and $d_{001} = 5.01$ Å. The oxygen atoms are at (000) $(\frac{1}{2}\ \frac{1}{2}\ 0)$, and the lead atoms at $(0\ \frac{1}{2}\ u)$ $(\frac{1}{2}\ 0\ \bar{u})$ with $u = 0.24$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

SCHIFF'S BASES FROM 3,5-DIBROMO-SALICYLALDEHYDE

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An examination of the literature has shown that comparatively few derivatives of dibromo-salicylaldehyde[1] have been prepared, as compared with salicylaldehyde itself, and as the Schiff's bases from the latter compound have in a number of instances shown unusual phototropic and thermotropic properties, the study of aldehydes already under way in this Laboratory has been extended to this field.

Of the fourteen new compounds described in this paper, five appear to exist in two modifications, the properties of which are stated in the experimental section. Some of these may be transformed from one modification to the other by suitable choice of solvents and temperature. None of these Schiff's bases from dibromo-salicylaldehyde shows phototropic properties.

Hantzsch[2] in studying the relation of color to constitution showed that by the introduction of halogen atoms in the molecule of salicylaldehyde, the tendency of the compound to form the yellow quinoid derivative is strengthened. Monobromo- and dibromo-salicylaldehyde give colorless solutions in non-dissociating solvents, but in water they form yellow solutions. In alcohol the color is weak, but distinctly yellow. The salts are bright yellow, not only the sodium and potassium but also the ammonium salts. The ammonium salt is more stable than that of salicylaldehyde, but decomposes on heating. It may be recrystallized from alcohol or ether. Hantzsch also stated that two forms of a salt may be expected only when the tautomeric forms are of nearly equal strength or of equal weakness as to acidity. An example is salicylaldehyde; this aldehyde-phenol is colorless and its ammonium salts are also colorless; therefore it is a true phenol salt, $C_6H_4ONH_4.CHO$. But a slight change in constitution shifts the equilibrium, for the dibromo-salicylaldehyde forms only yellow salts.

In the case of anils prepared in the present study, the influence of the bromine atoms on this equilibrium is very apparent. While in the forma-

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[1] Werner, *Bull. soc. chim.*, **46**, 277 (1886). Tummeley, *Ann.*, **251**, 174 (1889). Bradley, *Ber.*, **22**, 1135 (1889). Simonis and Wenzel, *Ber.*, **33**, 1964 (1900). Hantzsch, *Ber.*, **39**, 3080 (1906). Wentworth and Brady, *J. Chem. Soc.*, **117**, 1040 (1920).

[2] Hantzsch, *Ber.*, **34**, 882 (1901); *Ber.*, **39**, 3080 (1906); *Ber.*, **43**, 95 (1910).

tion of Schiff's bases of salicylaldehyde the anil of the phenol form is always the first product, which afterwards may be rearranged into the quinoid form or deeply colored derivative,[3] the anils of dibromo-salicylaldehyde give first the deeply colored form, which in some cases may then be changed into the yellow form: Synthesis ⟶ red form $\rightleftharpoons$ yellow form.

The *o*-toluidine derivative of dibromo-salicylaldehyde, first obtained in the red form, on recrystallization from alcohol changes to the yellow modification. The *bis*-*p*-phenylenediamine derivative is red when crystallized from nitrobenzene, but orange from toluene or amyl alcohol. The benzidine derivative when precipitated from alkaline solution is bright yellow, but on standing becomes orange-red. The *p*-bromo-aniline derivative obtained by dilution of the acetic acid solution is pale cream in color, but after ten minutes changes to the orange form. The tolidine derivative when prepared by neutralization of the alcoholic sodium hydroxide solution is yellow but changes on standing to the orange form. The first four mentioned possess thermotropic properties. Senier[4] and his co-workers state that phototropy seems to be inhibited by the entry into the nucleus of various substituents, and the present work confirms this, for none of our derivatives containing bromine in the nucleus was phototropic.

