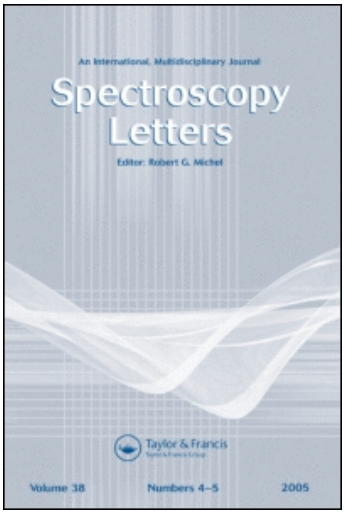

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The N-0xidation effect on the carbon-13 chemical shafts and. H-α in (Z)-H-Renzylidene arylamine and the orthohydroxy benzylidene analogue

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The N-Oxidation effect on the carbon-13 chemical shifts and H-α in (Z)-N-Benzylidene arylamine and the orthohydroxy benzylidene analogue

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Abstract:

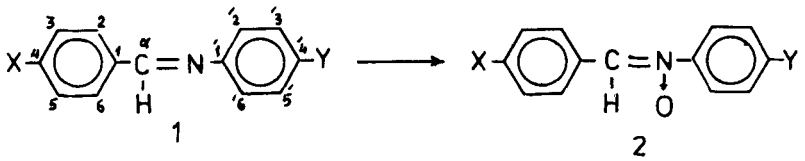
N-oxidation of Z-N-Benzylidene arylamine and their orthohydroxybenzylidene analogue resulted in unexpected upfield shift of the H-α and C-α chemical shifts. The predominant resonance forms of the nitrones are discussed. The N-oxidation effects on the ^{13}C chemical shift depend upon nitrogen as well as the attached carbon hybridization.

Introduction:

There has been a considerable discussion of the conformation at (Z)-N-benzylidene aniline 1 and it's derivatives[1] using various spectroscopic methods. Furthermore substituent effect on the ^{1}H and ^{13}C chemical shifts of (Z)-N-benzylidene phenylamine N-oxides[2] 2 and (Z)-N-orthohydroxy benzylidene phenylamine N-oxides[3] 4 were studied.

This communication reports a study of the N-oxidation effect on the H-α and C-13 chemical shifts of compounds 1 and 3 in addition to the stable resonance structures of the nitrones 2 and 4. The nitrogen hybridization effect on N-oxidation were also discussed.

Results and Discussion:

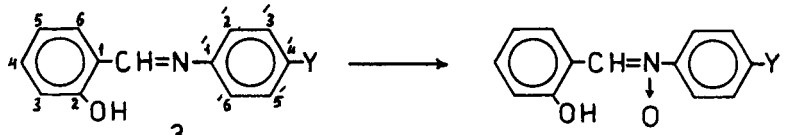


1 2

Y = H X ; a = H ; b = Cl ; c = OCH_3

d = $N(CH_3)_2$; e = NO_2

X = H Y; f = CH_3 ; g = Cl ; h = OCH_3



3 4

Y , a = H ; b = CH_3 ; c = OCH_3

The N-oxidation of compounds 1 and 3 gave the corresponding N-oxides 2 and 4 respectively. An unexpected upfield shift of the ^{1}H and ^{13}C chemical shifts of H-α and C-α was observed (see Table 1). The shielding of the carbon-13 chemical shift of C-α varied from 24.6 - 26.7 p.p.m. in going from 1 to 2, while this effect was in the range of 20 - 22 p.p.m. on going from 3 to 4. The ^{1}H chemical shift of the H-α shows shielding between 0.3 - 0.75 p.p.m. C-1 of the benzildene ring shows a shielding of - 3.6 to - 5.1 p.p.m. in

Table 1. N-oxidation effect[a] on the H_α and Carbon-13 chemical shift of Z-N-benzylidene arylamine and the corresponding Z-N-(o-hydroxy benzylidene arylamine.

