Enamine Chemistry. Part 22.[1] Carbon-13 Nuclear Magnetic Resonance Spectra of Acyclic Enamines

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The ^{13}C chemical shifts of a series of acyclic enamines derived from morpholine and pyrrolidine are reported. There is considerable variation in the contribution of the amine moiety to the chemical shift of the olefinic C-2, which is attributed principally to variation in the mesomeric contribution to the electron density. The amine contribution to the chemical shift of the olefinic C-1 is relatively constant if allowance is made for changes in the shift parameters of the alkyl substituents.

A RECENT report[2] on the ^{13}C n.m.r. spectra of cyclic enamines and enamino-ketones prompts us to report our preliminary studies of the ^{13}C n.m.r. spectra of acyclic enamines.

The chemical shifts of some acyclic enamines derived from morpholine and pyrrolidine are recorded in Table 1. Assignments are made from proton noise decoupled, off-resonance decoupled, and proton coupled spectra, relative intensities of signals, and comparison with reported data. These assignments are mostly straightforward and unambiguous. The signals of the methyl groups of the *cis*-enamines (1) occur to high field of those of the *trans*-enamines (2), presumably as a result of steric compression[3] by the adjacent amine residue. The assignments of the 2,2-disubstituted enamines (3) therefore follow, as indicated. The signals of the methyl groups in the 1,2-disubstituted enamines (5) could not be assigned on the basis of chemical shift differences alone, but the signal at δ 12.6 (5a) showed distinct doublet splitting by the single olefinic proton and was, therefore, assigned to the C-2 methyl group. This assignment was subsequently confirmed by a selective decoupling experiment with the pyrrolidine isomer (5b). Irradiation at δ *ca.* 1.0 (corresponding to the $CH_2{\cdot}CH_3$ proton signal) caused the low-field ^{13}C methyl signal (at δ 13.3) to collapse to a sharp singlet, whereas irradiation at δ *ca.* 1.7 (2-CH_3) caused the high-field ^{13}C methyl signal (at δ 12.5) to collapse to a singlet. The constitutional isomers (6a) and (7a) were obtained as an equilibrium mixture which we could not separate, but the signals of each isomer were readily identified because of their unequal populations. The signal at δ 12.9 was assigned to the 2-methyl group of (6a) by analogy with (5a), and the remaining assignments for this mixture followed from the relative intensities and splitting of the signals. The ^{13}C shifts of the geminal 2-methyl groups in the tetrasubstituted enamines (8a) and (10) are identical, or nearly so, suggesting that the steric shielding effects to which these groups are subjected are similar. These signals can readily be distinguished from those of the methyl carbon atoms of the 1-isopropyl substituent in (10) by the almost double intensity of the latter. The constitutional isomers (8b) and (9b) were also obtained as an equilibrium mixture, but in this case the high-field signals were overlaid and could not be distinguished readily by their relative intensities owing to the approximately equal populations of the two isomers. Only the olefinic signals were therefore assigned.

There are several unexpected features in Table 1. In saturated primary amines the amino-group deshields the α- and β-carbon atoms by 29 and 11.4 p.p.m., respectively, but shields the γ-carbon atom by 4.6 p.p.m.[4] Apart from the deshielding of the α-carbon atom (see later), these effects appear to be greatly attenuated in unsaturated amines. Comparison with the parent alkene[5] indicates a deshielding β-effect of only 1—3 p.p.m. on the α-carbon atom of a substituent R^1 by the morpholine and pyrrolidine rings, and the γ-effect,

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[1] Part 21, P. W. Hickmott and K. N. Woodward, *J.C.S. Perkin I*, 1976, 904.

[2] D. Tourwé, G. Van Binst, S. A. G. De Graaf, and U. K. Pandit, *Org. Magnetic Resonance*, 1975, **7**, 433.

