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Abstract

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On the Planarity of Molecules of Diazoamino Compounds

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Diazoamino compounds of the aromatic series (triazenes) are, as is known, colored substances characterized by maximum absorption of radiant energy in the region 350–365 mµ. In earlier works (1, 2) it is mentioned that 2,4,6—2′,4′,6′-hexachloro- and 2,4,6—2′,4′,6′-hexabromodiazoaminobenzene are colorless. Starting from chloro- and bromoanilines, we synthesized a large number of diazoamino compounds (with identical benzene nuclei) and became convinced that, alongside colored compounds, there are also quite a few colorless compounds.

Fig. 1. Absorption spectra of diazoamino compounds in various solvents: solid curves—in *n*-hexane, dashed—in alcohol, dotted—in cyclohexane; 1, 2, 3—2,4,6—2′,4′,6′-hexabromodiazoaminobenzene; 4, 5, 6—2,3,4—2′,3′,4′-hexachlorodiazoaminobenzene.

It is interesting to note that in the colorless compounds the halogen atoms occupy all four possible *o*-positions with respect to both nitrogen atoms; the situation does not change when a larger number of substituents is present. When, however, 2 or all 4 *o*-positions with respect to both nitrogen atoms are free from substituents—halogens—the diazoamino compound has a more or less deep yellow color.

Their electronic absorption spectra are characteristic: whereas the colored substances have a clearly expressed absorption maximum in the region 350–365 mµ, as well as in the region 240–260 mµ, the colorless ones are represented by more or less smooth curves with a small maximum in the region 270–280 mµ, or none at all.

Fig. 2. Absorption spectra of colorless diazoamino compounds in *n*-hexane:
a—2,4,6—2′,4′,6′-hexachloro-,
b—2,3,4,6—2′,3′,4′,6′-octachloro-,
c—2,3,5,6—2′,3′,5′,6′-octachloro-,
d—2,4,6—2′,4′,6′-hexamethyl-,
e—2,6—2′,6′-tetrabromo-,
f—2,4,6—2′,4′,6′-hexabromodiazoaminobenzene.

do not have an absorption maximum. The spectra of individual diazoamino compounds were recorded in various solvents (alcohol, cyclohexane, *n*-hexane), and no sharp difference in the nature of the curves for one and the same compound was observed (see Fig. 1) (^{4}).

Starting from mesidine, 2,4,6–2′,4′,6′-hexamethyldiazoaminobenzene was obtained, which also proved to be colorless (see Fig. 2). Thus, in the presence of bulky substituents in positions suitable with respect to the nitrogen atoms, the absorption of radiant energy by a given substance shifts into the short-wavelength region of the spectrum. Models of diazoamino compounds constructed by the Stuart-Briegleb method confirm our supposition that the absence of color is associated with sharp changes in the planarity of such molecules.

Fig. 3. Absorption spectra of colored diazoamino compounds: 1–2,4,5–2′,4′,5′-hexachloro-, 2–3,4,5–3′,4′,5′-hexachloro-, 3–2,3,4–2′,3′,4′-hexachloro-, 4–2,4–2′,4′-tetrachloro-, 5–2,4,5–2′,4′,5′-hexabromodiazoaminobenzene

It is known that, under the action of an excess of mineral acid, diazoamino compounds decompose with the formation of diazonium salts and amines; therefore diazoamino compounds are prepared in weakly acidic media. This also includes the method of obtaining them with amyl nitrite (^{1,3}) in ethanol in the presence of traces of HCl (see the preparation method B in Table 1). In this connection, the unusual stability of many halogen-substituted diazoamino compounds in a strongly acidic medium is of interest. On this basis, a method is proposed for obtaining a number of these compounds (see preparation method A in Table 1). Nitrosylsulfuric acid is mixed with a solution of the haloaniline in conc. H_2SO_4; upon completion of the reaction, the mixture is poured into water with ice, and the product precipitates almost immediately. The final concentration of the acid diluted with water is 10-12%. Some compounds could not be obtained in this way, for example 2,4,6–2′,4′,6′-hexachloro- and hexabromodiazoaminobenzene.

