

¹H-NMR STUDY OF A TRANSFER OF SUBSTITUENT EFFECTS IN 2,4-DINITRO-4'-SUBSTITUTED HYDRAZOBENZENES

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Dedicated to Professor V. Veselý on occasion on his 100th birthday.

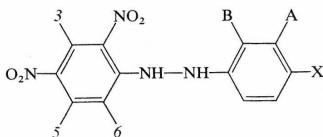
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Chemical shifts of hydrogen atoms signals of 2,4-dinitro-4'-substituted hydrazobenzenes have been correlated with the Hammett σ_p constants and with increments of chemical shifts a_i . Slope of the correlations for the hydrogen atoms in the vicinity of the NH—NH group indicates that change of a substituent influences the chemical shifts of these hydrogens not only by a change in the electron density but also by a change in the van der Waals repulsion of electron clouds.

Investigation of the course of reductive ring closure of 2-nitroazo compounds to the corresponding 2-phenylbenzotriazoles showed^{1,2} that 2-nitrohydrazobenzenes and 2-phenylbenzotriazol-1-oxides are intermediates of this reaction. For kinetic study³ of the second reaction step (*i.e.* cyclization itself) a series of 2,4-dinitro-4'-substituted hydrazobenzenes *I* was prepared. It was found³ that the cyclization rate depends on the nature of the 4'-substituent. Transmission of this substituent effect through the hydrazobenzene system has been studied by means of ¹H-NMR spectroscopy.

EXPERIMENTAL

Preparation of the hydrazobenzenes was described elsewhere^{2,3}. For measurements of ¹H-NMR spectra 0.1M solutions were prepared in a mixture of CDCl₃ and (CD₃)₂SO, 4:1 (by vol.); tetramethylsilane was used as internal standard. The spectra were recorded with a Tesla BS 487C spectrometer (80 MHz); accuracy of readings of chemical shifts was 0.25 Hz. The chemical shifts of hydrogen signals of dinitrophenylhydrazine grouping were read directly from the spectra, for the hydrogen signals of the *para*-substituted benzene the calculation of chemical shifts for an AA'BB' system was used.



I

X = OMe, CH₃, H, Cl, COOC₂H₅, CN, NO₂

RESULTS AND DISCUSSION

From Tables I and II it follows that the effect of 4'-substituent is spread over the whole molecule, which is indicated by changes of chemical shifts of all the hydrogen atoms present. In the *para*-substituted benzene ring the substituent effect is transmitted by inductive and resonance mechanisms up to the nearer nitrogen atom of NH—NH group. Transmission between the both nitrogen atoms is of inductive nature obviously, whereas further transmission to the dinitrophenyl ring is accomplished again by the both mechanisms.

Chemical shifts of hydrogen signals in 2,4-dinitrophenylhydrazine group can be correlated with the Hammett σ_p constants⁴ of the respective 4'-substituents X. Substitution of 4'-hydrogen by an electron-withdrawing group lowers electron density in the whole system, which is demonstrated by decreased shielding of hydrogen atoms and downfield shift of their ¹H-NMR signals. Naturally the most marked change in chemical shift is observed with the signal of hydrogen atom at the nitrogen adjacent to the *para*-substituted benzene ring (NH') — the correlation straight line has the largest slope (Table I). With increasing distance from the 4'-substituent the change in chemical shifts of hydrogen atoms diminishes and, hence, also the slopes for NH, H₃ and H₅. Correlation straight line of the H₆ hydrogen forms

TABLE I

Chemical Shifts^a of Signals of 2,4-Dinitro-4'-substituted Hydrazobenzenes in σ (ppm) and Correlation^b with σ_p Constants

Substituent	σ_p	δ_{H_3}	δ_{H_5}	δ_{H_6}	δ_{NH}	$\delta_{NH'}$
OCH ₃	-0.268	9.047	8.219	7.609	9.875	7.425
CH ₃	-0.170	9.050	8.209	7.566	8.875	7.537
H	0	9.059	8.222	7.569	9.900	7.734
Cl	0.227	9.047	8.228	7.512	9.925	7.997
COOC ₂ H ₅	0.450	9.059	8.231	7.447	9.987	8.487
CN	0.660	9.066	8.250	7.400	9.987	8.759
NO ₂	0.778	9.064	8.250	7.367	10.075	9.094
<i>b</i>	—	0.016	0.036	-0.225	0.173	1.565
<i>a</i>	—	9.052	8.221	7.550	9.905	7.773
<i>r</i>	—	0.8006	0.9418	-0.9893	0.9534	0.9923
<i>P</i>	—	95	99.8	99.9	99.9	99.9

^a 0.1M solution in solvent mixture CDCl₃ + (CD₃)₂SO 4 : 1 (by vol.); tetramethylsilane as internal standard; ^b $\delta = a + b\sigma_p$; *r* = correlation coefficient; *P* = correlation significance in %.

an exception, its slope being negative in contrast to the foregoing ones. Electron-withdrawing substituents and electron donors and shift this signal upfield downfield, respectively. It is obvious that in this case the chemical shift is not affected in decisive way by electron density at the adjacent carbon atom, but another effect is significant, its origin being the conformation of the investigated molecule.

