Nuclear Magnetic Resonance Studies of (*Z*)- and (*E*)-3-Amino-3-(*p*-substituted phenyl)propenenitriles

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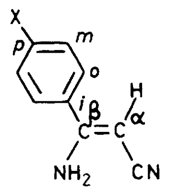
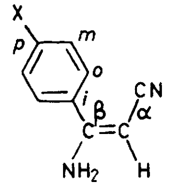
^{13}C N.m.r. shifts of (*Z*)- and (*E*)-3-amino-3-(*p*-substituted phenyl)propenenitriles [p-$XC_6H_4C(NH_2)$=CHCN; X = NMe_2, OMe, Me, H, Cl, or CF_3] in $(CD_3)_2SO$ are reported. Ethylenic and cyano carbon chemical shifts are compared with those of *trans*- and *cis*-cinnamonitriles. The effect of substituents on ^{13}C shifts, and correlations with σ^+ substituent constants and with ^{1}H and ^{13}C experimental shifts are also discussed.

Various aspects of the reactivity of 3-amino-3-arylpropenenitriles (**1**) have been investigated in our laboratory. Recent work has included studies on their dipolarophilic reactivity towards benzonitrile oxides,[1–3] compared with that of cinnamonitrile,[4] and on their nucleophilic reactivity towards *N*-phenyl- and *N*-methyl-*S*-chloroisothiocarbamoyl chloride.[5]

We here report the ^{13}C n.m.r. spectra of the enaminonitriles (**1**) (*Z*-isomers, used in previous synthetic work) and (**2**) (*E*-isomers), with the aim of obtaining information on the transmission of electronic effects of the amino group and of phenyl substituents, which, together with the configuration of the C=C double bond, appear to be responsible for the reactivity of the enaminonitrile system.[2,3]



(**1**) *Z*



(**2**) *E*

a; X = NMe_2
b; X = OMe
c; X = Me
d; X = H
e; X = Cl
f; X = CF_3

Results and Discussion

The preparation and characterization of the *Z*-enamines (**1**)[2,6] and the chemical shift of the methine proton of the *E*-enamine (**2d**) in $(CD_3)_2SO$ have been reported.[6]

Mixtures of *E*- and *Z*-isomers were obtained by irradiating solutions of pure *Z*-isomers (**1**) in $(CD_3)_2SO$ directly in the n.m.r. tube (see Experimental section). The relative yields and the methine ^{1}H chemical shifts are recorded in Table 1. The ^{13}C chemical shifts for the enamines (**1**) and (**2**) are listed in Table 2. The signals of the *E*-isomers could easily be identified in the spectra of the photoequilibrium mixtures.

Table 1. ^{1}H Chemical shifts for methine protons of (*Z*)- and (*E*)-3-amino-3-(*p*-substituted phenyl)propenenitriles in $(CD_3)_2SO$[a,b]

Substituent X	Photo-equilibrium population (%) of *E*-isomer[c]	*Z*	*E*
NMe_2	42	4.091	4.100
OMe	48	4.133	4.206
Me	41	4.156	4.252
H	41	4.188	4.302
Cl	48	4.201	4.293
CF_3	46	4.288	4.371

[a] Chemical shifts in p.p.m. relative to Me_4Si. [b] For the description of the solutions see Experimental section. [c] Yields of *E*-isomers in the photoequilibrium mixtures were determined from intensity ratios of the methine proton signals.

Phenyl Ring Carbon Atoms.—The assignment of phenyl ring carbon chemical shifts (Table 2) rests mainly on substituted chemical shift (SCS) considerations, with the aid of off-resonance decoupled spectra. The SCS values with respect to the unsubstituted derivative, which can be easily calculated from the shifts in Table 2, are in very good agreement with those for monosubstituted benzenes[7] and for substituted styrenes.[8]

Attempted correlations of the shifts for *ipso*-carbon atoms with single-substituent parameters (SSP) equations showed a good correlation with σ^+ constants (Table 3), with high sensitivity to the effects of the substituents X ($\rho^+ > 7$), in agreement with the behaviour of the analogous carbon shifts in (α-cyano-) cinnamates and cinnamamides.[9]

As expected, the similar ρ^+ values and the unit slope of the correlation between *ipso*-carbon (*i*) shifts for *Z*- and *E*-isomers (Table 3) confirm that the sensitivity to substituent effects in both isomers is the same.

