\Delta\delta(\text{O})_{\text{HB}} = -27 \pm 2$ ppm]. The shielding effects $[\Delta\delta(\text{O})_{\text{HB}}]$ of intramolecular hydrogen bonding of the type of $\text{NH} \cdots \text{C}=\text{O}$, ranging from -4 to -29 ppm have been reported previously for 2-amino-acetophenones,^{20a} 1-aminoanthraquinones^{20b} and 1-aminofluorenones.^{20b} It is generally accepted that $\Delta\delta(\text{O})_{\text{HB}}$ values indicate the strength of the hydrogen bond.^{21a} The high values of $\Delta\delta(\text{O})_{\text{HB}}$ (-33 to -45 ppm) found in acyclic enaminones 1 and 2 indicate a strong hydrogen bond.

Substituent effects on the benzene rings

The results of the correlations of the ^{13}C SCS values for the nuclei of the benzene ring in enaminones (1–4) with the SCS values of the corresponding carbon nuclei for the monosubstituted benzene^{6b} are listed in Table 11. The slopes of the correlations are all close to unity, indicating that the chemical shifts of the aromatic carbons are affected little by the enaminone moiety as a whole and mainly by the electronic effects of the substituents. However, a slope of 0.89 for C-1' was observed for the series 4-XC₆H₄NHCOCH₂Ph,^{10d} 0.86 for 4-XC₆H₄NHAc^{10e} and 1.26 for 4-XC₆H₄NHSO₂Me.²²

DSP analyses and DSP-NLR [Eqn (3)]^{6b} treatments for the *para* carbon to X, i.e. C-1' in 1 and 3 or C-6' in 2 and 4, are summarized in Table 12, in which DSP analyses for the *meta* carbon to X, i.e. C-2' in 1 and 3 or C-1' and C-5' in 2 and 4, are included. The results show that both field and resonance effects of the substituent X contribute to changes in chemical shifts at C-1' or C-6'. The ρ_I and ρ_R values for the *para* series (1 and 3), *ca.* 5.0 and 21.0, respectively, can be compared with those for C-4 of 4-substituted anilines ($\rho_I = 5.0$; $\rho_R = 17.8$)^{6b} and 7 ($\rho_I = 4.5$; $\rho_R = 19.5$).^{10d} In the *meta* series 2 and 4, the ρ_I and ρ_R values are close to those of 3-substituted anilines^{6b} and 8.^{10d} According to electron demand (ϵ), small positive values of ϵ for C-1' in the *para* series (1 and 3), as noted for 1,4-disubstituted benzenes^{6b} and

Table 11. Correlations of ¹³C SCS for series 1–4 with those for monosubstituted benzenes

Series	SCS ^a	SCS ^b	<i>b</i>	<i>a</i>	<i>r</i>	<i>n</i>	SD
1	C-1'	SCS _p	0.98	0.36	0.999	10	0.24
	C-3'	SCS _o	1.03	0.16	0.998	10	0.47
	C-4'	SCS _i	1.06	−1.24	0.998	10	1.11
2	C-2'	SCS _o	0.96	−0.64	0.996	8	0.63
	C-3'	SCS _i	0.99	0.01	1.000	8	0.25
	C-4'	SCS _o	0.99	−0.44	0.998	8	0.47
	C-6'	SCS _p	0.93	−0.41	0.998	8	0.29
3	C-1'	SCS _p	0.99	0.32	0.999	10	0.27
	C-3'	SCS _o	1.03	0.16	0.999	10	0.44
	C-4'	SCS _i	1.05	−0.96	0.999	10	0.99
4	C-2'	SCS _o	0.96	−0.54	0.998	8	0.47
	C-3'	SCS _i	0.99	−0.04	1.000	8	0.29
	C-4'	SCS _o	0.98	−0.47	0.998	8	0.49
	C-6'	SCS _p	0.97	−0.28	0.997	8	0.41

^a SCS = δ(X) − δ(H) = *a* + *b* SCS_{*i, o, p*}.

