

Proton magnetic resonance spectra of some aromatic nitriles and their Meisenheimer complexes

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The π -electron densities of carbon atoms of seven aromatic nitriles were calculated on a simple Hückel level and the results were correlated with the proton chemical shifts measured in deuterated chloroform and di(methyl-*d*₃) sulfoxide. In both cases the correlations were statistically significant on the 0.1% probability level. Nitro derivatives of benzonitrile give colour solutions in dimethyl sulfoxide in the presence of basic agents (RS⁻, RO⁻, etc.). The structure of Meisenheimer complexes was ascribed to the colour products of *o*- and *p*-nitrobenzonitrile.

Derivatives and hetero analogues of benzonitrile were recently broadly studied by means of the molecular spectroscopy and the MO theory [1–8]. Chemical shifts of hydrogens in the p.m.r. spectra of mono-, di-, and 2,4,6-tricyanopyridines were correlated with the π -electron densities of the corresponding carbon atoms on the HMO as well as SCF CI level [1, 5, 6].

The purpose of this work was to extend the correlation of the chemical shifts with the electron densities to benzonitrile derivatives, to evaluate the influence of dipolar complexes of benzonitrile with dimethyl sulfoxide on the position of the bands in the p.m.r. spectra, and to interpret the p.m.r. spectra of the Meisenheimer complexes of *p*- and *o*-nitrobenzonitrile.

Experimental

LCAO HMO calculations were performed on an Odra 1301 computer in the Laboratory of Computation Technique, Palacký University. The following empirical parameters [1, 4, 9] were used: $h_N = 0.5$, $k_{CN} = 1.4$ (nitrile group), $h_N = 2$, $h_O = 1$, $h_{C(NO_2)} = 0.2$, $k_{CN} = 0.8$, $k_{NO} = 0.7$ (nitro group), $h_O = 1$, $k_{CO} = 1$ (carboxylic group), $h_{N(CH_3)_2} = 0.6$, $k_{CN} = 0.9$ (dimethylamino group [4]), $h_{NH_2} = 1.5$, $k_{CN} = 0.8$ (amino group), $h_{CH_3} = 2$, $k_{CCH_3} = 0.7$ (model of hetero atom), $h_{OH} = 2$, $k_{CO} = 0.8$ (hydroxy group).

With the exception of benzonitrile (Koch–Light), *p*-amino- and *o*-nitrobenzonitrile (Fluka), the nitriles were prepared by a common procedure [10, 11].

The p.m.r. spectra were measured with a Varian T-60 instrument at 27°C in the 5% w/v concentration in chloroform-*d* and di(methyl-*d*₃) sulfoxide (DMSO-*d*₆). Tetra-

methylsilane was used as an internal standard. Experimental positions of the signals were determined with a frequency counter. The assignment of the signals to aromatic protons agrees with the chemical shifts calculated from the substituent shift constants for benzene derivatives in dimethyl sulfoxide [19]. The chemical shifts are given in the τ values. The spectra of Meisenheimer complexes were measured with the use of sodium ethoxide in a mixture DMSO- d_6 -ethanol.

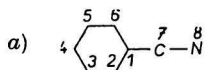
Results and discussion

Chemical shifts and the molecular HMO diagrams (I and II)

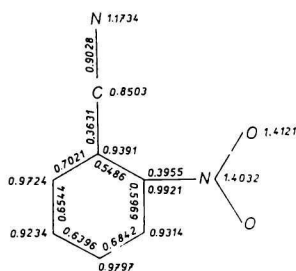
Although the chemical shifts of hydrogens in the p.m.r. spectra are influenced by many factors, specific for the p.m.r. spectra, some significant correlations between the π -electron density and values of the chemical shifts can be frequently found. These values measured in chloroform- d and DMSO- d_6 are listed in Table 1, together with the corresponding values of the electron densities of carbon atoms. For the nonpolar medium, the correlation of 15 determined pairs is statistically significant on the 0.1% probability level ($r = 0.831$) and the constants of the linear relationship ($\tau_r = bq_r + a$) have the expected values ($b = 9.705$, $a = -7.17$).

Table 1
Chemical shifts of hydrogens in the p.m.r. spectra and
the HMO electron densities of carbon atoms

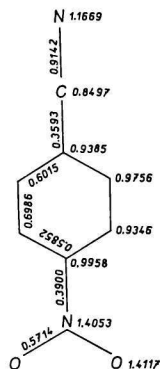
Nitrile	r^a	q_r	$\tau_r^{\text{DMSO-}d_6}$	$\tau_r^{\text{CDCl}_3}$
<i>o</i> -NO ₂	3	0.9314	<i>b</i>	1.67 ^c
<i>m</i> -NO ₂	2	0.9066	1.33	1.46
	4	0.9142	1.50	1.53
	5	0.9976	2.17	2.28
	6	0.8987	1.73	1.99
<i>p</i> -NO ₂	2	0.9756	1.92	2.12
	3	0.9346	1.63	1.65
<i>p</i> -COOH	2	0.9808	—	2.27
	3	0.9592	—	1.82
<i>p</i> -CH ₃	2	0.9749	—	2.58
	3	1.0310	—	3.38
<i>p</i> -NH ₂	2	0.9742	—	2.67
	3	1.0466	—	3.40
<i>p</i> -N(CH ₃) ₂	2	0.9752	2.52	2.50
	3	1.0860	3.28	2.77



- b) Multiplet in the region $\tau = 1.53-2.23$ p. p. m.
c) Multiplet in the region $\tau = 1.97-2.30$ p. p. m.



