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Table 1

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Abstract

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p-DIMETHYLAMINOPHENYLMERCURY DERIVATIVES OF NITROSOANILINES AND NITROSONAPHTHYLAMINES

In contrast to the extensively studied nitrosophenols and nitrosonaphthols, the structure of nitrosoanilines and nitrosonaphthylamines has been investigated much less fully. Thus, there is only one indication that the absorption spectrum of *p*-nitrosoaniline contains a band of the NO group of somewhat increased intensity, caused by conjugation of the NO group with the free electron pair of the amino group (^{1}). This band disappears upon acidification of the solution. On this basis it may be concluded that nitrosoaniline has a benzenoid structure, in contrast to its salt, which has a quinoid structure; i.e., the same relationships occur here as in nitrosodialkylanilines and their salts. Cu, Co, Ni, and Pd derivatives of nitrosonaphthylamines have been obtained and have found application in qualitative and quantitative analysis, but their structure has not been investigated ($^{2-5}$).

Table 1

No.	Compound	M.p. (decomp.), °C	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Hg, % found	Hg, % calcd.
1	Benzene ring bearing NHHgC$_6$H$_4$N(CH$_3$)$_2$ and NO	205 from C_7H_{16} — C_5H_5N	91	37.74 37.81	38.18	3.42 3.38	3.43	9.34 9.49	9.54	45.48 45.50	45.56

No.	Compound	M.p. (decomp.), °C	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Hg, % found	Hg, % calcd.
2	Benzene ring bearing NHHgC$_{6}$H$_{4}$N(CH$_{3}$)$_{2}$, two CH$_{3}$ groups, and NO	178 from C$_7$H$_{16}$ — C$_5$H$_5$N	89	41.17 41.13	40.89	4.13 4.16	4.07	8.78 8.83	8.94	42.65 42.56	42.09
3	Benzene ring bearing N[HgC$_{6}$H$_{4}$N(CH$_{3}$)$_{2}$]$_{2}$, CH$_{3}$, and NO	192 from C$_7$H$_{16}$ — C$_5$H$_5$N	82	35.42 35.56	35.71	3.45 3.41	3.38	7.19 7.08	7.22	51.66 51.57	51.82
4	Benzene ring bearing N[HgC$_{6}$H$_{4}$N(CH$_{3}$)$_{2}$]$_{2}$, OCH$_{3}$, and NO	206 from C$_7$H$_{16}$ — C$_5$H$_5$N	81	34.95 34.08	34.19	3.27 3.30	3.31	6.99 7.11	7.08	50.27 50.36	50.38
5	Naphthalene ring bearing NHHgC$_{6}$H$_{4}$N(CH$_{3}$)$_{2}$ and NO	162 from C$_4$H$_9$OH	95	43.92 43.85	43.95	3.44 3.63	3.48	8.57 8.56	8.54	40.42 40.27	40.78
6	Naphthalene ring bearing NO and NHHgC$_{6}$H$_{4}$N(CH$_{3}$)$_{2}$	207 from C$_6$H$_5$Cl	93	43.97 43.90	43.95	3.45 3.51	3.48	8.67 8.73	8.54	40.34 40.45	40.78

Table 2

No.	Compound	Solvent	ν, cm^{-1} $\cdot 10^{-3}$	ε_{max}
1	$H_2NC_6H_4NO-4$	C_2H_5OH	15.2	53.5
2	Same	CH_3COCH_3	14.1	58.0
3	Same	$CH_3COOC_2H_5$	14.2	53.0
4	Same	C_4H_8O	15.0	57.5
5	$(CH_3)_2NC_6H_4NO-4$	C_2H_5OH	15.0	58.5
6	Same	CH_3COCH_3	14.1	60.0
7	Same	$CH_3COOC_2H_5$	14.0	57.5
8	Same	C_4H_8O	13.9	60.0
9	$H_2NC_6H_3(CH_3-3)(NO-4)$	C_5H_5N	13.7	65.5
10	$(CH_3)_2NC_6H_3(CH_3-3)(NO-4)$	Same	13.6	69.5
11	$(RHg)_2NC_6H_3(CH_3-3)(NO-4)$	Same	14.2	90.0
12	$H_2NC_6H_3(OCH_3-3)(NO-4)$	Same	13.8	78.0
13	$(CH_3)_2NC_6H_3(OCH_3-3)(NO-4)$	Same	13.7	80.5
14	$(RHg)_2NC_6H_3(OCH_3-3)(NO-4)$	Same	14.3	117.0
15	$H_2NC_6H_2((CH_3)_2-2,5)(NO-4)$	Same	13.7	63.5
16	$(CH_3)_2NC_6H_2((CH_3)_2-2,5)(NO-4)$	Same	13.3	47.5
17	$RHgNHC_6H_2((CH_3)_2-2,5)(NO-4)$	Same	14.0	75.0
18	$1-H_2NC_{10}H_6NO-2$	Same	14.4	80.0

No.	Compound	Solvent	ν, cm^{-1} $\cdot 10^{-3}$	$\varepsilon_{\max}$
19	$1-\mathrm{RHgNHC_{10}H_6NO}-2$	Same	14.2	93.0