	H_α^c	C_α^d	$\Delta\delta$C-1	$\Delta\delta$C-2	$\Delta\delta$C-3	$\Delta\delta$C-4	$\Delta\delta$C-5	$\Delta\delta$C-6	$\Delta\delta$C-1	$\Delta\delta$C-2	$\Delta\delta$C-3	$\Delta\delta$C-4	$\Delta\delta$C-5	$\Delta\delta$C-6
2a-1a	-0.68	-26.7	-3.8	+1.0	+0.3	-0.3	+0.3	-1.0	-2.1	+1.4	+0.3	+4.6	+0.3	+1.4
2b-1b	-0.67	-26.0	-3.5	+1.0	+0.7	-1.6	+0.7	+1.0	-1.7	+1.5	+0.1	+4.2	+0.1	+1.5
2c-1c	-0.70	-26.6	-3.9	+0.5	+0.3	-0.3	+0.3	+0.5	-2.4	+1.8	+0.6	+4.6	+0.6	+1.8
2d-1d	-0.66	-26.5	-4.1	+0.2	+0.4	0.0	+0.4	+0.2	-3.0	+1.0	+0.7	+4.1	+0.7	+1.0
2e-1e	-0.59	-24.6	-3.6	+0.7	+0.4	-0.7	+0.4	+0.7	-1.1	+2.4	+0.7	+4.1	+0.7	+2.4
2f-1f	-0.69	-26.5	-3.6	+0.5	+0.3	-0.2	+0.8	+0.5	-2.4	+1.3	+0.5	+4.8	+0.5	+1.3
2h-1h	-0.71	-25.7	-3.8	+0.5	+0.7	-0.4	+0.7	+0.5	-1.5	+1.4	+0.2	+3.1	+0.2	+1.4
4a-3a	-0.57	-20.0	-2.4	+0.1	+2.9	+1.8	+1.6	+3.2	-0.8	+1.3	+1.2	+4.7	+1.2	+1.3
4b-3b	0.45	-22.0	-1.4	-0.5	+2.5	+0.9	+0.7	+1.4	-1.6	+0.5	-0.2	+4.2	-0.2	+0.5
4c-3c	- 0.5	-21.1	-1.7	-0.7	+2.3	+1.0	+0.2	+1.7	-1.7	+0.7	-0.2	+2.2	-0.2	+0.7

[a] $\Delta\delta C = \delta C$ of the N-oxides 2 or 4 - δC of the corresponding amines 1 or 3, the same applied for $\Delta\delta H_\alpha$.

[b] Numbering of the carbon atoms corresponds with that in the scheme.

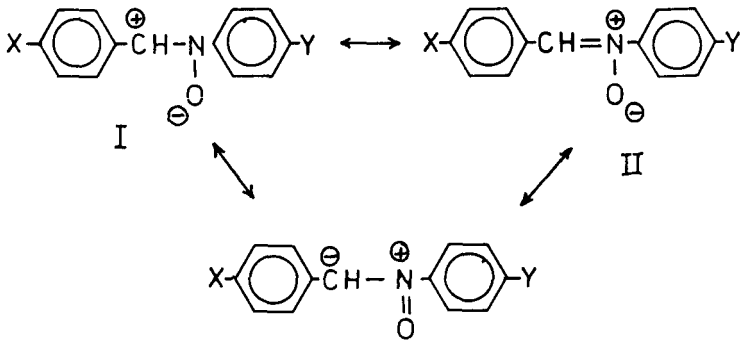
[c] H_α chemical shift of compound 1 and 2 were taken from ref. 1 and 3 respectively; for compound 4 were taken from ref. 2; compounds 3 were prepared from the condensation of salicylaldehyde with substituted aniline and the ^1H NMR spectra were obtained on a Bruker WH 90 DS spectrometer in $CDCl_3$ and TMS as internal reference.

[d] Carbon-13 chemical shift of compounds 1,2,3 and 4 were taken from ref. 7,3,8 and 2 respectively.

compound 2 and - 0.2 to - 2.4 p.p.m. in compound 4 while the remaining carbon atoms C-2, C-3, C-4, C-5 and C-6 shows very small shielding or deshielding (see Table 1.).

