[Contribution from the Chemical Laboratory of Iowa State College]

SILICON-CONTAINING AZO DYES. II[1]

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In previous publications (1, 2), we have reported the synthesis and properties of some silicon-containing azo dyes, prepared from *m*-trimethylsilyl- and *m*-triphenylsilyl-dimethylaniline, to study the effect of an R_3Si substituent on the dyeing properties of these compounds. In continuation of our study, we now have synthesized several dispersed cellulose acetate azo dyes, related to some commercial types, derived from *m*-trimethylsilyl- and *m*-triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline. This paper reports the synthesis and properties of these azo dyes.

Due to the unusual behavior of cellulose acetate in dyeing, the research in the synthesis of suitable dyes for this fiber progressed in a different way. Most of the acid wool and direct cotton water-soluble dyes, which generally are characterized by their water solubility due to the presence of a nuclear sulfonic group, had no affinity for cellulose acetate (3), while basic dyes lacked the necessary fastness (4). Therefore, the choice was left with basic azo dyes (Dispersols) and aminoanthraquinones (Duranols). Many of the dispersed azo dyes, however, showed a lack of proper affinity and necessary light fastness. Moreover, a low molecular weight of the dye was also desirable. Therefore, a large number of dyes was prepared by the introduction of appropriate substituents. For example, the substitution of 4′-nitro-4-aminoazobenzene was effected in two ways. N-Alkylation with suitable groups resulted in the solubilization and easy dispersion of the dyes, while the nuclear substitution facilitated a desirable change in hue, brightness, and fastness. The sulfoalkyl (5), hydroxyalkyl, alkoxyalkyl, cyanoalkyl (6), and polyethanoxyalkyl (7) are some of the groups used for N-alkylation.

Similarly, the replacement of 4-nitroaniline as a diazo component, with its 6-chloro, 2,6-dichloro, 2-trifluoromethyl, 2-methylsulfonyl, *etc.*, derivatives (8, 9), as well as the replacement of tertiary amine as a coupling component with its derivatives such as 3-methyl, 3-methyl-6-methoxy, *etc.*, (10), has led to the preparation of faster and deeper dyes. Among these, of particular importance are N,N-bis(β-hydroxyethyl)aniline and its derivatives. Accordingly, *m*-trimethylsilyl- and *m*-triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline were the compounds of choice for our investigation.

The organosilicon compounds were prepared by the action of trimethylchlorosilane and triphenylchlorosilane with the organolithium compound, prepared by the action of *n*-butyllithium with *m*-bromo-N,N-bis(β-hydroxyethyl) aniline. The preparation of these organosilicon compounds presented some difficulties. Considering the two hydroxyl groups present in the molecule, these difficulties were not unanticipated. From our past experience (11), it has been

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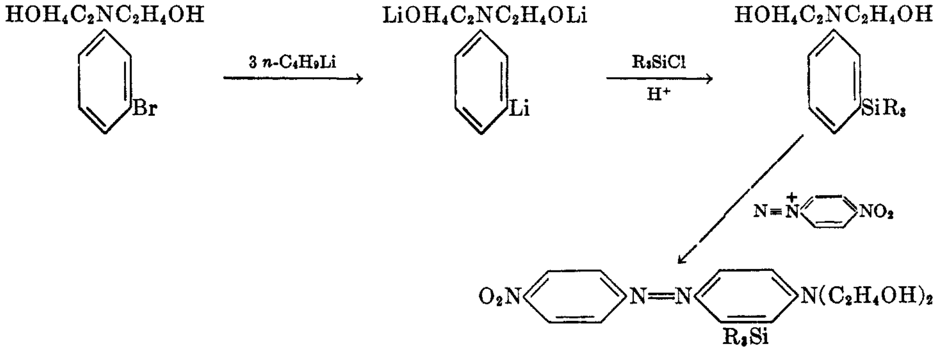
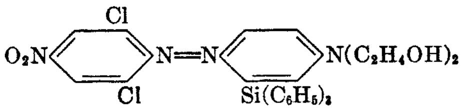
found that the reaction of the chlorosilanes with the organolithium compounds containing —OLi groups invariably leads, to some extent, to polymeric side products.



