The Effect of Charge and of Electron Density on the Nuclear Magnetic Resonance Parameters of Conjugated Systems: Some Isoelectronic Anions and Cations

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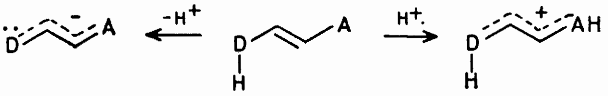
3-t-Butylaminoacrolein is readily *O*-protonated by trifluoroacetic acid and is *N*-deprotonated by sodium hydride in dimethyl sulphoxide, to give cationic and anionic species respectively, which both contain delocalised systems of 6π-electrons. The effect of the delocalisation is reflected in the equalisation of the vicinal coupling constants $^{3}J_{1,2}$ and $^{3}J_{2,3}$ compared with the neutral compound. The isoelectronic nature of the series is reflected in the similarity of ^{1}H and ^{13}C n.m.r. chemical shifts for anion, cation, and neutral compound. The effect of the overall charge is shown by the regular increase of $^{1}J_{CH}$ through negatively, neutral, and positively charged systems. Similar results are obtained for glyoxal t-butylhydrazone.

It has long been recognised that ^{1}H and ^{13}C n.m.r. chemical shifts of carbanions and carbocations are strongly dependent on the electron density at a given site.[1] However, it is often difficult to distinguish the influence of electron density from that of charge density, since the two effects usually act in parallel. For example, the one-bond coupling $^{1}J_{CH}$ is generally larger in carbocations than in carbanions, though it is not clear whether this is due to charge effects (+1 or −1) or to electronic effects (six or eight electrons in the carbon sp^2 orbital).

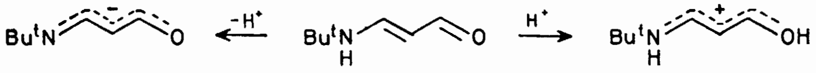


(C) (A) (B)

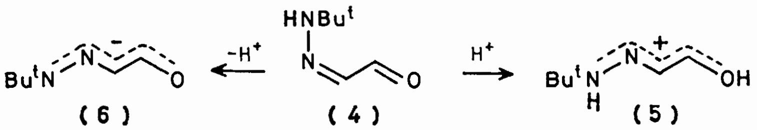
In order to differentiate charge and electronic effects, an isostructural series is required in which it is possible to vary the overall charge while the number of electrons is kept constant. These criteria can be met with a ' push–pull ' alkene [2] system (A) in which a heteroatom can donate a pair of electrons in the cation (B) or alternatively be itself deprotonated to give the anion (C). This paper reports the results of an empirical study of two such systems.

The compounds chosen were the enaminone (1) and the glyoxal monohydrazone (azaenaminone) (4), which were prepared as previously described.[3] It is well known that such systems are quantitatively *O*-protonated in strong acids [4,5] (*e.g.* trifluoroacetic acid) to give conjugated 6π-electron cations, *e.g.* (2) and (5). *N*-Deprotonation was conveniently effected using sodium hydride in dimethyl sulphoxide, but (4) was sufficiently acidic to generate the anion (6) with sodium methoxide in methanol. Assignment of the peaks in the spectra was generally possible by inspection, but the 1- and 3-positions in (2) and (3) could not be distinguished in this way. Their signals were assigned unambiguously using the spectra of the cation and anion derived from the specificially deuteriated compound (7).[3]

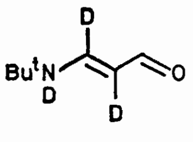
The spectra of enaminones and azaenaminones are strongly dependent on the shape of the system, and the structures of (1) and (4) have previously been assigned.[3] No long-range proton–proton coupling $^{4}J_{2,NH}$ is apparent in the cation (5), and so this, and the corresponding anion (6), are tentatively assigned the *E-s-E* configuration by analogy with the enaminone series. However, for comparison, the *Z-s-Z* series (8)—(10) of 6π-electron anions and 4π-electron cations was chosen since the literature data for these systems are complete [6,7] (Figures 1 and 2): homoconjugation has been ruled out in all cases.