The N-oxidation also affects aniline ring where C-$\bar{1}$ shows shielding of - 0.8 to - 3.0 p.p.m. while C-$\bar{4}$ showed deshielding between + 1.9 - + 4.8 furthermore, C-2 and C-3 carbon atoms showed a small deshielding.

The nitrone group is usually discussed in terms of the resonance structures I, II and III[3].



I II

III

From the above findings the large shielding at C-α on going from -C=N- to -$\overset{\frown}{C=N}$ is clear indication that the resonance structure III is the more predominant resonance form; indeed this can explain the large shielding effect on the chemical shifts at the C-α and H-α . Further confirmation for the stability of the resonance form III comes from the I.R. absorption of the C=N group in compound 1a at γ max (Nujole) 1640 cm^{-1} which changes to 1590 cm^{-1} upon N-oxidation (compound 2a), meaning that N-oxidation causes a decrease in the double bond character of C = N group.

The N-oxidation effect is also transmitted to C-1 and C-$\bar{1}$ (small shielding effect) as a result of the positive inductive effect of the negative charge of the C-α , while most other carbon atoms of the benzylidene ring and the aniline ring show a smaller deshielding or smaller shielding. This indicates that the localized negative charge on the C-α is not incorporated by resonance into the benzylidene ring. However, the positive charge on the nitrogen atom induced some resonance into the aniline ring which results in deshielding of C-$\bar{2}$ and C-$\bar{4}$. This suggests that benzylidene ring was twisted out of the C=N plane even for the 2-hydroxy benzylidene ring compounds 4a - 4c which was suggested previously[2] that it will form a strong hydrogen bonding with the N-O group which makes it coplanar with the C=N plane.

The N-oxidation effect and the hybridization of the nitrogen atom:

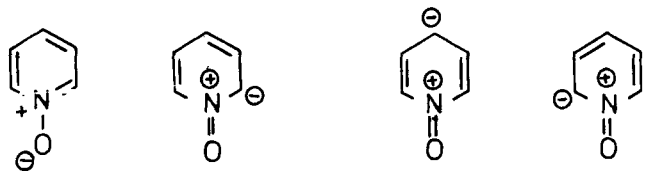
N-oxidation of Sp^2 nitrogen:

The N-oxidation of SP^3 nitrogen shows a deshielding of C-α /SP^2 or SP^3, e.g. the N-oxidation of N,N-dimethylaniline[4] caused a deshielding of N-CH_3 by 23 p.p.m.; C-1 of aromatic ring by 3.9 p.p.m. whereas the ortho-and para-carbons of the aromatic ring were also deshielded by 7.3 and 12.8 p.p.m. respectively.

N-oxidation of SP^2 nitrogen:

N-oxidation of pyridine causes an upfield shift of C-2,6 and C-4 by 10.4 and 17.1 p.p.m. respectively while C-3 and C-5 were not affected[5]. This confirms the formation of N=O and th negative charge which resonates between the C-2,6

and C 4 carbons. The total shielding effect by the N-oxidation of the pyridine ring is 37.9 p.p.m.



This is further confirmed by the data presented in this paper for the N-oxidation effect on C-α on going from 1 to 2 and 3 to 4.

N-oxidation effect of SP nitrogen on the ^{13}C chemical shift:

The N-oxidation of CH_3CN to $CH_3C{=}N{=}O$[6] caused the shielding of SP carbon by 81 p.p.m. Similarly the conversion of $(CH_3)_3$ C-CN to $(CH_3)_3C$-CN=O and $(CH_3)_3SiCN$ to $(CH_3)_3SiCN{=}O$ showed a shielding of the SP carbon by 84.4 and 90.3 p.p.m. respectively.

Conclusion:

N-oxidation effect can result in a valuable information on the type of resonance structures in the oxidized products, and that the N-oxidation depends on the hybridization state of the nitrogen atom as well as the attached carbon atom.

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