[3] D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315; W. R. Woolfenden and D. M. Grant, *ibid.*, 1966, **88**, 1466; B. V. Cheney, *ibid.*, 1968, **90**, 5386.

[4] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.

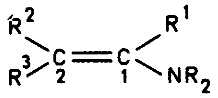
[5] J. W. de Haan and L. J. M. van de Ven, *Org. Magnetic Resonance*, 1973, **5**, 147.

transmitted through the double bond to the α-carbon atom of a substituent R^2, is deshielding to the extent of 0.5—1.5 p.p.m. Nevertheless, this difference is sufficient to differentiate between substituents attached to C-1 and C-2 in the same enamine [*viz.* (6a), δ (1-CH_3) 14.7; δ (2-CH_3) 12.9 p.p.m.] or in different enamines [*cf.* (7a), δ (CH_2) 26.6 with (4a), δ (CH_2) 23.7 p.p.m.], the deshielding of the carbon atom α to C-1 being slightly greater than that of the carbon atom α to C-2.

A systematic evaluation of alkyl shift parameters cannot be carried out since we do not have sufficient examples. However, the indications are that the effect of an alkyl group varies with its spatial relationship to the amine moiety. Thus a substituent R^3 deshields an R^2 α-carbon atom by *ca.* 7 p.p.m., whereas the reverse effect of a substituent R^2 on an R^3 α-carbon atom is *ca.* 5 p.p.m. A substituent R^3 shields an R^1 α-carbon atom by 2 p.p.m., but a substituent R^1 *deshields* an R^3 α-carbon atom by a similar amount. Surprisingly, although the amine residue shields a methyl substituent R^3, the α-carbon atom of the amine residue in *cis*-substituted enamines is deshielded to the extent of 1.6—4.6 p.p.m. As regards the olefinic carbon shifts the α-effect of an alkyl substituent is deshielding in all cases, but the magnitude of the shift varies greatly and depends upon whether the substituent is at C-1 or C-2. A substituent R^1 appears to deshield C-1 to the extent of 4—11 p.p.m., substituent R^2 deshields C-2 by 16—18 p.p.m., and a substituent R^3 deshields C-2 by 22—28 p.p.m. Clearly the effect of R^2 or R^3 is far greater than the deshielding effect (6.3—12.6 p.p.m.) normally attributed to a methyl substituent in an alkene hydrocarbon.[6] The explanation for this variation may be that the steric and *electronic* effects of introducing these substituents alters the electronic contribution of the amine moiety (see later) to the chemical shift of the carbon nucleus under consideration. Finally the effects of R^1 and R^2 on each other also differ. A substituent R^1 shields an R^2 α-carbon atom by 2.4—3.0 p.p.m., whereas a substituent R^2 shields an R^1 α-carbon atom by 5.5 p.p.m. However this difference could be attributed to different cosine factors in the expression [3] for the sterically induced polarization of charge in the relevant C–H bonds.