(3) (1) (2)



(6) (4) (5)



(7)

(8)

(9)

(10)

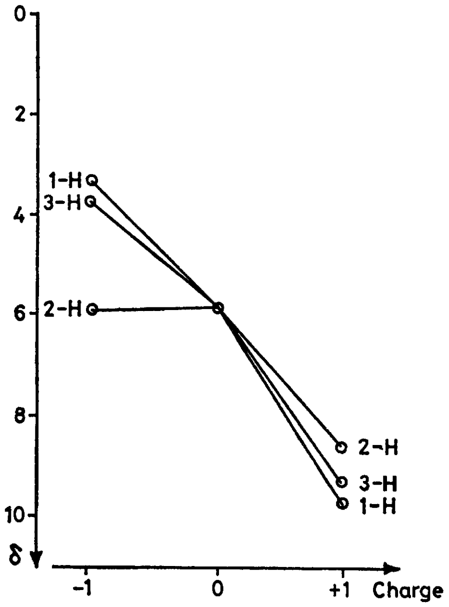


FIGURE 1 ^{1}H N.m.r. chemical shifts of (8)—(10)

The data for the present series (1)—(3) and (4)—(6) are collected in Tables 1 and 2 and shown in Figures 3—10. The delocalisation of the electrons in the vinylogous amide anions (3) and (6) and in the cations (2) and (5) is demonstrated by the increase in the vicinal coupling constant $^3J_{1,2}$, which reflects the increase in the bond order of the C-1–C-2 bond. This is accompanied in the case of (2) and (3) by a reduction in $^3J_{2,3}$, which is form-

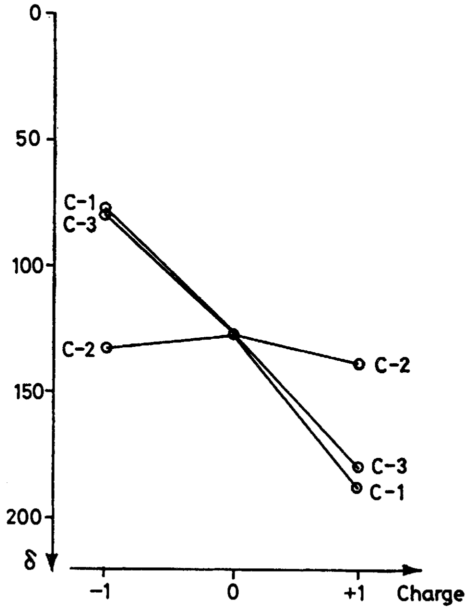


FIGURE 2 ^{13}C N.m.r. chemical shifts of (8)—(10)

TABLE 1

^{1}H N.m.r. spectra of 3-t-butylaminoacrolein and glyoxal t-butylhydrazone [a]

Species	Solvent	δ(Bu^t)	δ(1-H)	δ(2-H)	δ(3-H)	δ(NH)	$^3J_{1,2}$	$^3J_{2,3}$	$^3J_{3,NH}$	$^4J_{2,NH}$
(1)	[$^2H_6$]DMSO	1.20	8.88	5.11	7.37	7.96	8.7	12.5	13.0	
(2)	CF_3CO_2H	1.49	7.94 [b]	6.12	8.08 [b]	*ca.* 9.4	11.2	11.2	16.5	
(3)	[$^2H_6$]DMSO	0.99	8.01 [c]	4.69	7.59 [c]		10.0	9.6		
(4)	[$^2H_6$]DMSO	1.20	9.22	7.06		9.52	8.0			1.3
(5)	CF_3CO_2H	1.53	8.67	7.62			9.2			
(6)	[$^2H_6$]DMSO	1.00	8.56	6.56			9.5			

[a] Chemical shifts are to high frequency of Me_4Si; coupling constants are quoted in Hz. [b] Relative assignment confirmed by coupling of 1-H to NH, and by the spectrum of the [3-^{2}H] derivative. [c] Relative assignment confirmed by the spectrum of the [2,3-$^2H_2$] derivative.

