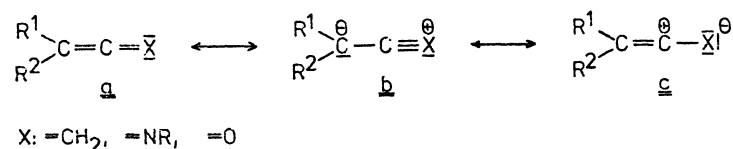


¹³C-NMR SPECTRA AND BONDING SITUATION IN KETENIMINES¹⁾

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¹³C-NMR spectra of a series of substituted ketenimines are reported. The terminal carbon resonances are found at unusual high fields between δ 37 and 78, while the central carbon signals appear around δ 189 - 196. On the basis of these results, the bonding situation in ketenimines has been discussed.

Ketenimines are π -isoelectronic with allenes and ketenes. According to the VB theory, the ground state π -electron distribution of these systems may be described by resonance structures such as a, b, and c contributing to a different extent for the individual cumulene. The problem is to get at least a qualitative idea of the relative importance of the contributing structures from experimentally consistent data.



Recently, it was concluded from ¹H-NMR data that structure b symbolizing a conjugative interaction of the C=C-bond π -orbital with the group X orbital of appropriate symmetry has no greater importance in ketenimines than in allenes.²⁾ On the other hand, we have shown by a comparative ¹³C-NMR study of allenes, ketenes,³⁾ and diazoalkanes⁴⁾ that the contribution of structure b becomes more important if the -CH₂-group in allenes is replaced by an electronegative atom with electron lone pairs. In order to test and substantiate our generalization, we wish to report here the first ¹³C-NMR investigation of ketenimines.

As can be seen from Table 1, the resonances of the central carbon (C^Z) of the ketenimine moiety appear in a characteristic narrow range at very low fields extending for N-phenyl derivatives from about δ 196 (cf. 3) to about δ 189 (cf. 1). The typical range for the terminal carbon (C^t) resonance is outlined by the parent compound 1 (δ 36.94) and the triphenyl derivative 6 (δ 77.79). Both, C^t and C^Z are deshielded though to a different extent if a proton at C^t is substituted by a methyl, and both are shielded if the N-phenyl group is replaced by a methyl. From the analytical point of view, the occurrence of the C^Z resonance in a spectral range where

Table 1. ^{13}C -NMR data on ketenimines, $\text{a) } \text{R}^1\text{R}^2\text{C}^{\text{t}}=\text{C}^{\text{z}}=\text{NR}^3$: $\delta_{\text{C}}^{\text{b)}}$ and $J_{\text{C}^{\text{t}}-\text{H}}$ (Hz)

compound	R^1	R^2	R^3	$\delta_{\text{C}^{\text{t}}}$	$\delta_{\text{C}^{\text{z}}}$	δ_{CH_3}	$J_{\text{C}^{\text{t}}-\text{H}}$
<u>1</u>	H	H	C_6H_5	36.94	189.21	---	172.0
<u>2</u>	H	CH_3	C_6H_5	48.02	193.41	8.48	167.0
<u>3</u>	CH_3	CH_3	C_6H_5	58.16	195.49	15.79	---
<u>4</u>	H	C_6H_5	C_6H_5	60.40	190.42	---	167.7
<u>5</u>	CH_3	C_6H_5	C_6H_5	67.06	193.93	12.08	---
<u>6</u>	C_6H_5	C_6H_5	C_6H_5	77.79	190.16	---	---
<u>7</u>	C_6H_5	C_6H_5	CH_3	74.41	186.55	38.92	---

a) Compounds 1-7 were prepared by the method of Stevens and French.⁵⁾ IR- and ^1H -NMR data, and elemental analyses are in agreement with the above structures.

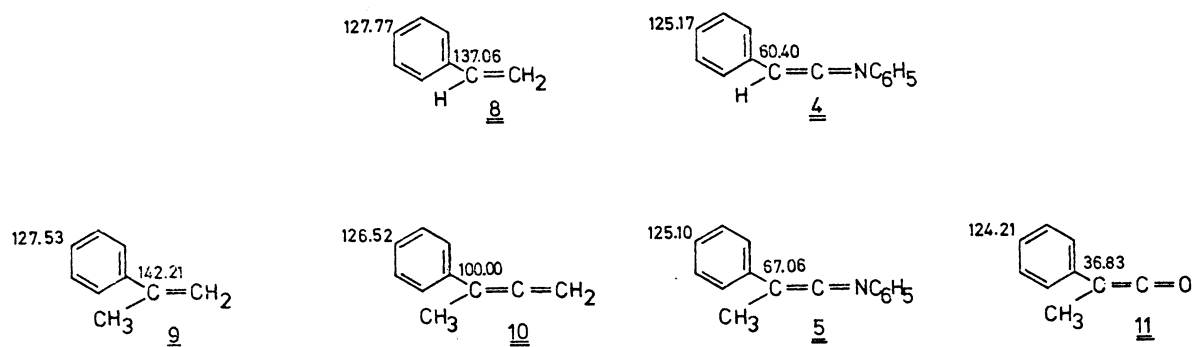
b) From ^1H -broad band decoupled PFT-spectra in CDCl_3 at 35° with TMS as an internal standard. The spectra were recorded on an Bruker HX-90-15" spectrometer at 22.63 MHz. Errors of δ_{C} are ± 0.04 ppm.