In the halogen-metal interconversion reaction of *n*-butyllithium with *m*-bromo-N,N-bis(β-hydroxyethyl)aniline, the replacement of bromine by lithium is preceded by the replacement of two active hydrogen atoms from the hydroxyl groups by lithium. When the reaction of triphenylchlorosilane was carried out at room temperature, a large amount of polymeric compound was formed, and a yield of only 10% of the desired organosilicon compound was obtained. Therefore, the halogen-metal interconversion reaction was carried out at −20°, and after adding triphenylchlorosilane to the resulting organolithium compound, the temperature of the reaction mixture was allowed to rise gradually to that of the room. By this procedure, the yield of the polymeric compound was considerably reduced, and the yield of the organosilicon compound was raised to 36.5%. In the case of trimethylchlorosilane, the reaction seemed to be smoother. Even by carrying out the reaction at room temperature, a yield of about 50% of the organosilicon compound was obtained. This compound also was contaminated with a polymeric side product, which made its purification difficult.

Both of the organosilicon compounds coupled readily with diazonium salts. The resulting dyes, however, especially in the case of trimethylsilyl derivatives, were obtained as sticky products. The purification of the dyes, therefore, was done by chromatographic fractionation, followed by crystallization from appropriate solvents.



I

While carrying out the chromatographic separations, it was noted that some of the dyes exist in two forms. Prominent among them was the dye (I), prepared by coupling the diazonium salt of 2,6-dichloro-4-nitroaniline with *m*-triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline. When the chloroform solution of the dye was passed through an alumina column, only one band of brown-red color was obtained. Even after development with a large amount of solvent, there was only one band. By repeated chromatographic separations, however, the two forms were obtained in pure states. Since the dye melts with decomposition, the conversion of the low-melting form of the dye to the high-melting one is not complete, and on slow heating, only a partial conversion resulted. However, when the compound was inserted into an oil-bath at 180–190°, it melted and then resolidified and remelted at 218° (dec.). In this way, the interconversion is achieved before decomposition. Similarly the dye, after melting at 218°, partly solidified on cooling, and on reheating melted at 218°. It seems, therefore, that the dye exists in two forms.

It has been well established that there are different kinds of isomerism, which can be shown by an azo dye. Cis-trans- (12), phototropic- (13), and chromoisomerism (14) are the three important types. The phototropic behavior is exhibited by dyes in solution, and the change in color on exposure to light is supposed to be due to conversion into a photomeric condition (13). The third type supposedly is due to a change in the molecular aggregation, which has also been attributed to the possibility of hydrogen bonding (14).

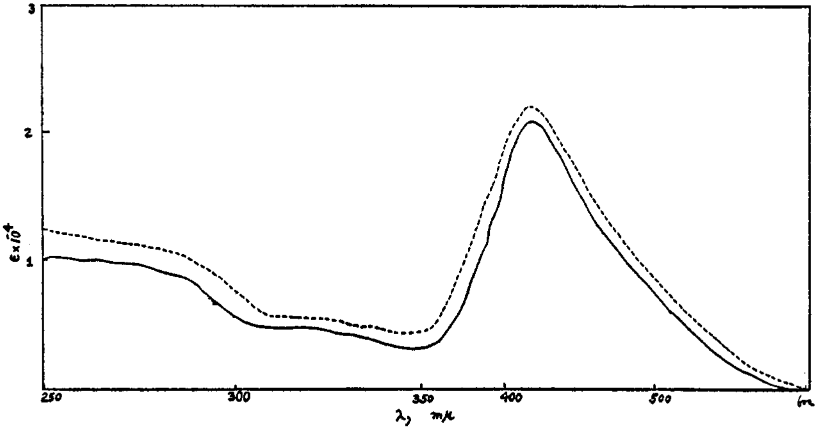


FIG. 1. ULTRAVIOLET AND VISIBLE SPECTRA OF THE AZO DYE I IN CHLOROFORM. ------------ Form (I) of m.p. 169–170°; ———— Form (II) of m.p. 218°

