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Abstract

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p-DIMETHYLAMINOPHENYLMERCURY DERIVATIVES OF AMINOAZO COMPOUNDS

As a result of a study of the ultraviolet and infrared absorption spectra of aminoazo compounds of the benzene and naphthalene series, it has been shown that, within the sensitivity limits of the spectral method, in solution and in the solid state they exist predominantly in the aminoazo form ($^{1-3}$):

[[structural formula: aminoazobenzene]]   [[structural formula: aminoazonaphthalene]]   [[structural formu

contrary to earlier ideas concerning the presence in some cases of a quinone imine hydrazone structure (^{4}). Metallic derivatives of *o*-aminoazo compounds and of metals possessing complex-forming ability are known (^{5,6}). It was found that aminoazobenzene is mercurated with considerably greater difficulty than aniline (^{7}). The literature contains no information on the preparation of metallic derivatives of *p*-aminoazo compounds or of mercury derivatives of aminoazo compounds in which the mercury is not bonded to the aromatic nucleus.

Fig. 1. Absorption spectra in ethyl acetate:
a–$R = NH_2$;
b–$R = (CH_3)_2N$;
c–$R = (CH_3)_2NC_6H_4HgNH$

In continuation of earlier work ($^{8-10}$) on arylmercury derivatives of tautomeric and pseudomeric systems, we have investigated the interaction of *p*-dimethylaminophenylmercury hydroxide with aminoazo compounds of benzene, naphthalene, and anthracene. Of the compounds studied, only 10-phenylazo-9-aminoanthracene did not react with arylmercury hydroxide, probably because of its quinone imine hydrazone structure (^{11}). The arylmercury derivatives of the remaining compounds were obtained according to the general scheme:

$$(CH_3)_2NC_6H_4HgOH + HA \rightarrow (CH_3)_2NC_6H_4HgA + H_2O,$$

where HA is the corresponding aminoazo compound.

The compounds obtained are crystalline substances of orange or dark-red color, insoluble in water, soluble in organic solvents, and melting with decomposition; see Table 1. They are not changed by the action of alkalis, but are decomposed by dilute acids. In the compounds under consideration, the arylmercury radical may either be bonded to the aromatic nucleus or replace a labile hydrogen atom.

We have found that aniline, dimethylaniline, and 4-phenylazodimethylaniline do not react with *p*-dimethylaminophenylmercury hydroxide, in contrast to aminoazo compounds. The arylmercury derivatives obtained by us, unlike bis(*p*-dimethylaminophenyl)mercury, are decomposed by the action of KI into an arylmercury halide, an aminoazo compound, and an equivalent amount-

Table 1

$(CH_3)_2NC_6H_4HgNHR$

R	Yield, %	M.p. (decomp.), °C	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Hg, % found	Hg, % calcd.
$C_6H_5N{=}N{-}C_6H_4{-}$	87	196 from $CH_3C_6H_5$	46,19 46,32	46,46	4,03 3,93	3,90	11,02 10,97	10,84	38,63 38,30	38,80
quinoline residue $-N{=}N{-}C_6H_4X$, $X{=}H$	86	189 from $CH_3C_6H_5$	50,83 50,79	50,74	4,09 3,95	3,90	9,63 9,59	9,86	35,41 35,73	35,32
same, $X{=}CH_3$	88	207 from C_3H_7OH	51,89 51,72	51,67	4,21 4,17	4,16	9,81 9,78	9,64	34,56 34,50	34,53
same, $X{=}CH_3O$	85	203 from C_3H_7OH	50,46 50,35	50,28	4,15 4,09	4,05	9,53 9,58	9,38	33,82 33,89	33,60
same, $X{=}Cl$	83	210 from $CH_3C_6H_5$	47,96 48,05	47,83	3,70 3,70	3,51	9,43 9,50	9,30	33,33 33,21	33,30
same, $X{=}O_2N$	89	218 from $CH_3C_6H_5$	46,91 46,88	47,01	3,57 3,63	3,45	11,74 11,69	10,43	32,69 32,66	32,72
naphthalene residue $N{=}N{-}C_6H_4X$, $X{=}H$	88	182 from $C_6H_6{-}C_6H_{12}$	50,60 50,53	50,74	3,92 3,76	3,90	10,11 10,15	9,86	35,32 35,27	35,32
same, $X{=}CH_3$	86	178 from C_2H_5OH	51,86 51,83	51,67	4,19 4,20	4,16	9,93 9,77	9,64	34,94 34,75	34,53
same, $X{=}CH_3O$	84	169 from C_2H_5OH	50,38 50,01	50,28	4,12 4,06	4,05	9,55 9,39	9,38	33,96 33,29	33,60
same, $X{=}Cl$	90	176 from C_3H_7OH	47,90 47,86	47,83	3,54 3,73	3,51	8,96 9,18	9,30	33,63 33,55	33,30
same, $X{=}O_2N$	87	198 from $CH_3C_6H_5$	46,99 46,85	47,01	3,49 3,53	3,45	11,78 11,65	10,43	32,96 32,61	32,72

amount of alkali, for example:

Fig. 2 and Fig. 3

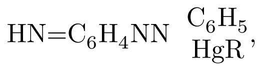
Figure 1: Fig. 2 and Fig. 3

$$(CH_3)_2NC_6H_4HgNHC_6H_4N{=}NC_6H_5 + KJ + H_2O \rightarrow$$

$$\rightarrow (CH_3)_2NC_6H_4HgJ + H_2NC_6H_4N{=}NC_6H_5 + KOH.$$

On this basis, taking into account, moreover, the passivating action of the phenylazo group on the aromatic nucleus ([7,12]), it should be concluded that in the derivatives obtained the arylmercury radical is not bonded to the aromatic nucleus of the aminoazo compound. Thus, they may have either a benzenoid or a quinoid structure, for example:

$$RHgNH{-}C_6H_4{-}N{=}NC_6H_5$$



$$HN{=}C_6H_4NN\begin{matrix}C_6H_5\\HgR\end{matrix},$$

or be tautomeric in solution.

To elucidate the structure of the compounds obtained, their absorption spectra were recorded in the region 15 000–40 000 cm^{-1} in ethyl acetate, and they were compared with the spectra of the initial aminoazo compounds and of several N,N-dimethyl-substituted compounds (see Figs. 1–3). Consideration of the spectral data shows that the spectra of 4-aminoazobenzene and of 4-phenylazo-1-naphthylamines substituted in the phenylazo group, as well as of their arylmercury derivatives, are very similar to the spectra of N,N-dimethyl-substituted compounds. The shape of the spectral curve remains unchanged in the region 20 000–30 000 cm^{-1} on going from one compound to another. Only a certain change in the absorption intensity and a shift of the maxima occur. We also found that, for 4-phenylazo-1-naphthylamines substituted in the phenylazo group, the shape of the absorption curve does not depend on the substituent in the phenylazo group.

The appearance of an additional maximum in the region 37 000 cm^{-1} is due to the intrinsic absorption of the arylmercury radical. The observed similarity

the nature of the absorption spectra indicates the benzenoid structure of the arylmercury derivatives of 4-aminoazobenzene and substituted 4-phenylazo-1-naphthylamines. An analogous picture is also observed in the case of arylmercury derivatives of 1-phenylazo-2-naphthylamine and its substituted compounds. Unfortunately, it was not possible to obtain N,N-dimethyl-substituted 1-arylazo-2-naphthylamines. Nevertheless

Fig. 2. Absorption spectra in ethyl acetate:
$a\ {-X} = H,\ R = NH_2;\ \ {-X} = H,\ R = (CH_3)_2N;\ \ {-X} = H,\ R =$

$(CH_3)_2NC_6H_4HgNH$; $-X = NO_2$, $R = NH_2$; $-X = NO_2$, $R = (CH_3)_2N$; $-X = NO_2$, $R = (CH_3)_2NC_6H_4HgNH$

Fig. 3. Absorption spectra in ethyl acetate:
a $-X = H$, $R = NH_2$; $-X = H$, $R = (CH_3)_2NC_6H_4Hg$; $-X = NO_2$, $R = H$; $-X = NO_2$, $R = (CH_3)_2NC_6H_4Hg$

comparison of the spectra of aminoazo compounds of this series and their arylmercury derivatives with the spectrum of 1-phenylazo-2-naphthylamine, for which the aminoazo structure has been established on the basis of IR spectra (^{3}), shows that the compounds under consideration likewise possess a benzenoid structure.

The independence of the shape of the spectral curve from the substituent in the phenylazo group indicates the absence of tautomeric equilibrium within the sensitivity limits of the spectral method. Thus, the structure of arylmercury derivatives is completely analogous to the structure of the corresponding aminoazo compounds and is determined by the stability of the benzenoid state of the aromatic ring entering into the pseudomeric system.

The arylmercury derivatives of 4-aminoazobenzene and substituted 4-phenylazo-1-naphthylamine are the first example of metallic derivatives of *n*-aminoazo compounds. Their stability, in contrast to compounds of other metals, is determined by the greater strength of the Hg–N bond in comparison with the Hg–O bond. As a result, there is no need for stabilization by a coordination bond with the azo group, as occurs in the case of Cu, Ni, and Co derivatives of *o*-aminoazo compounds.

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Note: Figure translations are in progress. See original paper for figures.