Fig. 4. Absorption spectra of colored diazoamino compounds in *n*-hexane: 1–diazoaminobenzene, 2–4,4′-dimethyldiazoaminobenzene, 3–3,4–3′,4′-tetramethyldiazoaminobenzene

It should be noted that there is no universal method for obtaining diazoamino compounds; for example, 3,4–3′,4′-tetramethyldiazoaminobenzene is obtained by the usual methods in a yield of 90% of theory (^{5}),

Table 1

Substance No.	Method of preparation	Yield, theor., %	m.p., °C	Color	In *n*-hexane, λmax	In *n*-hexane, ϵmax	In alcohol, λmax	In alcohol, ϵmax
I	A	68	156-157	colorless	shoulder 265–275	12 000	–	–
II	A	74	143-144	colorless	–	–	–	–

Substance No.	Method of preparation	Yield, theor., %	m.p., °C	Color	In n-hexane, λmax	In n-hexane, ϵmax	In alcohol, λmax	In alcohol, ϵmax
III	A	80	165–166	yellow	250300365	16 40011 80023 600	245305365	14 08011 24021 200
IV	A	90	186–187	yellow	250310–315365	18 40011 84023 000	250360	18 20023 400
V	A	82	170–171	yellow	245295360–365	16 0008 80017 400	245300360–365	18 00010 00019 960
VI	A		192–193	yellow	250310365	28 80014 40033 600	250310–315365	23 20012 60028 500
VII	B	85	138–139	colorless	275–280	10 200	255	16 800
VIII	B	88	157–158	colorless	270	13 100	–	–
IX	B		189–190	yellow	310370	12 96024 400	310370	14 40024 800
X	C	54	132–133	colorless	shoulder265–270	8 720	–	–
XI	C	90	126–127	yellow	235–240305365	13 70010 80020 200	240–245305360	15 40011 24022 200
XII	C	35	91–92	colorless	280	18 800	–	–
XIII	C	30	116–117	yellow	235295355	16 8009 70018 400	235290355	15 2007 80017 220
XIV	G	90	142–143	yellow	240295370	20 9209 64020 600	245295360	20 6008 60025 520
XV	G	92	98–99	yellow	235292375	15 8009 20017 300	235290350	16 4006 32019 200

formation of the isomeric 2,6–2′,6′-tetramethyldiazoaminobenzene does not occur under the same conditions. Many halogen derivatives, for example 2,4,6–2′,4′,6′-hexahalo-substituted compounds, are readily obtained with the aid of ethyl nitrite in ethanol in the presence of H_2SO_4 (final concentration of H_2SO_4 2%) at 18-20° (see method B in Table 1).

Experimental Part

2,3,5,6–2′,3′,5′,6′-Octachlorodiazoaminobenzene (I), method A. 4.6 g of symmetrical tetrachloroaniline in 35 ml of conc. H_2SO_4 was diazotized at 5-7° with nitrosylsulfuric acid (1.4 g of $NaNO_2$ in 20 ml of conc. H_2SO_4), stirred for 1 h, and 2.3 g of the same amine in 25 ml of conc. H_2SO_4 was introduced at 20°. After 3 h the mixture was poured into 1 l of water with ice, filtered, and washed with water. Colorless needles (from a mixture of benzene and ligroin).

2,3,4,6–2′,3′,4′,6′-Octachlorodiazoaminobenzene (II) was obtained analogously to I. 2.3 g of 2,3,4,6-tetrachloroaniline in 18 ml of H_2SO_4 and 0.7 g of $NaNO_2$ in 10 ml of H_2SO_4 were taken. 1.15 g of the same amine in 12 ml of H_2SO_4 was added. Colorless needles (from a mixture of ether and alcohol).

2,4,5–2′,4′,5′-Hexachlorodiazoaminobenzene (III) was obtained by method A, by the interaction of 3.9 g of 2,4,5-trichloroaniline in 25 ml of conc. H_2SO_4 with nitrosylsulfuric acid (0.7 g of $NaNO_2$ in 10 ml of H_2SO_4). Tufts of yellow needles (from acetone).

2,3,4–2′,3′,4′-Hexachlorodiazoaminobenzene (IV) was obtained analogously to III from 1.96 g of 2,3,4-trichloroaniline in 12 ml of H_2SO_4 and 0.35 g of $NaNO_2$ in 5 ml of H_2SO_4. Yellow needles (from benzene).