I



II

The interaction of aromatic nitriles with dimethyl sulfoxide was once intensively studied *via* the i.r. spectroscopy [12, 13]. In the medium of carbon tetrachloride and dimethyl sulfoxide, complexes with the 1 : 1 component ratio are formed. Owing to the stability of these complexes ($K_1 = 1.1$), practically the whole nitrile is present in the complex form in pure dimethyl sulfoxide. Since the stability constants of the four studied derivatives were independent of the substitution, the reaction was assumed to be limited to the nitrile group [12, 13]. The HMO molecular diagrams corroborate these conclusions. They also show only a slight influence of the substitution on the charge distribution in the nitrile group. Similar conclusions were obtained by other authors on the SCF level [8]. This specific solvation is manifested by a change in the chemical shifts. The chemical shifts of the nitro derivatives show more marked changes only in *o*-positions towards the nitrile group. It is noteworthy that in spite of these changes the regressions parameters practically do not vary and the significance level remains unchanged (0.1%, $r = 0.931$) ($\tau_r = 9.55 q_r - 7.17$). Since the chemical shifts of nitro derivatives in dimethyl sulfoxide are always shifted downfield, it may be assumed that the discussed interaction is not accompanied by a charge transfer in the ground state.

Meisenheimer complexes of mononitro derivatives of benzonitrile

Nitrobenzonitriles (*o*-, *m*-, and *p*-) give colour solutions [14] in some solvents (DMSO, acetone) in the presence of bases. The reactions are especially intensive in dimethyl sulfoxide where the colours can be observed after addition of 5% aqueous solution of hydroxide in the inert nitrogen atmosphere. *o*-Nitrobenzonitrile exhibits intensively green colour, the product of *m*-nitrobenzonitrile is red-orange and gradually changes into intensive red-brown, finally, *p*-nitrobenzonitrile gives red solutions. Colour changes are observed also in the presence of sulfur bases, *e.g.* sodium mercaptoethoxide. Furthermore, nitrobenzonitriles give colour solutions in dimethyl sulfoxide after addition of saturated solution of sodium sulfide (*o*-derivative red colour, *m*-derivative yellow-brown, and *p*-derivative violet colour, fading in the course of time).

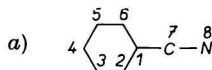
We studied the mentioned coloured products by means of the p.m.r. spectroscopy

in the mixture of DMSO—EtOH (90% v/v) after addition of 2 M sodium ethoxide in ethanol. The chemical shifts of hydrogens in *o*- and *p*-nitrobenzonitrile are listed in Table 2.

Table 2

Chemical shifts of hydrogens in the p.m.r. spectra of σ complexes (I) and (II)

Complex	r^a	τ_r	Type of splitting
I	2	2.97	<i>ortho</i>
	3	2.33	
II	3	2.40	<i>ortho/meta</i>
	4	3.00	<i>diortho/meta</i>
	5	2.37	<i>diortho/meta</i>
	6	2.83	<i>ortho/meta</i>



The signals of hydrogens are shifted upfield in a corresponding way. In the spectrum of *o*-nitrobenzonitrile, both the signals of the original compound and the new upfield signals can be simultaneously seen. While the original signals disappear with increasing concentration of sodium ethoxide, the position of the new signals remains unchanged. It corroborates a slow exchange of the nucleophilic agent which is usually regarded as a detection of Meisenheimer complexes under the described conditions. Otherwise the donor-acceptor interactions usually exhibit a simple spectrum which only shifts upfield [15] with the increasing concentration of the donor. The structure of the Meisenheimer complexes (III) and (IV) was ascribed to the formed products.



The upfield shift of the signals of the Meisenheimer complexes is frequently explained by an increase of the π -electron densities on the transition to anion [16], though it may be also affected by the decreased diamagnetic anisotropy owing to the decrease of the ring current [17].

Both the products show absorption bands in the visible spectral region. In the mixture of DMSO—EtOH (90% v/v) after addition of sodium ethoxide, the absorption maxima of the complexes III and IV are at 565 and 430 nm respectively.

The study of the Meisenheimer complexes by the MO theory leads to diverse conclusions. The primary results on the HMO level indicated the localization of the negative charge on the nitro group with the rest of the aromatic nucleus bearing a positive charge [17]. More recent calculations on the PPP SCF level and the composite molecule method produced more reasonable results, admitting a delocalization

of the negative charge in the whole π -system of the complex [18]. For example, the distribution of the π -electron densities in the anion derived from 2,4,6-trinitrobenzene is qualitatively analogous to the distribution in cyclohexadiene anion. Both the complexes exhibit signals in the range of $\tau = 2.33$ – 2.40 p.p.m. as well as $\tau = 2.83$ – 3.00 p.p.m. In accordance with the results of the calculations on the SCF level [18] it seems to be reasonable to assign the upfield signals to the hydrogen atoms bonded in the active positions of the cyclohexadiene anion and the downfield signals to the hydrogens in the inactive positions. With respect to the type of splitting, it is then possible to assign unambiguously the chemical shifts to the corresponding hydrogen atoms (Table 2).

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