TABLE 2

^{13}C N.m.r. spectra of 3-t-butylaminoacrolein and glyoxal t-butylhydrazone [a]

Species	Solvent	δ(C*Me*$_3$)	δ(*C*Me$_3$)	δ(C-1)	δ(C-2)	δ(C-3)	$^1J_{CH}$	$^nJ_{CH}$ [b]
(1)	[$^2H_6$]DMSO	29.42	51.91	187.72	102.05	156.85	C-1 159.5 C-2 155.3 C-3 160.9	*c* 3.1, 20.3
(2)	CF_3CO_2H	29.27	60.79	176.93 [d]	104.68	167.53 [d]	C-1 180.8 C-2 164.9 C-3 168.4	3.6 9.6,[e] 4.1 [e] 3.6
(3)	[$^2H_6$]DMSO	30.93	53.66	176.80 [d]	100.27	159.41 [d]	C-1 148.7 C-2 149.2 C-3 140.0	 9.1, 17.9 2.3
(4)	[$^2H_6$]DMSO	28.25	54.68	189.36	132.24		C-1 170.8 C-2 164.6	8.7 4.3, 22.9
(5)	CF_3CO_2H	27.56	65.46	184.85	131.54		C-1 186.4 C-2 172.3	 5.1
(6)	[$^2H_6$]DMSO	28.66	59.56	178.59	126.76		C-1 153.3 C-2 155.8	*c* 15.1

[a] Chemical shifts are to high frequency of Me_4Si; coupling constants are quoted in Hz, and are estimated to be accurate to ±0.5 Hz. [b] Not specifically assigned (see text). [c] Minor couplings poorly resolved. [d] Relative assignment confirmed by the spectrum of the [(2),3-$^2H_{(2)}$] derivative. [e] Measured for the [3-^{2}H] derivative: an additional small coupling to 3-H in the parent gives a poorly resolved multiplet for this carbon.

ally a double bond in the neutral species (Figures 3 and 4).

Both the ^{1}H and ^{13}C n.m.r. chemical shifts of the series (1)—(3) and (4)—(6) in general follow similar trends (Figures 5—8). In all cases, the most shielded nucleus of the conjugated portion of the molecule is the central C-2 or 2-H nucleus, although a slight trend to high frequency (1—2 p.p.m. in ^{1}H n.m.r.; 4—5 p.p.m. in ^{13}C n.m.r.) is apparent as the series is scanned from anion to cation. It is well known that the *electron* density of charged pentadienes is located at the termini and at the central position[6] (Scheme). The slight differences observed may reflect differences in the electron distribution in the 6π systems: in particular the tripolar resonance structure in the cation is probably relatively disfavoured. As expected, these results are in spectacular contrast with those of the 4π-cation (9) and 6π-anion (10) (Figures 1 and 2), where the ^{1}H and ^{13}C n.m.r. chemical shift differences for the corresponding position (3-position) are 5.6 and 100.1 p.p.m., respectively.

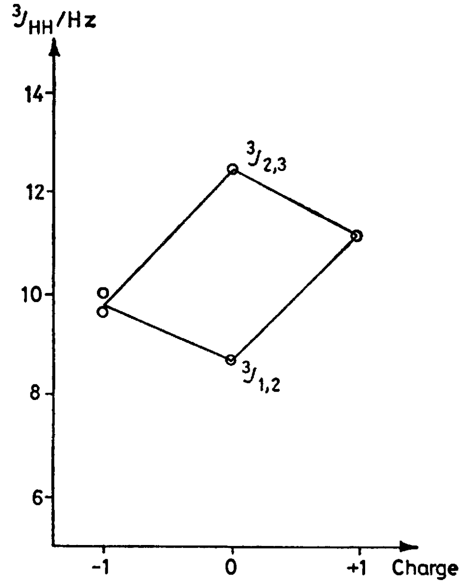


FIGURE 3 $^3J_{HH}$ of (1)—(3)