Table 1

^{13}C Chemical shifts of acyclic enamines



	Compound				Ref. to synthesis	^{13}C Chemical shift						
No.	R^1	R^2	R^3	R_2N		C-1	C-2	R^1	R^2	R^3	α-CH_2	β-CH_2
(1a)	H	H	Me	M	*a*	140.0d	107.5d			12.4q	52.3t	66.7t
(1b)	H	H	Me	P	*a*	137.6d	97.1d			12.7q	52.5t	25.7t
(2a)	H	Me	H	M	*b*	141.0d	95.8d		15.3q		49.9t	66.5t
(2b)	H	Me	H	P	*b*	136.6d	92.3d		15.5q		49.2t	25.1t
(3a)	H	Me	Me	M	*b*	135.9d	123.5s		22.1q	17.2q	53.4t	66.7t
(3b)	H	Me	Me	P	*b*	135.0d	114.75s		22.9q	18.0q	53.8t	25.4t
(4a)	H	Et	H	M	*b*	139.5d	103.5d		23.7t (CH_2) 15.9q (CH_3)		49.8t	66.4t
(4b)	H	Et	H	P	*b*	135.2d	100.6d		24.1t (CH_2) 16.5q (CH_3)		49.15t	25.1t
(5a)	Et	Me	H	M	*c*	150.9s	97.7d	21.1td (CH_2) 13.1q (CH_3)	12.6qd		49.9t	67.15t
(5b)	Et	Me	H	P	*c*	147.4s	90.5d	22.1t (CH_2) 13.3q (CH_3) *	12.5q *		48.0t	25.0t
(6a)	Me	Me	H	M	*d*	144.9s	97.6d	14.7 †	12.9 †		49.7t	67.0t
(7a)	Et	H	H	M	*d*	156.8s	85.6t	26.6t (CH_2) 13.40 (CH_3)			48.6t	67.0t
(8a)	Et	Me	Me	M	*e*	144.2s	121.6s	19.15t (CH_2) 14.6q (CH_3)	19.15q	19.15q	51.5t	67.5t
(8b)	Et	Me	Me	P	*e*	140.8s	117.5s					
(9b)	Pr^i	Me	H	P	*e*	151.5s	95.4d					
(10a)	Pr^i	Me	Me	M	*e*	147.2	125.2s	30.1d (CH) 21.5q (CH_3)	20.6 †‡	20.2 †‡	51.8t	67.7t
(10b)	Pr^i	Me	Me	P	*e*	144.6	123.5	31.1d (CH) 21.6q (CH_3)	20.4 †‡	20.0 †‡	51.95t	26.1t

M = morpholino; P = pyrrolidino.

* Assignments confirmed by single proton decoupling. † Overlaid. ‡ Assignments may be reversed.

[a] J. Sauer and H. Prahl, *Tetrahedron Letters*, 1966, 2863; [b] C. Mannich and H. Davidsen, *Ber.*, 1936, **69**, 2106; [c] G .Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207; [d] P. W. Hickmott, B. J. Hopkins, and C. T. Yoxall, *J. Chem. Soc. (B)*, 1971, 205; [e] W. A. White and H. Weingarten, *J. Org. Chem.*, 1967, **32**, 213.

The most interesting feature of Table 1 is the variation in ^{13}C shifts for the olefinic carbon atoms, since these will reflect the inductive, mesomeric, and steric effects of the amine moiety, superimposed on any changes in bond lengths, excitation energy, and other influences. The C-1 shifts vary over a range of 20 p.p.m., and the

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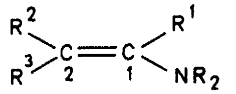
[6] D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, 1971, **36**, 2757.

C-2 shifts span a range of 40 p.p.m. If we assume that the α- and β-effects of the alkyl substituents in an olefin are not affected by the introduction of an amine substituent, the contribution ($\Delta\delta_C$) of the amino-group to the olefinic chemical shifts can be derived from the expression $\Delta\delta_C = [\delta\ (\text{enamine}) - \delta\ (\text{alkene})]$. These values are shown in Table 2. However, Roberts *et al.*[7] have shown that the deshielding α-effects of hydroxy and alkyl substituents in highly branched bicyclic systems decrease with increasing substitution at the α- and β-positions, and have attributed this to lengthening of the C_α–C_β bond. Also the value of the parameters α, β, and α′, developed for the prediction of the ^{13}C chemical shifts of olefinic carbon atoms, are not constant, and in fact decrease in magnitude as the degree of substitution of the double bond increases. It follows that the introduction of a bulky amine residue could alter the contribution of the alkyl substituents to the ^{13}C shifts of C-1 and C-2 in the enamine in comparison with the parent alkene, and thus invalidate the derived ($\Delta\delta_C$) values. We have attempted to allow for this by modifying the value of $\Delta\delta_C$ by the amounts the parameters α, β, and α′ are reported[6] to change when these parameters appear more than once in the expression used to predict the chemical shift of the trigonal carbon atoms in an acyclic alkene, assuming that the effect of the amine residue is similar to that of an isopropyl substituent on the shift parameters of the residual alkyl substituents. The α, β, and α′ correction factors, and *cis* factor where applicable, quoted in solution 5, Table 2 of ref. 6, were used for this purpose and the values obtained ($\Delta\delta_C$*) are given in Table 2.