Experimental Part

3,5-Dibromo-salicylaldehyde, $Br_2OH.C_6H_2.CHO$.—This compound was obtained in nearly quantitative yield by dissolving 20 g. of salicylaldehyde in 100 cc. of glacial acetic acid, and adding in small portions a solution of 20 cc. of bromine in 100 cc. of glacial acetic acid. The methods of Heerlein[5] and of Werner[6] were tried but were not as satisfactory as the above method. The pale yellow-green crystals melt sharply without decomposition at 81–82°. They have an aromatic odor, and like salicylaldehyde the compound colors the skin bright yellow. It is readily soluble in ether, benzene, chloroform and hot alcohol. It imparts a yellow color to cold water, and is slightly soluble in boiling water so that it may be purified by distillation with steam. On the addition of sodium hydroxide the brilliant yellow sodium salt separates; it is difficultly soluble in cold water or alcohol but more readily soluble when heated with these solvents.

In one experiment a condensation product was obtained by heating salicylaldehyde with bromine for 24 hours. After extracting the mixture with alcohol, there remained a white granular product which did not melt but decomposed when heated above 250°. It is insoluble in cold or hot alcohol, acetone, ether, benzene, ligroin, carbon tetrachloride or ethyl acetate, but can be purified by crystallization from hot aniline. It is not soluble in aqueous sodium hydroxide, but readily dissolves when alcohol is added to the alkali. The exact experimental conditions for formation of this condensation product are not known, as repeated trials gave only the dibromo-salicylaldehyde.

3,5-Dibromo-salicylidene-aniline, $Br_2.OH.C_6H_2.CH:N.C_6H_5$.—To a solution of 3 g.

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[3] Manchot and Furlong, *Ber.*, **42**, 3030 (1909).

[4] Senier, *J. Chem. Soc.*, **113**, 28 (1918).

[5] Heerlein, *Berz. Jahresber.*, **25**, 486.

[6] Werner, *Bull. soc. chim.*, **46**, 277 (1886). See also Bradley, *Ber.*, **22**, 1135 (1889). Tummeley, *Ann.*, **251**, 170 (1889).

of 3,5-dibromo-salicylaldehyde in 20 cc. of glacial acetic acid, 2 g. of freshly distilled aniline was added. As the mixture cooled, beautiful, transparent, orange-red crystals were obtained, which after repeated recrystallization from alcohol melted at 91°.

Anal. Calc. for $C_{13}H_9ONBr_2$: Br, 45.07. Found: 45.18, 45.19.

The compound is readily soluble in alcohol, benzene, chloroform, ether and ligroin. It is insoluble in cold aqueous sodium hydroxide, but is slowly decomposed on boiling. It is not affected by boiling dil. sulfuric acid. In contact with dry hydrogen chloride the red crystals turn yellow. When the substance is dissolved in benzene and hydrogen chloride added, a yellow precipitate is formed, which returns to orange-red on evaporation.

3,5-Dibromo-salicylidene-*o*-toluidine, $Br_2.OH.C_6H_2CH:N.C_6H_4.CH_3$.—One mole of 3,5-dibromosalicylaldehyde was dissolved in one mole of *o*-toluidine, and the solution heated gently for fifteen minutes. When cold, the product was dissolved in boiling alcohol, from which it crystallized on cooling in orange-red plates. On recrystallization from hot alcohol the pure substance was obtained in the form of orange needles; m. p., 120–121°.

Anal. Calc. for $C_{14}H_{11}ONBr_2$: N, 3.80. Found: 3.48.

It is soluble in alcohol, benzene, chloroform, ether and ligroin. Its solution in amyl alcohol is a deep orange; on evaporation, a reddish film is formed, which becomes much paler on cooling; when this film is recrystallized from alcohol, the pale orange form is obtained, with unchanged melting point.

3,5-Dibromo-salicylidene-*p*-toluidine, $Br_2.OH.C_6H_2CH:N.C_6H_4.CH_3$.—The two compounds were melted together in molecular proportions. Glistening, orange-red needles were obtained from alcohol; m. p., 130°.

Anal. Calc. for $C_{17}H_{11}ONBr_2$: N, 3.80. Found: 3.56.