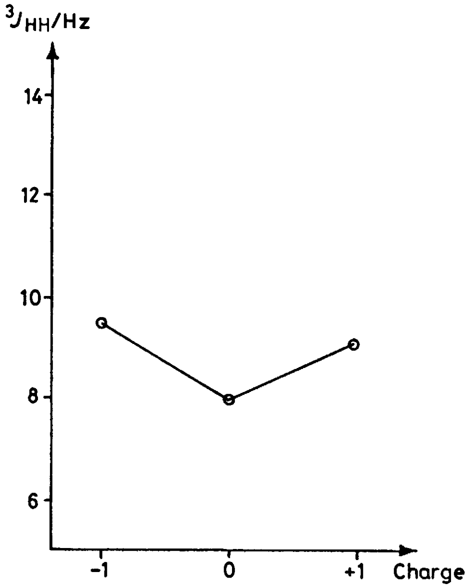


FIGURE 4 $^3J_{HH}$ of (4)—(6)

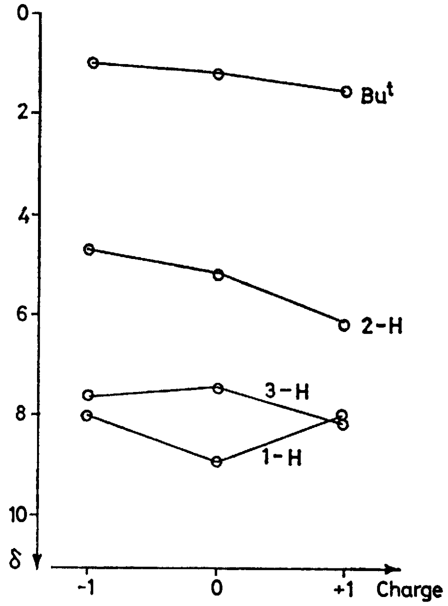


FIGURE 5 ^{1}H N.m.r. chemical shifts of (1)—(3)

The situation is rather different for the 1- and 3-positions of (1)—(6), since these sites do not formally bear charge (Scheme). The signals for the C-3 or 3-H nucleus in (1)—(3) are most shielded in the case of the neutral species, a situation which also obtains for the correspond-

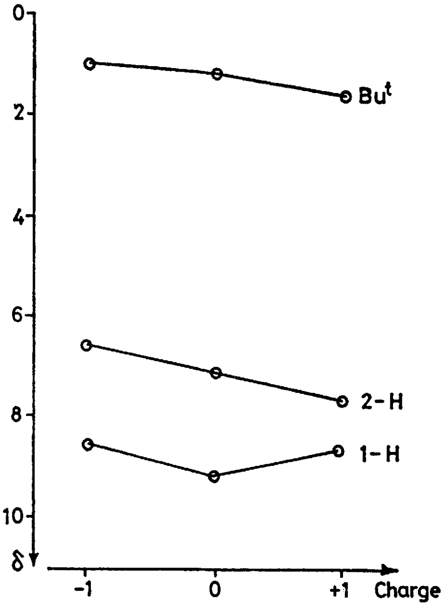


FIGURE 6 ^{1}H N.m.r. chemical shifts of (4)—(6)

ing position (2-position) in the 4π and 6π species (8)—(10). Similar factors are presumably involved. In contrast, the signals due to the 1-position in (1)—(3) and (4)—(6) are most deshielded for the neutral species. In this case the shift to low frequency in the delocalised systems is probably due to a reduction in the anisotropic effect of the aldehyde function in the neutral species (1) and (4).

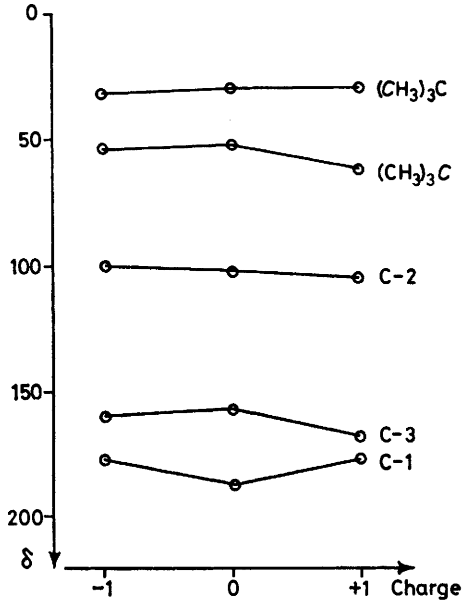


FIGURE 7 ^{13}C N.m.r. chemical shifts of (1)—(3)