TABLE 2

Contribution ($\Delta\delta_C$) of the amine moiety to the chemical shift in acyclic enamines



a ; R_2N = morpholino

b ; R_2N = pyrrolidino

	Compound			Morpholine enamines (a)					Pyrrolidine enamines (b)				
No.	R¹	R²	R³	$\lambda_{max.}$ nm	$\Delta\delta_{C-1}$	$\Delta\delta_{C-1}$ *	$\Delta\delta_{C-2}$	$\Delta\delta_{C-2}$ *	$\lambda_{max.}$ nm	$\Delta\delta_{C-1}$	$\Delta\delta_{C-1}$ *	$\Delta\delta_{C-2}$	$\Delta\delta_{C-2}$ *
(1)	H	H	Me		+24.6	+25.7	−28.2	−27.1		+22.2	+23.3	−38.6	−37.5
(2)	H	Me	H	227	+25.6	+25.6	−40.1	−39.9	234	+21.2	+21.2	−43.4	−43.4
(3)	H	Me	Me	228	+26.1	+27.2	−17.7	−16.6	236	+25.2	+26.3	−26.4	−25.4
(4)	H	Et	H	227	+26.7	+26.7	−36.7	−36.7	229	+22.4	+22.4	−39.6	−39.6
(5)	Et	Me	H	227	+18.5	+25.6	−25.1	−27.6	230	+15.0	+22.1	−32.3	−34.8
(6)	Me	Me	H	225 †	+21.6	+26.4	−25.7	−28.2					
(7)	Et	H	H		+16.6	+23.7	−27.2	−29.7					
(8)	Et	Me	Me	232	+18.5	+25.6	−8.5	−9.9	235	+14.2	+22.2	−12.6	−14.0
(9)	Prⁱ	Me	H							+12.7	+22.4	−26.4	−28.4
(10)	Prⁱ	Me	Me	227	+24.0 ‡	+24.5	−3.4 ‡	−4.8		+11.4 ‡	+21.9	−5.1 ‡	−6.5

† Mixture of enamines (6) and (7). ‡ Parent alkene (2,4-dimethylpent-2-ene): δ_C (neat liquid) 17.7 (q, C-1 *cis* to Prⁱ), 25.8 (q, C-1 *trans* to Prⁱ), 128.6 (s, C-2), 133.2 (d, C-3), 27.8 (d, C-4), and 23.4 (q, C-5).

Table 2 reveals that the magnitude of the $\Delta\delta_{C-1}$ values is unaffected by introduction of substituents at C-2, but appears to decrease with increasing substitution at C-1. However, the $\Delta\delta_{C-1}$* values do not follow this trend, remaining fairly constant, as one would expect if the α-effect of the amine moiety is mainly determined by its electronegativity. Nevertheless there is one intriguing feature about the $\Delta\delta_{C-1}$* values in that their magnitude, particularly for the pyrrolidine moiety, is very similar to the computed[6] and observed deshielding α-effect of an isopropyl substituent on the chemical shift of an attached olefinic carbon atom (*i.e.* +23 p.p.m.). Since the β-effect of a substituent is independent of the atom through which it is transmitted,[6] the α-methylene groups of the amine should exert a deshielding influence on C-1 similar to that of the methyls of an isopropyl substituent and, in view of the greater electronegativity of the nitrogen atom, the α-effect of the amine moiety would be expected to be greater. A possible explanation for this anomaly is that the mesomeric contribution to the electron density at C-1 is not entirely passed on to C-2. In other words, as suggested by Clark, Murrell, and Tedder,[8] the mesomeric effect increases the electron density at C-1 as well as at C-2 (*viz.* ${}^{\delta-}\mathrm{C}{=}{}^{\delta\delta-}\mathrm{C}{-}{}^{\delta+}\mathrm{N}$, *not* ${}^{\delta-}\mathrm{C}{=}\mathrm{C}{-}{}^{\delta+}\mathrm{N}$), thus partially compensating for the inductive electron withdrawal by the nitrogen atom. However if this were the case a substituent R³ would be expected to increase the $\Delta\delta_{C-1}$* value, owing to the resulting $A^{(1,3)}$-strain[9] which must cause twisting about the C(1)–N bond, unless there are shielding steric effects, or other influences, which compensate for this.