^b SCS_{*i, o, p*} = SCS for monosubstituted benzenes (Ref. 6b).

p-NHCOR groups,^{10d} indicate that the enaminone moiety is weak electron donor in presence of a strong electron acceptor at the *para* position, whereas negative values of ϵ for C-6' in the *meta* series (2 and 4) mean that the enaminone moieties are weak electron acceptors. These results suggest that the electronic effects of the enaminone moieties are very similar to those of RCONH groups.

σ Values of enaminone moieties

In order to determine whether the enaminone moiety as a whole is an electron donor or acceptor, its σ values were evaluated. The σ_p^+ values for the enaminone moieties of 1 and 3 can be estimated from the ¹⁷O SCS

values of *para*-substituted nitrobenzenes.^{20b} The influences of the enaminone moiety in 1j (563.6 ppm) and 3j (565.1 ppm) on the ¹⁷O chemical shifts of the nitro groups are −8.8 and −8.7 ppm, respectively, compared with nitrobenzene (572.4 ppm at 40 °C and 573.8 ppm at 70 °C, acetonitrile, new measurement). Using a ρ^+ value of 14.3,²³ the σ_p^+ value of *ca.* −0.61 is obtained for the enaminone moieties. Similarly, σ_m and σ_p values were estimated by using the correlations of the ¹³C SCS of the C=N carbon in benzonitriles with σ_m ($\rho_m = -3.21$) and σ_p ($\rho_p = -2.39$)²⁴ and the chemical shift differences between enaminones (1i, 2i, 3i and 4i) and unsubstituted benzonitrile (118.81 ppm).²⁴ From the relationships of ¹³C SCS values for the *meta* and *para* carbon atoms of monosubstituted benzene derivatives in CDCl₃ [Eqns (4) and (5)],^{6b} the σ_i and σ_R^0 values for the enaminone moiety were obtained by using the ¹³C data for 1a and 3a. Since the *meta* SCS data for monosubstituted benzenes fitted poorly to substituent parameters by DSP [Eqn (5)], the estimated σ_i should have a large deviation. It has been shown that ¹⁹F SCS data of *meta*-substituted fluorobenzenes correlate well with σ_i values [Eqn (6)].²⁵ Therefore, more precise values of σ_i and σ_R^0 for the enaminone moiety can be estimated by using the corresponding ¹⁹F data and Eqns (4) and (6).

$$\text{SCS}(^{13}\text{C}_{\text{para}}) = 4.6\sigma_i + 21.5\sigma_R^0 \quad (4)$$

$$\text{SCS}(^{13}\text{C}_{\text{meta}}) = 1.6\sigma_i - 1.3\sigma_R^0 \quad (5)$$

$$\text{SCS}(^{19}\text{F}_{\text{meta}}) = 7.1\sigma_i - 0.6 \quad (6)$$

The σ constants (Table 13) for both acyclic and cyclic enaminone moieties are very close, indicating that they have essentially identical electronic properties. Correlations of ¹³C SCS for carbons at the aryl ring in the cyclic series (3 and 4) with the those in acyclic series (1 and 2) further support the contention that the effects of the two enaminone moieties on the chemical shifts at these sites are identical, as evidenced by the near unity slopes (Table 6, lines 6–9 and 14–19). Comparison of

Table 12. DSP and DSP-NLR correlations of ¹³C chemical shifts for nuclei at the benzene ring in series 1–4

Series	δ ^a	ρ _i ^b	ρ _R ^{0 b}	δ ⁰	SD	ε ^c	<i>r</i>	<i>n</i>	f ^d
1	C-1'	5.09	20.70	138.76	0.14	0.00	0.9996	10	0.03
	C-1'	5.09	20.62	138.76	0.14	−0.01	0.9996	10	0.03
	C-2'	−0.13	−6.56	124.06	0.76	0.00	0.886	10	0.44
2	C-6'	3.48	20.40	124.57	0.16	0.00	0.999	8	0.04
	C-6'	3.62	19.77	124.56	0.15	−0.11	0.999	8	0.04
	C-1'	2.45	−1.28	138.77	0.12	0.00	0.978	8	0.11
	C-5'	2.10	−0.66	128.97	0.12	0.00	0.969	8	0.13
3	C-1'	5.02	21.13	138.35	0.19	0.00	0.999	10	0.04
	C-1'	4.99	21.62	138.34	0.19	0.06	0.999	10	0.03
	C-2'	0.11	−7.01	123.28	0.70	0.00	0.908	10	0.38
4	C-6'	3.79	21.13	123.90	0.34	0.00	0.997	8	0.08
	C-6'	3.89	20.72	123.89	0.34	−0.07	0.997	8	0.08
	C-1'	1.78	−1.48	138.55	0.24	0.00	0.886	8	0.27
	C-5'	2.15	−0.77	129.10	0.11	0.00	0.977	8	0.11