$R = 4-(\mathrm{CH_3})_2\mathrm{NC_6H_4}$

Continuing the investigation of arylmercury derivatives of tautomeric and pseudomeric systems, in the present work we studied the interaction of *p*-dimethylaminophenylmercury hydroxide with a series of nitrosoanilines and nitrosonaphthylamines, which were obtained by methods available in the literature$^{(6-8)}$. The arylmercury derivatives were synthesized according to the general equation:

$$(\mathrm{CH_3})_2\mathrm{NC_6H_4HgOH} + \mathrm{RNH_2} \rightarrow (\mathrm{CH_3})_2\mathrm{NC_6H_4HgNHR} + \mathrm{H_2O}$$

(where $\mathrm{RNH_2}$ is the corresponding nitrosoaniline or nitrosonaphthylamine) in the reaction of arylmercury hydroxide with nitrosoanilines and nitrosonaphthylamines in methanolic solution (Table 1). The compounds obtained are brightly colored crystalline substances, insoluble in water, very poorly soluble in most organic solvents, with the exception of pyridine, and melting with decomposition. The arylmercury radical in them is not bonded to the aromatic nucleus of the nitrosoaniline, which is confirmed by the following data: 1) N,N-dimethyl-substituted nitrosoanilines and dimethylaniline do not react with arylmercury hydroxide; 2) the compounds obtained, in contrast to bis-*p*-dimethylaminophenylmercury, are cleaved by the action of potassium iodide according to the equation

$$(\mathrm{CH_3})_2\mathrm{NC_6H_4HgNHR} + \mathrm{KJ} + \mathrm{H_2O} \rightarrow (\mathrm{CH_3})_2\mathrm{NC_6H_4HgJ} + \mathrm{RNH_2} + \mathrm{KOH}.$$

Consequently, they may have either a benzenoid or a quinoid structure

$$(\mathrm{CH_3})\mathrm{NC_6H_4HgNH}\langle\text{benzene ring}\rangle\mathrm{NO} \quad \text{or}$$

$$\mathrm{HN} = \langle\text{benzene ring}\rangle = \mathrm{NOHgC_6H_4N(CH_3)_2}.$$

To establish the structure of nitrosoanilines, nitrosonaphthylamines, and their arylmercury derivatives, the characteristic absorption of the NO group was used.

For this purpose, absorption spectra were recorded for nitrosoanilines, nitrosonaphthylamines, their arylmercury derivatives, and N,N-dimethyl-substituted nitrosoanilines in the region 10–20 cm^{-1} $\cdot$ 10^{-3} (see Figs. 1, 2 and Table 2)*.

Owing to the poor solubility of the arylmercury derivatives, the spectra were recorded in pyridine with cuvette thicknesses of 50–100 mm.

Fig. 1. Absorption spectra in C_5H_5N:

1 — p-$H_2N{-}C_6H_4{-}NO$;
2 — p-$(CH_3)_2N{-}C_6H_4{-}NO$;
3 — p-$NO{-}C_6H_4{-}NHHgC_6H_4N(CH_3)_2$;
4 — $HN{=}C_6H_4{=}NONa$.

Fig. 2. Absorption spectra in C_5H_5N:

1 — nitrosonaphthylamine ($NO,\ NH_2$);
2 — arylmercury derivative $NO{-}C_{10}H_5{-}NHHgC_6H_4N(CH_3)_2$;
3 — sodium salt form $NONa,\ {=}\,NH$.

All nitrosoanilines and their arylmercury derivatives possess in this region a characteristic absorption maximum of the NO group, clearly expressed and fairly distinctly separated from absorption in the ultraviolet region. Comparison of the absorption intensity of the NO group in the spectra of the N,N-dimethyl-substituted compounds with the spectra of the free compounds shows that the nitrosoanilines are present in solution entirely in the benzenoid form, in contrast to the nitrosophenols, for which the quinoid form predominates. The small difference in absorption intensity is caused by the influence of the substituting methyl groups. The lowered value of $\varepsilon_{\max}$ for N,N-dimethylnitrosoxylidine is probably due to disruption of conjugation of the NO group with the amino group as a result of steric hindrance. In the spectra of the arylmercury derivatives the absorption intensity of the NO-group maximum is greatly increased, which, together with a certain hypsochromic shift, indicates

* The spectra were recorded on an SFD-1 spectrophotometer in the optical laboratory of I. V. Obreimov.

electron-donating nature of the n-dimethylaminophenylmercury radical. It is possible that, in the present case, the specific influence of pyridine as a solvent is also manifested. Thus, comparison of the absorption intensity of n-nitrosoaniline and n-nitrosodimethylaniline in different solvents reveals its considerable increase on going to pyridine.

In the spectra of nitrosonaphthylamines and their arylmercury derivatives there is likewise an absorption band of the NO group, possessing normal intensity, which indicates their nitrosoamine structure. In contrast to this, in the spectra of the Na derivatives of nitrosoanilines and nitrosonaphthylamines the maximum of the NO group is absent, on the basis of which we have concluded that the anions of nitrosoanilines and nitrosonaphthylamines have a quinoid structure:

HN = ⟨benzene ring⟩ = NO$^-$ NO$^-$ naphthalene ring = NH

Thus, the results obtained show that nitrosoanilines and nitrosonaphthylamines, as well as their arylmercury derivatives, have a benzenoid structure, in contrast to nitrosophenols, nitrosonaphthols, and their arylmercury derivatives, which exist mainly in the quinoid form (9). This thereby once again confirms the great similarity in the behavior of the arylmercury radical and the hydrogen atom in tautomeric and pseudomeric systems.

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