Since it is widely held that ^{13}C shifts of unsaturated systems can be correlated with variations in local electron density,[10] and show an upfield shift when the π-

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[7] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

[8] D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1963, 1250.

[9] F. Johnson, *Chem. Rev.*, 1968, **68**, 375.

[10] (*a*) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 1961, 468; P. C. Lauterbur, *ibid.*, p. 274; (*b*) P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 1838; *J. Chem. Phys.*, 1963, **38**, 1415; G. E. Maciel, *ibid.*, 1965, **42**, 2746; *J. Phys. Chem.*, 1965, **69**, 1947; T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, 1964, **41**, 2796; J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, 1968, **72**, 716; Gurudata and J. B.Stothers, *Canad. J. Chem.*, 1969, **47**, 3601; T. Higashimura, S. Okamura, I. Morishima, and T. Yonezawa, *Polymer Letters*, 1969, **7**, 23; K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Japan*, 1970, **43**, 3195; R. H. Levin and L. Weingarten, *Tetrahedron Letters*, 1975, 611; D. H. O'Brien, A. J. Hart, and C. R. Russell, *J. Amer. Chem. Soc.*, 1975, **97**, 4410; G. Myajima, K. Takahashi, and K. Nishimato, *Org. Magnetic Resonance*, 1974, **6**, 413.

electron density is increased, the amine contribution to the chemical shift of C-2 ($\Delta\delta_{C-2}$ or $\Delta\delta_{C-2}^*$) must reflect the magnitude of the $p\pi$-interaction between the amine moiety and the double bond, superimposed on steric shielding effects and other influences. The wide variation in the $\Delta\delta_{C-2}$ values, which agree closely with the corrected $\Delta\delta_{C-2}^*$ values, indicates that the amine contribution, and hence the $p\pi$-interaction in the enamine system, is critically dependent upon the degree of substitution at C-1 and C-2. These variations cannot be attributed to changes in the excitation energy, although these are predicted to produce significant changes in the chemical shift,[11] since there is no obvious correlation with $\lambda_{max.}$ values (Table 2) (we assume that the energy of the $\sigma \longrightarrow \pi^*$ transition would be affected to an extent similar to that of the band in the 230 nm region). Unfortunately we do not have ^{13}C data for the unsubstituted enamine double bond, since the literature methods for the synthesis of *N*-vinylpyrrolidine failed in our hands (see Experimental section). However it appears that the introduction of a substituent R^1, R^2, or R^3 reduces the amine contribution to the C-2 shift ($\Delta\delta_{C-2}^*$) by *ca.* 8—12, 10—12, and 18—23 p.p.m., respectively. The reductions are smaller for the pyrrolidine than for the corresponding morpholine enamines, presumably owing to the lower steric requirements of the pyrrolidine ring. Since the effects of steric interactions on the ^{13}C shifts of the trigonal carbon atoms in substituted ethylenes may be shielding or deshielding,[5] it is not possible to decide definitely to what extent these reductions are steric in origin. However since the differences between the olefinic shifts of *E*- and *Z*-monoalkene isomers are rarely more than a few p.p.m., even when very bulky substituents are involved,[5,12] it seems probable that reductions in the $\Delta\delta_{C-2}^*$ values greater than 3—5 p.p.m. are electronic in origin and may be attributed to the reduced mesomeric electron donation by the amine moiety to C-2, caused by the introduction of substituents R^1, R^2, and R^3. There appears to be an analogous reduction in mesomeric energy in alkyl vinyl ethers on introduction of alkyl substituents at the olefinic positions C-1 or C-2.[13]