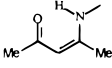
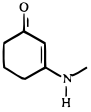
^a δ = δ⁰ + ρ_iσ_i + ρ_Rσ_R⁰ or δ = δ⁰ + ρ_iσ_i + ρ_Rσ_R⁰/(1 − εσ_R⁰).

^b σ_i and σ_R⁰ were taken from Ref. 6a.

^c Demand parameter for C_p-SCS in 1,4- or 1,3-disubstituted benzenes (Refs 6b and c).

^d f = SD/rms.

Table 13. Estimated substituent constants for the enaminone moieties

Substituent	σ_m	σ_p	σ_p^+	σ_I	σ_R^0
NH ₂	-0.16 ^a	-0.66 ^a	-1.30 ^a	0.17 ^b	-0.51 ^b
AcNH	0.21 ^a	0 ^a	-0.60 ^a	0.28 ^b	-0.35 ^b
	0.21	0.04	-0.62	0.29 ^c (0.33) ^d	-0.19 ^c (-0.20) ^d
	0.23	0.08	-0.61	0.36 ^c (0.40) ^d	-0.21 ^c (-0.22) ^d

^a Taken from Ref. 16a.^b Taken from Ref. 7b.^c Estimated from the ¹³C and ¹⁹F data.^d Estimated from the ¹³C data for **1a** and **3a**.

the σ constants (Table 13) for the enaminone moieties with those for the acetamino group shows that their electronic properties are essentially similar. The slightly more positive σ_I values reflect that the nitrogens in enaminone moieties are slightly more electronegative, and the less negative σ_R^0 values demonstrate that the enaminone moieties are poorer π -donors than the NHAc group. This can be attributed to the delocalization of the lone pair of the nitrogen into the enone moiety. These results confirm that in presence of a strong acceptor the enaminone moiety, as acetamino group, is a weak electron donor.

CONCLUSION

Correlations of ¹⁷O, ¹³C and ¹H chemical shifts for four series of enaminones showed that there is transmission of inductive (field) and resonance effects from *N*-aryl ring to the enaminone moiety. The correlation of O, H-2, C-2 with σ_R^- , and C-1, C-3 with σ_R^0 suggests that the resonance structures for enaminones can be described as A–D (Scheme 1). The effects of the enaminone moiety as a whole are very similar to those of the acetamido group. The enaminone moiety as a whole is a weak electron donor in the presence of the strong electron-withdrawing group, as evidenced by its σ constants. The correlations of ¹⁷O, ¹³C and ¹H chemical shifts with the pK_a values of anilines suggests that the nuclear shielding parameters depend on the strength of the basicity of anilines.

EXPERIMENTAL

Spectra

The ¹⁷O 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 micro-computer. The instrumental settings were as follows: spectral width 50 kHz (1025 ppm), 2K data points, pulse

width 33 μ s, acquisition time 20 ms, preacquisition delay 5 μ s, 150 000–300 000 scans, sample spinning (28 Hz). An even number (28–32) 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 $\delta(^{17}\text{O})$, measured in 0.25–0.5 M acetonitrile solution at 40 °C for series 1 and 2 and at 70 °C for series 3 and series 4 at natural isotopic abundance, are reported relative to $\delta(^{17}\text{O})(\text{H}_2\text{O})$ (= 0.0 ppm); dioxane [$\delta(^{17}\text{O})$ = 0 ppm] was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shifts values is *ca.* ± 1 ppm (± 0.2 ppm within the same series).