The compound is readily soluble in alcohol, benzene, ether, chloroform, carbon tetrachloride and difficultly soluble in ligroin.

3,5-Dibromo-salicylidene-α-naphthylamine, $Br_2.OH.C_6H_2.CH:N.C_{10}H_7$.—A mixture of the two compounds in molecular proportions when heated effervesced during the progress of the reaction. When effervescence ceased the liquid was cooled and the yellow residue dissolved in alcohol. As the solution cooled, pale orange-yellow, opaque crystals separated; m. p., 138°. The same product was obtained by dissolving the original materials in glacial acetic acid, or in alcohol, and mixing the cold solutions.

Anal. Calc. for $C_{17}H_{11}ONBr_2$: Br, 39.46. Found: 39.14.

The compound is soluble in alcohol, benzene and ether, but difficultly soluble in ligroin. When the fused mixture was heated for more than ten minutes a second reaction took place; the liquid gave off moisture and frothed, becoming a dark greenish-black. This mass when cool was insoluble in water, acids or alkalies. When warmed with concd. sulfuric acid this second condensation product dissolved readily, giving on dilution a flocculent, maroon-red precipitate.

3,5-Dibromo-salicylidene-β-naphthylamine, $Br_2.OH.C_6H_2CH:N.C_{10}H_7$.—The mixed reaction compounds melted to a clear red liquid when heated together. The residue dissolved readily in an alcoholic solution of sodium hydroxide, and after dilution with water and filtering, the solution was acidified with sulfuric acid, which gave a brilliant, orange-red, flocculent precipitate. This was redissolved in alcoholic sodium hydroxide solution, precipitated, washed and dried at 120°. The light powder sintered at 168° and melted at 171°.

Anal. Calc. for $C_{17}H_{11}ONBr_2$: N, 3.45. Found: 3.20.

It is readily soluble in toluene, difficultly soluble in amyl alcohol, and butanol, from which it crystallizes on cooling. The compound is insoluble in cold aqueous sodium hydroxide, and shows no change when heated to boiling with this solution.

bis-**3,5-Dibromo-salicylidene-*m*-phenylenediamine,** $(Br_2.OH.C_6H_2CH)_2N_2C_6H_4$.—Two molecules of dibromo-salicylaldehyde and one molecule of *m*-phenylenediamine hydrochloride were heated together for fifteen minutes. The mass was extracted with alcohol, and the residue dissolved in boiling nitrobenzene. On recrystallization from nitrobenzene and dilution with an equal volume of alcohol, a voluminous mass of salmon-colored crystals formed. The crystals were filtered, refluxed with alcohol, washed and dried; m. p., 225°.

Anal. Calc. for $C_{20}H_{12}O_2N_2Br_4$: N, 4.40. Found: 4.24.

The compound is very slightly soluble in hot alcohol, carbon tetrachloride, toluene, and insoluble in ether or ligroin. It is difficultly soluble in benzene, chloroform, amyl alcohol or butanol, and crystallizes from these solvents on cooling. It is insoluble in cold aqueous sodium hydroxide, but dissolves slowly when the solution is boiled.

When heated, the compound melts to a red liquid which becomes light yellow as it cools. When the substance is remelted, the color deepens, but always returns to the yellow shade as the compound cools.

bis-**3,5-Dibromo-salicylidene-*p*-phenylenediamine,** $(Br_2.OH.C_6H_2CH)_2N_2C_6H_4$.—The dry solids in the proportion of two molecules of the aldehyde to one of the amine were heated over the free flame for fifteen minutes. A red-black solid remained; this was extracted with alcohol, leaving a flocculent red material which was dried, and dissolved in hot nitrobenzene. As the solution cooled, deep red crystals were formed which were removed, washed with hot alcohol, and recrystallized from nitrobenzene; the process was repeated until two successive crystallizations gave crystals with the same melting point, 310°, with decomposition.

Anal. Calc. for $C_{20}H_{12}O_2N_2Br_4$: Br, 50.58. Found: 50.26.