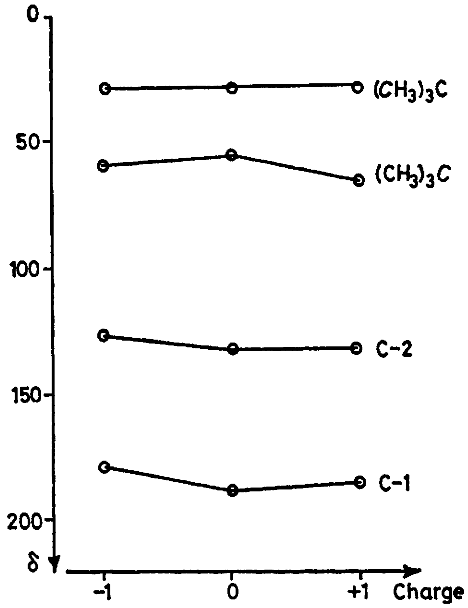


FIGURE 8 ^{13}C N.m.r. chemical shifts of (4)—(6)

The chemical shift of the quaternary carbon of the t-butyl group will reflect to some extent the electron density at the nitrogen atom. Once again, the delocalised systems show a deshielding effect at this position, which is probably due to the non-equivalence of the resonance structures (Scheme). Because of the electronegativities of the heteroatoms, the most favourable canonical form of the cation will be that in which the nitrogen carries the charge, whereas in the anion, the most favourable structure will be that in which the oxygen carries the charge and the nitrogen adopts an imine (or azo) structure. Hence the nitrogen atom in both anion and cation will be electron-withdrawing relative to its influence in the neutral species.

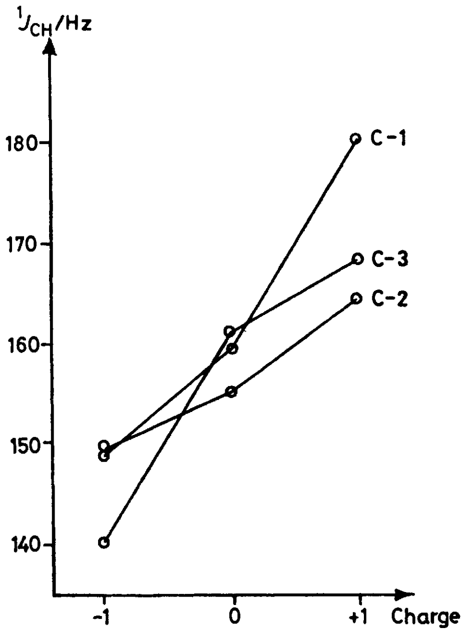


FIGURE 9 $^1J_{CH}$ of (1)—(3)

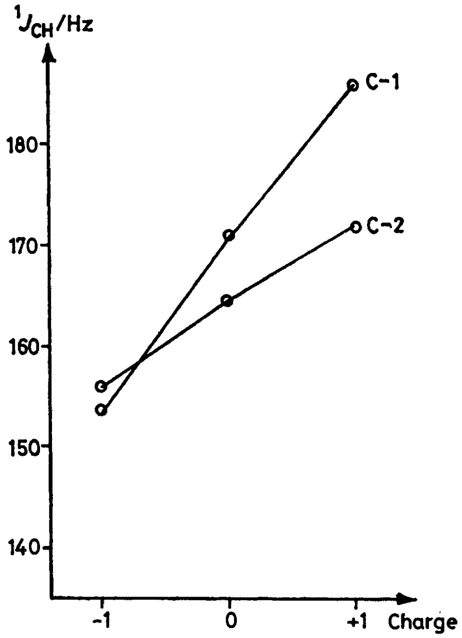
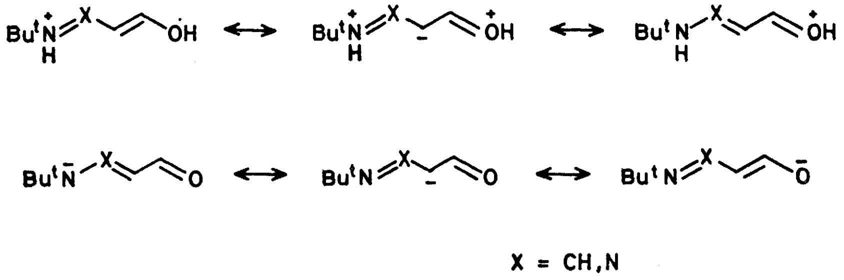