2,5–2′,5′-Tetrachlorodiazoaminobenzene (V), method A. From 1.6 g of 2,5-dichloroaniline in 12 ml of H_2SO_4 and 0.7 g of $NaNO_2$ in 10 ml of H_2SO_4.

Added 0.8 g of the same amine in 6 ml of H_2SO_4. Light-yellow needles (from ligroin).

3,4,5–3′,4′,5′-Hexachlorodiazoaminobenzene (VI) was obtained analogously to I by method A. Yellow needles (from benzene).

2,4,6–2′,4′,6′-Hexachlorodiazoaminobenzene (VII), method B. 1.96 g of symmetrical trichloroaniline, 1.9 g of conc. H_2SO_4, 17 ml of ethanol, and 0.7 g of $NaNO_2$ were stirred for 3 hours at 20°, after which the mixture was poured into 80 ml of water with ice, filtered, and washed with water and cold alcohol. Bundles of colorless needles (from ligroin). Molecular weight found: 396.0; 402.10; calculated: 403.93.

2,4,6–2′,4′,6′-Hexabromodiazoaminobenzene (VIII) was obtained by method B. Taken were 6.6 g of symmetrical tribromoaniline, 3.8 g of H_2SO_4, 70 ml of ethanol, and 0.7 g of $NaNO_2$. Bundles of colorless needles (from benzene).

2,4,5–2′,4′,5′-Hexabromodiazoaminobenzene (IX) was obtained analogously to VIII. Yellow needles (from benzene).

2,6–2′,6′-Tetrabromodiazoaminobenzene (X), method B. A solution of 5 g of 2,6-dibromoaniline in 70 ml of ethanol and 2.4 g of amylnitrite was stirred for 4 hours at 20°. On the following day the mixture, cooled to 0°, was filtered and washed with cold alcohol. Colorless needles (from ligroin).

2,4–2′,4′-Tetrachlorodiazoaminobenzene (XI) was obtained analogously to X. Straw-yellow needles (from ligroin).

2,4,6–2′,4′,6′-Hexamethyldiazoaminobenzene (XII). 4.0 g of mesidine, 5 ml of ether, and 3.5 g of amylnitrite were mixed and left to stand in an open vessel for 3 hours at 25–30°. The mixture was cooled in ice, filtered, and washed with cold alcohol. Bundles of colorless needles (from cyclohexane), elongated prisms (from a mixture of ether and alcohol). Molecular weight found: 273.6; 267.0; calculated: 281.39.

4,4′-Dimethyldiazoaminobenzene (XIII) was obtained analogously to XII. Light-yellow needles (from alcohol).

3,4–3′,4′-Tetramethyldiazoaminobenzene (XIV), method . A solution of 1.2 g of 3,4-dimethylaniline and 3.0 g of HCl in 1.5 ml of water was mixed with a diazonium solution prepared from 1.2 g of 3,4-dimethylaniline, 4.6 g of HCl in 10 ml of water, and 0.7 g of $NaNO_2$. After mixing, 4.8 g of sodium acetate in 15 ml of water was added immediately. Yellow needles (from benzene).

Diazoaminobenzene (XV) was obtained by method . Yellow needles (from benzene).

Diazoamino compounds I, III, V, VII, VIII were also obtained by another method. For example, VIII: at 5–7°, 3.3 g of 2,4,6-tribromoaniline in 300 ml of alcohol was mixed with 1.2 g of amylnitrite and 0.5 g of HCl and stirred for 3 hours at 20°. On the following day the cooled mixture was filtered and washed with cold alcohol. 2.7 g (82% of theory) of VIII was obtained.

Purification of diazoamino compounds sometimes presents considerable difficulties. Many of the diazoamino compounds described were purified by chromatographic adsorption on aluminum oxide, using solvents–acetone, benzene, *n*-hexane–after which they were recrystallized from various suitable solvents.

The electronic absorption spectra data were obtained on an SF-4 spectrophotometer in solutions of *n*-hexane, alcohol, and cyclohexane; the concentration of the solutions was 10^{-4} mol/l.

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