In the present dye (I), since there are substituents in three of the four positions *ortho* to the azo linkage, it is improbable that the *cis* form of the dye will be stable (15). Furthermore, in such a configuration there will be crowding of the *ortho* substituents, and as a result the dye molecule may be forced to deviate from coplanarity. Such a situation would cause a greater bathochromic effect on the color of the dye in this form (16). However, there is very little difference in the color of the dye in the two forms. Also, the examination of the absorption spectra of the two forms of the dye (I) indicated no evidence of any geometric difference in the molecule of the dye in these two forms. Both the curves were similar, and the maxima and minima in the curves were at the identical wave

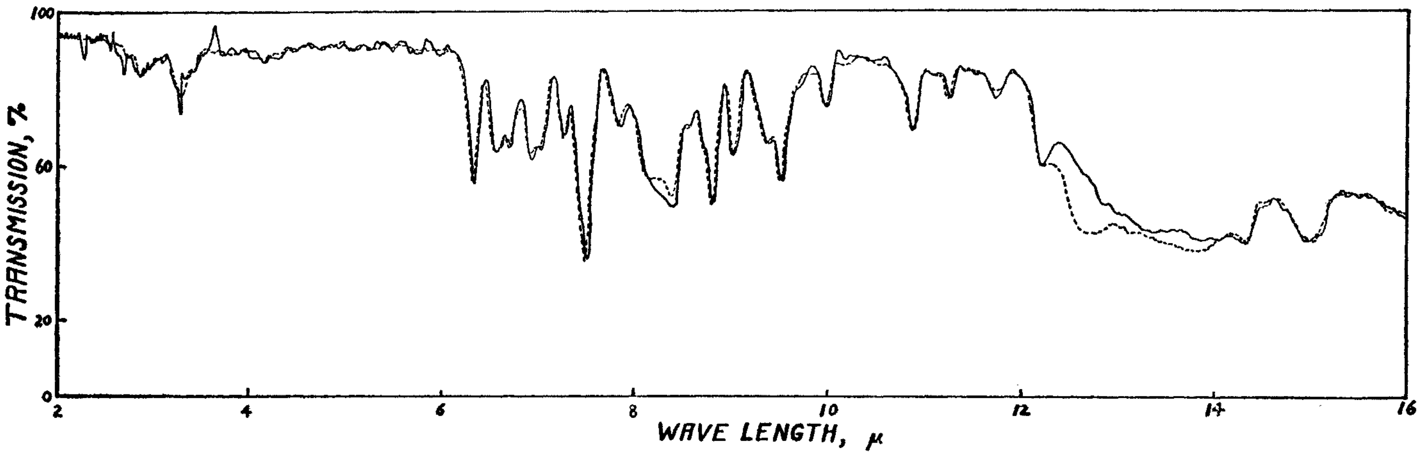


FIG. 2. INFRARED SPECTRA OF THE AZO DYE I IN CHLOROFORM. ------------ Form (I) of m.p. 169–170°; ———— Form (II) of m.p. 218°

lengths. Therefore it seems that these two forms are probably chromoisomeric or polymorphic.

The dyeing properties of the dyes will be reported elsewhere.