Ethylenic and Cyano Carbon Atoms.—The ethylenic carbon atoms C_β of the enaminonitrile (**1**) and (**2**) are deshielded by *ca.* 12 p.p.m. with respect to the analogous carbon atoms of the parent cinnamonitriles.[10–12] The carbon atoms C_α are shielded by *ca.* 35 p.p.m., and the cyano carbon atoms are deshielded by *ca.* 4 p.p.m.

It is known that ^{13}C shifts of unsaturated systems can be correlated with variations in local electron density, and show an upfield shift when the π-electron density is increased. Comparison of the charge density by CNDO/2 calculations in 3-nitro- and 3-amino-acrylonitriles reveals that conjugative electron donation produces decreases and increases in the π-electron densities on alternate carbon atoms.[12]

Although CNDO/2 calculations of electron densities are not available for cinnamonitriles and the enaminonitriles (**1**) and (**2**), comparison of ethylenic and cyano chemical shifts for the latter compounds with those of the cinnamonitriles reveals that in the enamines the amino group produces a decrease in electron density (*i.e.* a downfield shift) at the cyano and β-carbon atoms and an increase in electron density (*i.e.* an upfield shift) at the α-carbon atoms. The relatively low deshielding (only 1—3 p.p.m.) at the *ipso*-carbon atom (*i*) can be ascribed to the β-effect of the amino group, similar to that found for ^{13}C n.m.r. shifts in acyclic enamines.[13]

Table 2. ^{13}C Chemical shifts for (*Z*)- and (*E*)[a]-3-amino-3-(*p*-substituted phenyl)propenenitriles in $(CD_3)_2SO$[b]

Carbon	X = NMe_2		X = OMe		X = Me		X = H		X = Cl		X = CF_3	
atom	(**1a**)	(**2a**)	(**1b**)	(**2b**)	(**1c**)	(**2c**)	(**1d**)	(**2d**)	(**1e**)	(**2e**)	(**1f**)	(**2f**)
CN	121.5	(0.0)	121.0	(+1.7)	120.7	(+1.8)	120.6	(+1.8)	120.4	(+1.7)	120.0	(+1.8)
C_α[c]	56.2	(+1.9)	57.9	(+1.6)	58.5	(+1.6)	59.2	(+1.2)	59.7	(+1.2)	60.8	(+0.7)
C_β[c]	162.1	(+2.3)	161.7	(+2.2)	162.1	(+2.3)	162.3	(+2.1)	161.0	(+2.2)	160.7	(+2.3)
C_i	121.9	(+0.3)	127.7	(−1.3)	132.8	(0.0)	135.8	(−1.2)	134.6	(−0.7)	139.8	(+0.2)
C_o	127.4	(+1.5)	128.0	(+1.5)	126.4	(+1.4)	126.6	(+1.3)	128.5	(+1.3)	127.5	(+1.4)
C_m	111.5	(−0.2)	114.1	(−0.3)	129.3	(−0.2)	128.7	(−0.1)	128.8	(0.0)	125.6	(−0.4)
C_p	152.1	(−0.2)	161.3	(−0.3)	140.5	(−0.4)	130.6	(−0.3)	135.3	(−0.4)	133.5	(+0.2)
Others	39.8	(−0.1)	55.4	(+1.0)	29.8	(0.0)					124.1[d]	(0.0)

[a] Reported in parentheses, as substituent chemical shifts (SCS) with respect to the corresponding shifts of the *Z*-isomers. [b] Chemical shifts in p.p.m. relative to Me_4Si, calculated by adding 36.9 to the shift relative to the centre peak of $(CD_3)_2SO$. [c] According to the nomenclature adopted in this paper. [d] J_{CF} 272 Hz.