The ¹H and ¹³C NMR spectra were measured at 400.13 and 100.62 MHz, respectively on a Bruker DPX-400 spectrometer. The ¹H and ¹³C chemical shifts, measured in *ca.* 0.05 and 0.5 M CDCl₃ solutions, respectively, in a 5 mm o.d. tube at 20 °C, are reported relative to TMS as an internal reference (δ = 0). The 1D proton decoupling ¹³C NMR spectra were recorded using the following conditions: 16K data points, spectral width 26 315 Hz, 200–1000 scans, acquisition time, 0.311 s pre-acquisition delay 4.5 μ s and pulse width 6.5 μ s (90°). FID signals were zero filled to 32K and an exponential multiplier with LB of 3 Hz prior to FT. The accuracy of the results is within ± 0.03 ppm.

The ¹⁹F NMR spectra were measured at 376.48 MHz on a Bruker ARX-400 spectrometer under the following conditions: 32K data points, spectral width 62 500 Hz, 8 scans, pulse width 16.9 μ s (90°), acquisition time 0.262 s and preacquisition delay 4.5 μ s. The proton decoupling ¹⁹F NMR spectra were recorded by using a frequency of 7280 Hz at 300 K (27 °C). The samples were run as *ca.* 0.05 M solutions in CDCl₃ with 0.05 M fluorobenzene as an internal reference (δ = 0).

Melting points were observed under a microscope using a Mettler FP-52 instrument.

Materials

The general procedure for the preparation of 4-arylamino-pent-3-en-2-ones (**1** and **2**) was as follows. A mixture of Na₂SO₄ (5.0 g), the appropriate arylamine (10 mmol) and pentane-2,4-dione (11 mmol) in a sealed tube was heated at 120 °C for 1 h. After cooling, the

Table 14. Yields and melting points of enaminones (1–4)

Compound	Yield (%)	M.p. (°C) ^a	Compound	Yield (%)	M.p. (°C)
1a	86	45.3–46.5 (48) ²⁷	3a	91	174.9–175.3 (176–177) ³¹
1b	88	64.5–65.8 (65–67) ^{3a}	3b	85	134.4–135.5 (140–141) ³¹
1c	80	40.5–42.1 (41–43) ^{3a}	3c	83	164.5–165.0 (160–161) ³¹
1d	73	58.5–59.5 (59–61) ²⁸	3d	81	206.5–207.2
1e	81	oil (semisolid) ²⁹	3e	83	174–175.1
1f	89	58.6–60.3 (60–61) ²⁷	3f	86	188.5–189.5 (190) ³²
1g	83	57.3–58.5 (58–60.5) ^{3a}	3g	80	184–185.5
1h	86	71.9–73	3h	82	203.5–204.5 (203–204) ^{3a}
1i	78	86.5–87.5	3i	61	214–215
1j	82	143.6–144.1 (144–145) ^{3a}	3j	50	180.5–181.8 (178–80) ³¹
2b	90	oil	4b	87	142–142.8
2c	83	oil	4c	83	124–125
2e	80	26.8–28.3 ^b	4e	78	175–177.3
2f	79	40–42.7 (42) ²⁷	4f	81	155–156
2h	71	62.3–62.8	4h	75	156.5–157.0 (158) ³²
2i	85	87.3–88.0	4i	76	142.1–142.8
2j	77	75.5–76.0 (78–80) ³⁰	4j	73	169.7–170.8

^a Values in parentheses are taken from the References cited.

^b Bulb-to-bulb distillation at 150 °C/0.05 Torr.

mixture was flash chromatographed on a silica gel column (ethyl acetate) to afford the pure sample (71–90%).

The general procedure for the preparation of 3-arylaminocyclohex-2-en-1-ones (**3** and **4**) followed the modified method.²⁶ A mixture of the appropriate arylamine (10 mmol) and cyclohexane-1,3-dione (10 mmol) in a sealed tube was heated at 140 °C for 20 min. After cooling, the solidified product was crushed and washed with ethyl acetate. Recrystallization from acetonitrile

provided the pure sample (50–91%). The melting points and yields of enaminones are given in Table 14.

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