normally only a limited number of signals appears, together with the unusual strong shielding of the sp^2 -carbon makes the ^{13}C -NMR spectroscopy to an efficient tool for identification of ketenimines. With respect to the π -bonding situation, the most important feature is the unusual strong shielding of C^{t} . Compared with the corresponding carbon atoms in analogously substituted olefins ($\text{R}^1\text{R}^2\text{C}^{\text{t}}=\text{CH}_2$) and allenes ($\text{R}^1\text{R}^2\text{C}^{\text{t}}=\text{C}=\text{CH}_2$), the terminal carbon of ketenimines is shifted to a higher field by more than 70 and 30 ppm, respectively. Thus the terminal carbon of ketenimines is one of the most shielded sp^2 -carbons in organic molecules exceeded only by the corresponding carbon atoms in ketenes³⁾ and diazoalkanes.⁴⁾

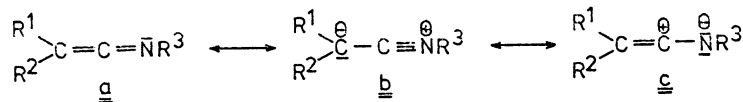
For discussion of these experimental results, it is important to note that the coupling constants $J_{\text{C}^{\text{t}}-\text{H}}$ for ketenimines (167-172 Hz, see Table 1) are of the same magnitude as $J_{\text{C}^{\text{t}}-\text{H}}$ of allene (168.2 Hz)⁶⁾ and ketene (171.5 Hz),³⁾ respectively. This indicates a very similar hybridization⁷⁾ and σ -bonding situation for the terminal carbon in these isoelectronic cumulenes. Therefore, the stronger shielding observed for C^{t} in ketenimines compared with C^{t} in allenes (see Table 2 for an explicit example) seems to be mainly a consequence of the higher π -electron density at C^{t} and differences in the π -bond order, by neglecting the possible influence of the mean excitation energy ΔE to a first approximation.⁸⁾

This conclusion can be supported further. It is known from ^{13}C -NMR studies of monosubstituted benzene derivatives that electron releasing groups shield the para-carbon of the benzene ring parallel to their π -electron-releasing ability.⁹⁾

As can be seen from Table 2, the C^{D} resonance of ketenimine 4 is found 3.3 ppm upfield from benzene (δ 128.5)⁹⁾ and 2.5 ppm upfield from styrene, respectively. This clearly indicates the higher electron-releasing ability of the

Table 2. δ_{C^p} and δ_{C^t} for some phenyl-substituted cumulenes and their olefin analogues.

$\text{C}=\text{C}=\text{N}-\text{C}_6\text{H}_5$ group compared to a vinyl group. This experimental result can only be explained if one accepts a conjugative interaction between the $\text{C}=\text{C}$ bond π -orbital and the electron lone pair at nitrogen in ketenimines which is symbolized by resonance structure b.



Concerning the relative importance of this resonance structure in the present series of isoelectronic cumulenes, a comparison of the ^{13}C -NMR data of the analogously substituted compounds 9, 10, 5, and 11 is useful. It is evident from Table 2 that C^p in each of the cited cumulenes is more shielded than in α -methylstyrene. This fact suggests that resonance structure b contributes even in the case of allenes. Furthermore, the comparison of δ_{C^p} and δ_{C^t} , which are sufficiently linearly related, reveals increasing importance of resonance structure b in the sequence, allene < ketenimine < ketene. From these results, it is apparent that the mesomeric interaction between the $\text{C}=\text{C}$ -bond π -orbital and the group X orbitals of appropriate symmetry is more important where X is =NR than where X is =CH₂, but less significant where X is =O. In this respect, the π -bonding situation of ketenimines is intermediate between that of allenes and that of ketenes.

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