Table 3. Correlation of C_i, C_α, and C_β chemical shifts with σ^+ constants for substituents X[a] or with other experimental shifts

Chemical shifts	σ^+ or chemical shifts	r[b]	Slope[c]
$C_i(Z)$	σ^+	0.990	7.99 (0.57)
$C_i(E)$	σ^+	0.976	7.85 (0.87)
$C_i(Z)$	$C_i(E)$	0.994	0.997 (0.056)
$C_\alpha(Z)$	$H_\alpha(Z)$	0.964	22.6 (3.1)
$C_\alpha(E)$	$H_\alpha(E)$	0.986	12.5 (1.1)
$C_\alpha(Z)$	σ^+	0.990	1.99 (0.14)
$C_\alpha(E)$	σ^+	0.994	1.50 (0.08)
$C_\alpha(Z)$	$C_\alpha(E)$	0.996	1.33 (0.06)
$C_\beta(Z)$	$C_\beta(E)$	0.994	1.02 (0.05)

[a] From O. Exner, 'Correlation Analysis in Chemistry. Recent Advances,' ed. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978, ch. 10. [b] Correlation coefficient; six substituents in regression analysis. [c] Standard deviation of slope in parentheses.

Both ethylenic and cyano carbon atoms as well as the methine protons of the *E*-form resonate at somewhat lower fields with respect to the *Z*-isomers (*cf.* Tables 1 and 2). The intensities of the methine proton signals can be used conveniently to determine the isomeric ratios (see Table 1).

The presence of the substituents X affects significantly both α-carbon and proton shifts in both *Z*- and *E*-isomers, as evidenced by the correlations reported in Table 3. α-Carbon shifts are correlated with σ^+ substituent constants, the sensitivity being slightly higher for the *Z*-isomer. Moreover, the chemical shifts of the ethylenic carbon atoms of the *Z*-form are correlated with the corresponding shifts for the *E*-form. This correlation is excellent for both α-carbon atoms (shifts of which were also found to be dependent on substituent effects as evaluated by σ^+ constants) and β-carbon atoms (which show no correlation with substituent constants). This result confirms that ^{13}C n.m.r. shifts exhibit markedly systematic behaviour in the series (**1**) and (**2**), and emphasizes the importance of direct comparison of experimental shifts for both interpretation and prediction of chemical shifts.

Experimental

Materials.—The enamines (**1**) were synthesized by condensation of cyanomethanide anion with the appropriate substituted benzonitriles, giving the *Z*-stereoisomers.[2,6] The *Z*-configuration was established by Dedina *et al.* on the basis of nuclear Overhauser effects.[6]

Photoequilibrium mixtures of *E*- and *Z*-isomers were obtained directly in a n.m.r. tube by irradiation 0.5M-solutions of pure *Z*-isomers in $(CD_3)_2SO$ with a 450 W Hanovia lamp equipped with a Pyrex filter for 5 h. Attempts to separate the isomers by chromatographic methods were unsuccessful, probably owing to a rapid interconversion catalysed by the chromatographic support. Irradiation of the *Z*-isomers produces an equilibrium mixture of the two isomers, as confirmed by the hypsochromic shift in the u.v. absorption maximum (due to *cis–trans* isomerization), by the presence of an isosbestic point, and by the ^1H n.m.r. spectra of the reaction mixtures, revealing signals at lower fields, which can be assigned to the methine hydrogen atoms of the *E*-form. The relative yields and methine ^1H n.m.r. chemical shifts are reported in Table 1.

Spectra.—The ^{13}C n.m.r. spectra were obtained with a Bruker WP 80 FT spectrometer operating at 20.11 MHz and 300 ± 2 K. Typical conditions were: spectral width 5 kHz; data points 16 K; pulse width 1.0 μs (15°); decoupler frequency 6 kHz; decoupler power 2 W; pulse repetition time 0.82 s; number of pulses 500—6 000. The accuracy of the ^{13}C chemical shift measurements was within ±0.1 p.p.m. ^1H N.m.r. spectra were measured at 80 MHz with the same instrument.

Acknowledgments

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