FIGURE 10 $^1J_{CH}$ of (4)—(6)

Whereas the trends in chemical shift can be satis-



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factorily explained by consideration of *electron* density, it is clear from Figures 9 and 10 that the variation in one-bond coupling $^1J_{CH}$ is dependent on *charge*.[8] The magnitude of the effect is itself dependent on the site, but an increase of as much as 30% may be observed in $^1J_{CH}$ of the cation relative to that of the anion. Similar increases in $^1J_{CH}$ have been previously noted in carbanions and carbocations,[1] and also in unprotonated and protonated heterocycles;[9] in sp^3-hybridised systems $^1J_{CH}$ is known to increase with additional electronegative substituents.[10] However, in these cases the increase in coupling constant is usually accompanied by a substantial deshielding of the carbon atom. The present results demonstrate that these effects are quite separate, and depend on charge and on electron density factors, respectively.

A number of minor couplings were resolved in the ^{13}C n.m.r. spectra of the species (1)—(6) and these are listed in Table 2. In view of the caution expressed earlier,[3] no attempt has been made to completely assign these unambiguously. Nevertheless it is clear that the coupling $^2J_{C\text{-}2,1\text{-}H}$ [which is >20 Hz in the neutral species (1) and (4)] is substantially reduced on delocalisation [*e.g.* $^2J_{C\text{-}2,1\text{-}H}$ (5) $\leqslant$ 5.1 Hz: $^2J_{C\text{-}2,1\text{-}H}$ (6) 15.1 Hz].

As might be expected of isoelectronic species, the cations (2) and (5) show similar chemical properties to the anions (3) and (6). For example, deuterium exchange at the 2-position is well known for enaminones and azaenaminones in acid solution, with the former exchange being faster than the latter.[5] Similarly, the anion (6) shows exchange at the 2-position in [^{2}H$_4$]-methanol (*ca.* 1 h): no reaction was observed at nuclear sites in an *NN*-dimethyl analogue.[5] Although (3) represents only a small proportion of the equilibrium when (1) is treated with sodium methoxide in [^{2}H$_4$]methanol, deuterium exchange again takes place at the 2-position at a similar rate. The reaction under neutral conditions is detectable only after many days.

EXPERIMENTAL

^{1}H and ^{13}C n.m.r. spectra were recorded at 100 and 20 MHz, respectively, unless otherwise stated.

3-t-Butylaminoacrolein, [2,3,N-^{2}H$_3$]-3-t-butylaminoacrolein, and glyoxal t-butylhydrazone were made as previously described.[3]

Generation of Cations of 3-t-Butylaminoacrolein and of Glyoxal t-Butylhydrazone.—These *O*-protonated species were generated when the acrolein or the hydrazone was dissolved in trifluoroacetic acid. Such solutions of the acrolein were indefinitely stable, but those of the hydrazone decomposed rapidly in the probe of the ^{13}C n.m.r. spectrometer. The spectra quoted for this species were therefore recorded at −15 °C (25.2 MHz).

Generation of Anions of 3-t-Butylaminoacrolein and of Glyoxal t-Butylhydrazone.—The following procedure is typical. Sodium hydride (50% dispersion in oil, 0.143 g, *ca.* 3 mmol) was added to a solution of 3-t-butylaminoacrolein (0.102 g, 0.8 mmol) in [^{2}H$_6$]dimethyl sulphoxide (0.8 ml) and the mixture was shaken vigorously at room temperature for 5 min. After this time, the mixture was filtered through a cotton-wool plug to give a clear solution which was used for recording the spectra.

The anion of glyoxal t-butylhydrazone, but *not* of 3-t-butylaminoacrolein could be generated by reaction with a two-fold excess of sodium methoxide in [^{2}H$_4$]methanol.

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