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NMR CHARACTERIZATION OF ZWITTERIONIC NITROGEN-BONDED σ-COMPLEXES : THE IMIDAZOLE/4,6-DINITROBENZOFUROXAN SYSTEM

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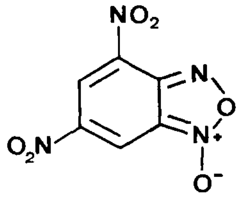
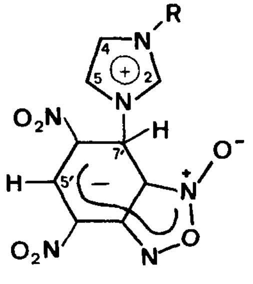
Abstract : Imidazole (ImH) and N-methylimidazole react with 4,6-dinitrobenzofuroxan to form the σ-complexes $1a,H^+$ *and* $1b,H^+$*. In excess of ImH,* $1a,H^+$ *is deprotonated to give the anionic σ-complex 1a.* $1a,H^+$ *and* $1b,H^+$ *are the first zwitterionic nitrogen-bonded σ-complexes to be firmly characterized by spectroscopy.*

Imidazolide anion (Im^-) but not neutral imidazole (ImH) add to electron-deficient aromatics like 1,3,5-trinitrobenzene (TNB) in dimethylsulfoxide (DMSO)-methanol mixtures rich in DMSO[1]. The reaction gives first a N-bonded complex which then undergoes a slow conversion into a C-bonded complex, providing the first example of the ambident nucleophilic character of Im^- towards an aromatic electrophile.

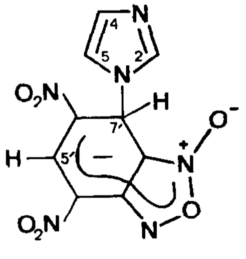
4,6-Dinitrobenzofuroxan (DNBF) is known to be a much stronger electrophile than TNB[2-6]. One can therefore wonder whether this compound will react directly with the weakly basic neutral imidazoles, including N-alkylimidazoles, to give zwitterionic N-bonded σ-complexes like $1,H^+$. Although there is indirect evidence that such zwitterions are intermediates in the reactions of aliphatic, alicyclic or aromatic amines as well as amidines with electrophilic aromatics, no spectroscopic identification of these species has been made so far.[6-10] We report here on the direct ^1H nmr observation of the zwitterionic complexes $1a,H^+$ and $1b,H^+$ in DMSO.



DNBF



1a,H⁺ R=H
1b,H⁺ R=Me



1a

Addition of imidazole to a solution of DNBF in DMSO-d_6 results in the development of intense colors typical of a σ-complex. Proton nmr spectra show a disappearance of the AB system due to DNBF and the concomitant formation of a new set of five signals the position of which depends on the ratio $\rho = [DNBF]/[ImH]$. Analysis of the chemical shifts is consistent with equation (1) :

$$\text{DNBF} + \text{ImH} \rightleftharpoons \underline{1a,H^+} \overset{\text{ImH}}{\rightleftharpoons} \underline{1a} + \text{ImH}_2^+ \qquad (1)$$

The formation of the zwitterionic complex 1a,H$^+$ is observed in experiments carried out with an excess of DNBF over ImH : $\rho \sim 2.5$. The main feature of the ^{1}H nmr spectrum (1a,H$^+$: δ_2 9.54, δ_4 7.71, δ_5 7.89, $\delta_{5'}$ 8.80, $\delta_{7'}$ 7.22, J_{24} 1.0, J_{25} 1.2, J_{45} 1.8) is the position of the H_2,H_4 and H_5 imidazolium protons of 1a,H$^+$ which resonate at lower field than the AX_2 system associated with the imidazolium cation ImH_2^+ under similar experimental conditions (ImH_2^+, $CF_3SO_3^-$: δ_2 9.08, $\delta_{4/5}$ 7.69).

A drastic upfield shift of the three imidazole protons and, to a least extent, of the $H_{7'}$ proton of the complex occurs when an excess of ImH over DNBF is used : $\rho \sim 0.46$. Concomitantly, the excess of ImH gives rise to an AX_2 system, the chemical shifts of which (δ_A 8.64, δ_X 7.48) lie between those of ImH_2^+ and ImH(ImH : δ_2 7.70, $\delta_{4/5}$ 7.06) i.e. it is partly protonated. These results indicate that excess of ImH deprotonates 1a,H$^+$ to form 1a (1a : δ_2 8.00, δ_4 6.95, δ_5 7.16, $\delta_{5'}$ 8.81, $\delta_{7'}$ 6.94, J_{24} 0.9, J_{25} 1.3, J_{45} 1.3$_5$). This was to be expected since the negatively charged DNBF moiety in σ-complexes is known to be strongly electron-withdrawing.[2] Hence, it increases appreciably the acidity of the imidazolium moiety of 1a,H$^+$ relative to that of ImH_2^+. Moreover, it explains the low-field shift of the imidazole protons in 1a,H$^+$ and 1a relative to those of ImH_2^+ and ImH respectively. Further evidence for the equilibrium 1a,H$^+$ $\rightleftarrows$ 1a is provided by the results observed at 1:1 stoechiometry (ρ=1). In this case, the $H_{7'}$ proton and the imidazole protons of the complex have chemical shifts approximatively half-way between those observed for 1a,H$^+$ and 1a (δ_2 8.70, δ_4 7.30, δ_5 7.51, δ_5 8.83, $\delta_{7'}$ 7.09). This points out the reversibility of the reaction 1a,H$^+$ + ImH $\rightleftarrows$ 1a + ImH_2^+

That the pyridine-like nitrogen of ImH directly attacks the electrophilic carbon $C_{7'}$ of DNBF to yield 1a,H$^+$ is confirmed by a parallel study of N-methylimidazole. In this case, the zwitterionic adduct 1b,H$^+$ is the only formed species. Its chemical shifts are very similar to those of 1a,H$^+$ but insensitive to the presence of an excess of N-methylimidazole (1b,H$^+$: δ_2 9.43, δ_4 7.68, δ_5 7.95, δ_{Me} 3.85, $\delta_{5'}$ 8.81, $\delta_{7'}$ 7.18).

1a,H$^+$ and 1b,H$^+$ are the first nitrogen-bonded zwitterionic σ-complexes to be unambiguously characterized. The reactivity of DNBF towards weak bases like imidazoles is also of interest in itself since it further emphasizes the very high electrophilic character of DNBF[2-5].

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