Hydrazines are known⁵ to have the non-bonding orbitals with free electron pairs at the NH—NH nitrogen atoms mutually perpendicular so that their overlap might be minimum. In phenylhydrazines and hydrazobenzenes the free electron pair at nitrogen is involved in conjugation with the neighbouring benzene ring; hence it is perpendicular to it. Steric effect of 2-nitro group in 2,4-dinitrophenylhydrazine causes the free electron pair of NH₂ group to be directed predominantly towards the 6-hydrogen

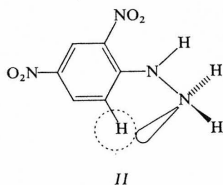


TABLE II

Chemical Shifts^a of Signals of 2,4-Dinitro-4'-substituted Hydrazobenzenes in δ (ppm) and Correlation^b with a_i Increments

Substituent	a_{ortho}	δ_A	a_{meta}	δ_B
OCH ₃	-0.48	6.777	-0.09	6.751
CH ₃	-0.20	7.013	-0.12	6.709
H	0	7.213	0	6.812
Cl	0.03	7.144	-0.02	6.772
COOC ₂ H ₅	0.71	7.864	0.11	6.817
CN	0.36	7.478	0.18	6.872
NO ₂	0.95	8.080	0.26	6.861
<i>b</i>	—	0.921	—	0.389
<i>a</i>	—	7.187	—	6.781
<i>r</i>	—	0.9965	—	0.9364
<i>P</i>	—	99.9	—	99.5

^a See Table I; ^b $\delta = a + ba_i$; *r* = correlation coefficient; *P* = correlation significance in %.

atom, which brings about deformation of electron cloud round this proton, its deshielding, and a downfield shift of the resonance signal. Substitution of NH_2 hydrogen atom by phenyl group to give 2,4-dinitrohydrazobenzene causes the free electron pair of this nitrogen to be involved in conjugation with π -electrons of the phenyl group and delocalized towards this benzene ring. The deformation effect of the free electron pair on the electron cloud round the H_6 proton is thus diminished and, consequently, its deshielding is decreased, too. The values δ_{H_6} are 7.793 and 7.569 ppm for 2,4-dinitrophenylhydrazine and 2,4-dinitrohydrazobenzene, respectively. Electron-withdrawing substituents in *para* position support the participation of n electrons of nitrogen atom in the conjugation, which causes a further lowering of their deforming effect on the electron cloud of the H_6 proton and upfield shift of its signal. On the contrary, a substituent with electron-donor effect, suppresses this conjugation and causes a downfield shift of the H_6 signal. The shifts caused by the changed deformation of the electron cloud are thus reverse to those due to electron density changes and are obviously predominant, which is manifested in negative slope of the correlation.

Our interpretation is supported by the fact that chemical shift of the signal of the hydrogen B in the *para* substituted benzene ring is affected in similar way by n electron cloud of the NH nitrogen atom adjacent to the dinitrophenyl group.

Chemical shifts of signals of aromatic hydrogen atoms in *para*-disubstituted benzenes are preferably correlated with the values a_i of increments⁶ for one variable substituent (X), the other substituent being kept constant during correlation. The correlation can be expressed as follows⁷:

$$\delta = (7.27 + a_j) + a_i(1 + Ka_j). \quad (1)$$

Eq. (1) expresses the deviation from additivity of the influence of the both substituents characterized by the increments a_i and a_j . The given correlation can be used to check correct assignment of chemical shifts to aromatic protons, determine effect of 2,4-dinitrophenylhydrazine group on the proton A and B, and confirm the effect of deformation of electron clouds on chemical shifts of the protons B which are sterically close to the NH nitrogen atom adjacent to 2,4-dinitrophenyl group. As far as the substituent X exerts only electronic effects, then slope of the correlation (b) is close to unity⁷, which, in our case, is true only for the hydrogen atoms A (Table II). However the correlation slope for B hydrogen atoms is much smaller.

The chemical shift of the hydrogen atoms B is affected (as in the case of hydrogens 6) by deformation of the electron cloud due to van der Waals repulsion by free electron pair at the sterically close NH nitrogen atom. Electron-withdrawing substituents will lower electron density at this nitrogen atom as well as in the adjacent dinitrobenzene ring, and thus they will support conjugation in this grouping. The result is lowering of the deformation effect of the free electron pair on the electron

cloud of hydrogen B and an upfield shift of their NMR signals. As the B hydrogens are much closer to the substituent X than hydrogens H₆, they are affected predominantly by change in electron density, whereas the influence of the changed deformation of electron cloud is only small. The resulting slope of correlation is positive, but it is considerably lower than the correlation for the hydrogens A.

The above results as well as those of another series of *para*-substituted benzenes^{8,9} indicate that the slope of the given correlation can be used for evaluation of substituent effects on chemical shift. A marked deviation of this slope from unity indicates that steric effects of the substituent are operating besides its electronegativity.

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