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THE STRUCTURE OF THE PROTONATED FORMS OF 1-HYDRAZINOPHTHALAZINE AND PHTHALAZONE HYDRAZONE DERIVATIVES

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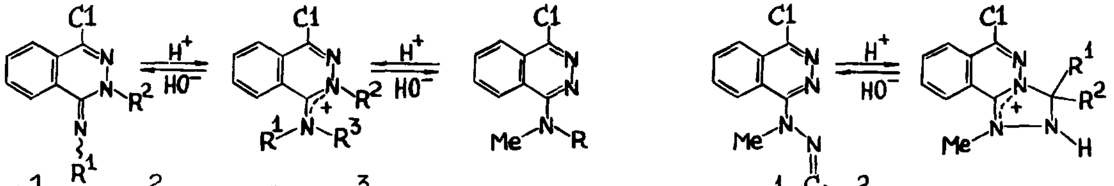
Abstract. Phthalazone derivatives Ia-h are protonated at the exocyclic nitrogen and phthalazine derivatives IIa-c at the N-2 of the ring. The cations of hydrazones Va-e have the cyclic structures VIa-e.

The protonated forms of hydrazones Ia,b and hydrazine IIa have similar UV spectra as regards the shapes and positions of the absorption bands (Fig.). Addition of the alkali yields the original bases, which indicate the absence of hydrolysis or symmetrization of the hydrazones in the azines in the protonated conditions (25°C, MeCN, 1 ml 57% $HClO_4$ in 9 ml MeCN). Therefore, the cations IIIa,b and IVc have the same electronic structures. A similar situation occurs with their benzylidene derivatives (ν_{max}, cm^{-1} 10^{-3}: IIIc - 28.5, 34.0, 35.0; IIId - 28.5, 33.4, 34.5; IVb - 27.4, 33.0, 34.3), the imines Ie,f and amine IIc (IIIe - 32.8, 38.0; IIIf - 31.8, 37.0, 38.0; IVc - 31.3, 36.3, 37.3), and isopropylidenehydrazones Ig,h (IIIg - 30.1, 35.3, 36.4; IIIh - 30.0, 34.6, 35.5).



	R^1	R^2
Ia	NH_2	H
b	NH_2	Me
c	N=CHPh	H
d	N=CHPh	Me
e	H	Me
f	Me	Me
g	$N=CMe_2$	H
h	$N=CMe_2$	Me

IIIa-h R^3=H
IVa-c R^2=H, R^3=Me

	R
IIa	NH_2
b	N=CHPh
c	Me

V VI

V,VI	a	b	c	d	e
R^1	H	H	Me	Me	Me
R^2	H	Me	Me	Ph	$CH=CMe_2$

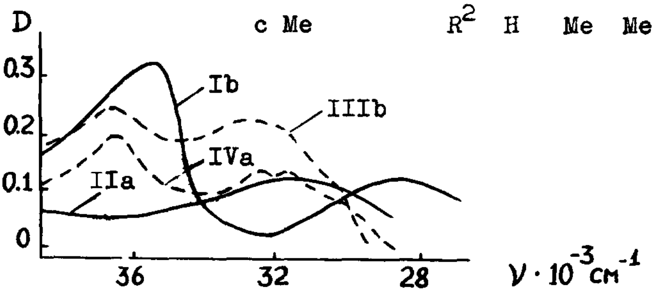


Figure. UV spectra of Ib, IIa and their protonated forms IIIb and IVa.

These data make it possible to draw the conclusion, that the hydrazones Ia,b, ilydenehydrazones Ic,d,g-h and imines Ie,f are protonated at the exocyclic nitrogen yielding the cations III, and hydrazine IIa, its benzylidene derivative IIb and amine IIc at N-2 of the cycle leading to the cations IV.

The hydrazones Va-e yield the cyclic cations VIa-e which yield the original hydrazones upon deprotonation. The UV spectra of cations VIa-e are not depend upon the nature of R^1 and R^2 (ν_{max}, $cm^{-1} \cdot 10^{-3}$: VIa-e - 30.2 (±0.1), 34.5, 35.5). The cyclic structure is also confirmed by the difference of UV spectra of VId and IVb and by the PMR spectra of V and VI. The transition from Va to VIa is followed by the downfield shift of aromatic protons and $N-CH_3$ signals (the shielding effect of the charge), which is typical of cations, whereas the signal of proton group $N=CH_2$ is undergone the characteristic upfield shift (Table) and instead of a quartet is shown by the single line (transition effect $C_{sp^2} \rightarrow C_{sp^3}$). The transition from Vc to VIc is also accompanied by the upfield shift of two protons signals of $N=CMe_2$ and their transformation into the singlet. The shift of the signal of CMe in VId is analogous, whereas the transition from acetone methylphenylhydrazone (VII) to its cation (VIII) is followed by the downfield shift of the signals of all protons, including $N=CMe_2$, two singlets (Z-Me and E-Me) being invariable. Protonation of VII at the imine nitrogen has been shown by UV spectroscopy method /1/.

It is interesting to note that the extent of the protonation of the hydrazones Va-e depends on the atrength of acid. At the progressive addition of more weak acid (DMSO-d_6, CF_3COOH) the protons signals of the hydrazone Vd and cyclic cation VId are shown in the PMR spectrum (a noncyclic cation is not found), the latter content being increased with acid.

^{1}H n.m.r. Chemical shifts, δppm, Varian T-60, DMSO-TMS[a]

	Va	VIa	Vc	VIc	Vd	VId	VII	VIII
H-5-H-7	8.08	8.25	7.98	8.25	7.88	8.28	6.62[e]	7.05[e]
H-8[b]	8.70	8.50		8.56		8.59		
Me[c]	3.58	3.84	3.18	3.85	3.33	3.93	2.80	3.00
R^1(Z)	6.89d[d]	5.23s	2.25s	1.72s	2.65s	2.15s	1.98s	2.28s
R^2(E)	6.59d[d]		2.10s		7.41m	7.50m	1.83s	2.18s

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[a] The protonation was carried out in the cell by addition of 1-2 drops of 57% $HClO_4$ to 5-10% solution. [b] A multiplet. [c] A singlet. [d] J_{HH} 10 hz, $\Delta\nu_{AB}$ 24 hz, [e] The protons of Ph.

Reference 1. V.V.Zverev, T.N.Pylaeva, A.P.Stolyarov, Yu.P.Kitaev, Izv. Acad. Nauk SSSR, ser. khim., 1977, 1280.

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