EXPERIMENTAL

m-Trimethylsilyl-N,N-bis(β-hydroxyethyl)aniline. To a solution of 13.0 g. (0.05 mole) of *m*-bromo-N,N-bis(β-hydroxyethyl)aniline in 75 ml. of ether there was added 0.15 mole of *n*-butyllithium in 100 ml. of ether at −20° (external), and the mixture was stirred for one hour, allowing the temperature to rise gradually to that of the room. The mixture was stirred for an additional 15 minutes. Color Test I (17) was positive, and Color Test IIA (18) was almost negative. To the resulting organolithium compound was added a solution of 7 g. (0.068 mole) of trimethylchlorosilane in 50 ml. of ether, and the mixture was stirred for one hour at room temperature. The product was hydrolyzed by pouring into ice-cold dilute hydrochloric acid. The ether layer was extracted with dilute hydrochloric acid, and the extracts were added to the aqueous layer. The combined aqueous layers were made basic by adding sodium carbonate. The oily product, which separated, was extracted with ether. On removing ether by distillation, 11 g. (87%) of oily residue was obtained. When attempts were made to purify the product by distillation, a thick jelly was obtained. However, the compound solidified on cooling by Dry Ice. The product was washed with petroleum ether (b.p., 30–40°) to remove the contaminating oily impurities, and then it was crystallized from petroleum ether (b.p., 60–70°). The product, 6.5 g. (51.4%), melted at 60–65°. After repeated crystallizations, the pure compound melted at 67–68°. The compound develops a pale blue color when exposed to the atmosphere for a long time.

Anal. Calc'd for $C_{13}H_{18}NO_2Si$: N, 5.54; Si, 11.08. Found: N, 5.72, 5.80.

Since the amount of the pure analytical sample of the compound was very small, the silicon analysis of the compound by the macro (19), or Parr bomb method could not be done, and the micro analytical sulfuric acid method (20) gave low results (8.48%) due to the presence of a trimethylsilyl group in the molecule of the compound.

m-Triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline. To a solution of 13.0 g. (0.05 mole) of *m*-bromo-N,N-bis(β-hydroxyethyl)aniline in 100 ml. of ether there was added 0.148 mole of *n*-butyllithium in 100 ml. of ether, keeping the temperature of the reaction mixture below −20°. The mixture was stirred for 30 minutes. Color Test I was positive, and Color Test IIA was almost negative. The mixture was stirred for one-half hour more, and to it was added a solution of triphenylchlorosilane, 12.0 g. (0.041 mole), in 100 ml. of ether. The temperature of the reaction mixture was allowed to rise gradually to that of the room, and the mixture was stirred for four hours. The product was poured into 10% hydrochloric acid. The compound, which was contaminated with a polymeric oily substance, was collected and was crystallized from dilute acetone. The air-dried product (15 g.) was crystallized from methanol. The pure product, 3 g. (13.7%), melted at 127°. From the mother liquors there was recovered 5 g. of the product, making a total yield of 8 g. (36.5%). On exposure to the atmosphere, the compound developed a pale blue color.

Anal. Calc'd for $C_{28}H_{29}NO_2Si$: Si, 6.38. Found: Si, 6.45, 6.40.

Preparation of the dyes. The dyes were prepared by coupling diazonium salts with the silicon compounds in acetic acid solution. The amines were diazotized by standard procedures (1) and after proper dilution, were added through filter paper to the ice-cold solution of the silicon compounds in acetic acid (in the case of triphenylchlorosilane, an acetic acid-ethanol mixture was used as a solvent to get a clear solution of the compound). After stirring for about one-half hour, the mineral acid present in the reaction mixture was neutralized with solid sodium acetate; and after stirring for a few minutes more, the mixture was diluted with water. The dilution of the reaction mixture was necessary as it was found that, on long standing, the dyes are partly decomposed in acetic acid. The dyes were collected and purified by chromatographic separation, followed by crystallization from appropriate solvents.