The red crystals are insoluble in alcohol, carbon tetrachloride and ether. They are very difficultly soluble in benzene, toluene, glacial acetic acid, amyl alcohol and butanol. From toluene and from amyl alcohol solution a light orange substance separates as the solutions cool, instead of the red compound dissolved. It is insoluble in cold aqueous sodium hydroxide.

ORANGE FORM.—On repeated crystallization from nitrobenzene, the color of the compound deepened from bright red to dark red; but on treatment of the deep red substance with hot alcohol, or more quickly when toluene or amyl alcohol was used, the filtrate on cooling deposited a small amount of a yellow compound, which when recrystallized and dried was found to have the same melting point as the red form. However, when this was heated in the melting-point tube the color became deeper so that between 200° and the melting point both forms had the same appearance. When the orange-yellow form is recrystallized from nitrobenzene, the red form is obtained. When the red form is refluxed with toluene or amyl alcohol, and the solution concentrated, the orange-yellow form is produced.

bis-**3,5-Dibromo-salicylidene-benzidine,** $Br_2.OH.C_6H_2CH:N.C_6H_4.C_6H_4.N:CH.C_6H_2.OH.Br_2$.—The dry substances were heated together to 150° for ten minutes and the mixture was allowed to cool slowly. The product was extracted with hot alcohol, and with glacial acetic acid, leaving a finely-divided scarlet powder. It was found to be insoluble in most solvents, except nitrobenzene, and was therefore purified by dissolving it in hot nitrobenzene, and diluting the filtered solution with alcohol, when a fine scarlet, crystalline substance was formed. The crystals turned dark red but did not melt when heated to 300°.

Anal. Calc. for $C_{26}H_{16}O_2N_2Br_4$: N, 3.96. Found: 4.04, 4.24.

The crystalline powder is insoluble in aqueous sodium hydroxide; there is no change when heated to boiling with sodium hydroxide. It is soluble in an alcoholic solution of sodium hydroxide, and on acidification of the solution by hydrochloric acid, a bright yellow precipitate is produced which slowly turns to orange-red on standing. A yellow sulfuric acid solution on dilution gives a voluminous red precipitate.

***bis*-3,5-Dibromosalicylidene-dianisidine,** $Br_2.OH.C_6H_2.CH:N(OCH_3)C_6H_4.C_6H_4(OCH_3)N:CH.C_6H_2.OH.Br_2$.—Upon mixing alcoholic solutions of two molecular proportions of 3,5-dibromo-salicylaldehyde and one of dianisidine, a dark red precipitate appeared. The product was dissolved in hot nitrobenzene, the solution filtered, and the filtrate diluted with three volumes of alcohol. Microscopic, maroon-red, rhomboid crystals were obtained, which melted with decomposition at 305°.

Anal. Calc. for $C_{28}H_{20}O_4N_2Br_4$: Br, 41.62. Found: Br, 41.3.

The compound is insoluble in alcohol, benzene, carbon tetrachloride, acetone, ether, and slightly soluble in glacial acetic acid and butanol. It is soluble in boiling nitrobenzene or aniline, from which it crystallizes on dilution with alcohol. It is not affected by boiling aqueous sodium hydroxide solution. Concd. sulfuric acid gives an orange-yellow solution; when this is poured into a large volume of water a brilliant cherry-red, flocculent precipitate is formed, the color of which gradually deepens.

3,5-Dibromo-salicylidene-*p*-phenylenediamine, $Br_2.OH.C_6H_2CH:NC_6H_4NH_2$.—Molecular proportions of the ingredients were mixed and heated to slightly above the melting point for ten minutes. The filtrate from the alcoholic extract gave fine orange-brown crystals, melting, after recrystallization, at 191°.

Anal. Calc. for $C_{13}H_{10}ON_2Br_2$: N, 7.5. Found: 7.2.

The compound is soluble in alcohol, glacial acetic acid, chloroform, ether, benzene and aqueous sodium hydroxide solution. It is insoluble in ligroin. It is not affected by continued exposure to sunlight.