The results reported here are in qualitative agreement with those expected from electron density calculations,[14] except that the calculated effect of substituents in reducing the $\Delta\delta_{C-2}^*$ values, with an assumed proportionality factor of 160 p.p.m. per electron,[10a] are too small (*i.e.* R^1 1.5; R^2 3.3 p.p.m.).

EXPERIMENTAL

The ^{13}C n.m.r. spectra were recorded at 20 MHz with a Varian CFT-20 spectrometer for neat liquids. The selective decoupling experiments were carried out by the Physico-Chemical Measurements Unit, Harwell. Chemical shifts are given in p.p.m. relative to internal Me_4Si (negative values indicate a high field shift). The enamines were prepared by literature methods (see Table 1) and were freshly distilled before determination of their spectra. Their purity and isomer distributions were checked by i.r. and ^{1}H n.m.r. spectroscopy. U.v. spectra were determined with a Unicam SP 800 spectrophotometer for solutions in hexane.

Attempted Synthesis of N-*Vinylpyrrolidine*.—(*a*) Freshly distilled acetaldehyde (3.08 g, 0.070 mol) was added dropwise to a mixture of pyrrolidine (5.12 g, 0.072 mol) and anhydrous magnesium sulphate (8 g) in anhydrous ether (30 ml) with stirring at 0 °C during 10 min. The mixture was kept at 0 °C overnight, then filtered, and the filtrate was evaporated to give a clear liquid showing strong i.r. absorption at 1 642 cm^{-1}, as previously reported.[15a] However, the ^{1}H and ^{13}C n.m.r. spectra showed this to be a mixture of the dimer [1,3-dipyrrolidinobut-1-ene (A)] and 1,1-dipyrrolidinoethane (B): τ (A) ($CDCl_3$) 3.75 (d, H-1), 5.85 (dd, H-2), 7.45 (m, H-3), 8.8 (d, H-4), 7.0 (t, C-1 $CH_2{\cdot}N{\cdot}CH_2$), 7.45 (t, C-3 $CH_2{\cdot}N{\cdot}CH_2$), and 8.25 (t, β-CH_2); δ_C (A) (neat liquid) 135.3 (d, C-1), 102.5 (d, C-2), 61.1 (d, C-3), 23.1 (q, C-4), 48.9 (t, C-1 $CH_2{\cdot}N{\cdot}CH_2$), 51.6 (t, C-3 $CH_2{\cdot}N{\cdot}CH_2$), 25.1 (t, C-1 β-CH_2), and 23.8 (t, C-3 β-CH_2); τ (B) ($CDCl_3$) 7.45 (q, H-1), 8.8 (d, H-2), 7.0 (t, α-CH_2), and 8.25 (t, β-CH_2); δ_C (B) (neat liquid) 75.8 (d, C-1), 12.1 (q, C-2), 48.9 (t, α-CH_2), and 23.8 (t, β-CH_2).

(*b*) A solution of acetaldehyde (15 g) in benzene (40 ml) was added to pyrrolidine (3 g) in benzene (40 ml) over 15 min, and the mixture was heated under reflux until the theoretical amount of water had been collected. Evaporation, and distillation of the residual oil gave a liquid (0.75 g), b.p. 85° at 0.2 mmHg.[15b] However, the complicated nature of the i.r. and ^{1}H and ^{13}C n.m.r. spectra indicated that this was not *N*-vinylpyrrolidine, but probably a telomer.

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