TABLE I

Silicon-Containing Azo Dyes. II

No.	DIAZO COMPONENT, ANILINE DERIVATIVE	COLOR OF DYE	M.P.,[a] °C. (UNCORR.)	YIELD, %	FORMULA	ANALYSIS			
						Si[b]		N	
						Calc'd	Found	Calc'd	Found
	COUPLER: *m*-TRIPHENYLSILYL-N,N-BIS (β-HYDROXYETHYL) ANILINE								
1	4-Nitro-	Brown-red	178–179[c]	50	$C_{34}H_{32}N_4O_4Si$	4.76	5.04	9.52	9.76
2	2-Chloro-4-nitro-	Bordeaux	189–190[c]	50	$C_{34}H_{31}ClN_4O_4Si$	4.50	4.58	9.00	8.74
3	2,6-Dichloro-4-nitro-	Brown-red I	169–170[d]	57	$C_{34}H_{30}Cl_2N_4O_4Si$	4.26	4.33	8.52	8.66
		II	218[c] (dec.)			—	4.28	—	8.61
4	2-Methylsulfonyl-4-nitro-	Blue-violet	209–210[e]	25	$C_{35}H_{34}N_4O_6SSi$	4.21	4.50	8.42	8.51
5	2,4-Bis(methylsulfonyl)-	Dark-red	211–212[c]	20	$C_{36}H_{37}N_3O_6S_2Si$	4.06	4.32	6.10	6.32
	COUPLER: *m*-TRIMETHYLSILYL-N,N-BIS (β-HYDROXYETHYL) ANILINE								
6	4-Nitro-	Brown-red	165–167[c, e]	50	$C_{19}H_{26}N_4O_4Si$	6.97	6.63[f]	—	—
7	2-Chloro-4-nitro-	Blue-violet	158–159[c]	60	$C_{19}H_{25}ClN_4O_4Si$	6.42	6.53	12.84	13.02
8	2,4-Dichloro-4-nitro-	Brown-red	163–164[c]	60	$C_{19}H_{24}Cl_2N_4O_4Si$	5.95	6.17	11.90	11.92
9	2-Trifluoromethyl-4-nitro-	Blue-violet	158–159[e]	50	$C_{20}H_{25}F_3N_4O_4Si$	—	—	11.93	12.42 12.63
10	2-Methylsulfonyl-4-nitro-	Blue-violet	195–197[c]	52	$C_{20}H_{28}N_4O_6SSi$	5.84	6.06	11.67	11.70
11	2,4-Bis(methylsulfonyl)-	Brown-red	164–165[c]	34	$C_{21}H_{31}N_3O_6S_2Si$	5.45	5.66	8.19	8.52

[a] Most of the dyes sinter 2–3° before melting. [b] Silicon analysis of the dyes was done by the microanalytical sulfuric acid fusion method (20). [c] Crystallized from dilute ethanol. [d] Crystallized from chloroform. [e] Crystallized from benzene. [f] Even after repeated crystallization, the compound was not obtained in an analytically pure state. [g] The compound gave high values for nitrogen, although it was purified by chromatographic separations and several crystallizations.

In some cases the dyes could not be obtained in an analytically pure state, even after these procedures. The dyes are soluble in most of the organic solvents. Ethanol or benzene was found to be a convenient solvent for crystallization.

The yields and properties of the compounds are reported in Table I.

N,N-Bis(β-hydroxyethyl)-m-triphenylsilyl-p-(2,6-dichloro-4-nitrophenylazo)aniline. To a solution of 2.19 g. (0.005 mole) of *m*-triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline in 100 ml. of glacial acetic acid and 50 ml. of ethanol there was added an aqueous solution of 2,6-dichloro-4-nitrobenzene diazonium sulfate, prepared by the nitrosyl sulfuric acid method (21). The brown-red mixture was stirred for one-half hour. Solid sodium acetate was added to neutralize the excess of mineral acid. The product was stirred for 15 minutes more, and the brown-red dye was collected, 2.7 g. (82.3%). It melted over the range of 150–180°. It was purified chromatographically. The dye obtained from the earlier fractions was crystallized from chloroform. The pure dye melted at 169–170° (dec.); on rapid heating it melted, solidified, and remelted at 218°. The dye obtained from the later fractions melted at 218°.

Form I, m.p. 169–170°

Anal. Calc'd for $C_{34}H_{30}Cl_2N_4O_4Si$: N, 8.52; Si, 4.26.

Found: N, 8.66; Si, 4.33.

Form II, m.p. 218°

Found: N, 8.61; Si, 4.28.

Chromatographic fractionation of the azo dye (I). A solution of 2.8 g. of the crude azo dye in 150 ml. of chloroform was poured onto a column of 35 g. of alumina (24 × 1½ cm.). There was only one band of brown-red color. Even after irradiating the solution by a mercury vapor lamp, at a distance of 12 inches, for about 30 minutes but one band was observed. The column was eluted with chloroform, and the colored filtrate was collected in eight fractions. The substance (1.6 g., 57%) from the first five fractions started sintering at 160°, became dark red in color and melted at 166–168° (dec.). The next two fractions, which were collected by eluting the column with chloroform containing methanol (5%), gave a substance (0.2 g.) melting at 166–167° (dec.). The substance (1.6 g.) obtained from the first five fractions was dissolved in 100 ml. of chloroform and again poured onto an alumina column (24 × 1½ cm.). The column was eluted with chloroform, and the colored filtrate was collected in 12 fractions, 20–30 ml. each. The first three fractions contained impurities melting over the range 130–160°. The substance obtained from the other fractions softened at 165–170°, with a change in color from brown-red to dark-red, and melted at 218°. Only the substance (300 mg.) from the 11th fraction melted at 168–169°. This was dissolved in 100 ml. of chloroform, and the solution was passed through an alumina column (17 × 1 cm.), and the column was eluted with chloroform. The substance (210 mg.) obtained from the first four fractions changed its color, softened at 168–170°, resolidified partly, and melted at 216–218°. The substance obtained from the last three fractions melted at 218°. The substance melting at 168–170° was crystallized from chloroform. The dark-red small square plates melted at 169–170° (dec.), and when inserted into an oil-bath at 180–190°, melted, solidified, and remelted at 218°. A portion of it when crystallized from ethanol melted at 218°. The product melting at 218°, when crystallized from ethanol, gave orange-red colored plates melting at 218°. Both of the pure compounds were analyzed for nitrogen and silicon.

Ultraviolet and visible absorption spectra of the dye (I). A solution of the dye in freshly distilled chloroform was used for the absorption spectra. In order to get optical density from 0–3, a solution of 5×10^{-5} *M* concentration had to be used. A Cary Recording Quartz Spectrophotometer, Model 12, was used to record the spectra of the compound. In each of the spectra there is a sharp high intensity band (422–423 mμ; ϵ, 2.55×10^4), a low intensity band (320 mμ; ϵ, 7×10^3), and a broad band (240–270 mμ; ϵ, 1.3×10^4). The spectra are reported in Fig. 1.

Infrared absorption spectra of the dye (I). The infrared spectra were determined with a Baird Infrared Double Beam Recording Spectrophotometer, Model B, using a sodium chloride prism. The spectra of both of the forms of the dye were taken as a 2.5% solution in pure chloroform, with the same solvent in the reference beam, and are recorded in Fig. 2.

SUMMARY

m-Trimethylsilyl- and *m*-triphenylsilyl-N,N-bis(β-hydroxyethyl)aniline have been prepared.

The synthesis and properties of several azo dyes, prepared by coupling selected diazonium salts with *m*-trimethylsilyl- and *m*-triphenylsilyl-N,N-bis-(β-hydroxyethyl)aniline, have been described.

In the case of the azo dye, N,N-bis-(β-hydroxyethyl)-*m*-triphenylsilyl-*p*-(2,6-dichloro-4-nitro)aniline, two forms have been isolated by chromatographic separation. A study of their absorption spectra has indicated that these two forms are probably polymorphic or chromoisomeric.

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