3,5-Dibromo-salicylidene-*p*-bromo-aniline, $Br_2.OH.C_6H_2CH:N.C_6H_4Br$.—Alcoholic solutions of molecular porportions of the reaction materials described above were heated together to boiling for fifteen minutes. A bright pink, flocculent precipitate was formed, which was filtered off, washed, dried and then recrystallized from carbon tetrachloride. Large glistening leaflets of brilliant crimson color were obtained, but as analyses showed too high a percentage of halogen, repeated crystallization from alcohol was necessary, giving a product which melted without decomposition at 160°.

Anal. Calc. for $C_{13}H_8ONBr_3$: Br, 55.24. Found: 55.45.

The compound is readily soluble in benzene, chloroform, carbon tetrachloride, difficultly soluble in alcohol or ether, and insoluble in ligroin. It is slightly soluble in aqeuous sodium hydroxide; when the solution is warmed it forms a light yellow sodium salt. In glacial acetic acid the compound dissolves readily, and on dilution gives a cream precipitate, which gradually changes to orange on standing for ten minutes. When the latter precipitate is dried and warmed to 120°, the color changes to brilliant crimson but the melting point is unaltered, 160°.

3,5-Dibromo-salicylidene-*p*-phenetidine, $Br_2.OH.C_6H_2CH:NC_6H_4OC_2H_5$.—When the component materials were warmed in alcoholic solution, a bright orange precipitate separated. The residue was purified by repeated crystallization from carbon tetrachloride. The transparent, orange-yellow, rhomboid crystals changed to crimson at about 100°, and melted at 133°.

Anal. Calc. for $C_{15}H_{13}O_2NBr_2$: Br, 40.1. Found: 40.0.

The crystals are readily soluble in benzene, ether, glacial acetic acid and carbon tetrachloride, difficultly soluble in alcohol, and insoluble in ligroin or aqueous sodium hydroxide.

***bis*-3,5-Dibromo-salicylidene-*o*-tolidine** $(Br_2.OH.C_6H_2CH:)_2(N.C_6H_3.CH_3)_2$.—When the reaction materials were mixed in alcoholic solution, an orange-red precipitate appeared, which was filtered, washed repeatedly with hot alcohol, and dissolved in boiling nitrobenzene; the solution was filtered hot, and the clear filtrate allowed to stand overnight, when microscopic, red crystals separated. The scarlet, crystalline product melted sharply at 302° with decomposition.

Anal. Calc. for $C_{28}H_{20}O_2N_2Br_4$: Br, 43.49. Found: 43.2.

This compound is difficultly soluble in benzene, carbon tetrachloride, chloroform, glacial acetic acid and ether, but insoluble in acetone, ligroin, alcohol or aqueous sodium hydroxide. It is readily soluble in alcoholic sodium hydroxide; on neutralization a yellow precipitate is formed which turns red in a few minutes.

3,5-Dibromo-salicylaldehyde-*p*-bromophenylhydrazone, $Br_2.OH.C_6H_2CH:N.NH.C_6H_4Br_3$.—To an alcoholic solution of dibromo-salicylaldehyde was added in molecular proportions *p*-bromophenylhydrazine hydrochloride and sodium hydroxide. The solution became warm and a fine, light yellow, amorphous precipitate separated, which was washed with alcohol, dried and recrystallized from boiling nitrobenzene. As the solution cooled, glistening yellow needles formed, and were filtered off, refluxed with alcohol and dried. They melted at 224° with decomposition.

Anal. Calc. for $C_{13}H_9ON_2Br_3$: Br, 53.45. Found: 53.12.

The compound is insoluble in aqueous sodium hydroxide solution; even on continued boiling only a very small proportion dissolved, although the solution was colored slightly yellow.

Summary

1. Of a series of Schiff's bases prepared from 3,5-dibromo-salicylaldehyde, five appear to exist in two forms.

2. The deeply colored form is produced by direct synthesis, and afterwards may be converted into the light colored form.

3. Four of these Schiff's bases are thermotropic, but none of them appears to have phototropic properties.

4. The substitution of bromine in the salicylaldehyde nucleus favors the formation of the deeply colored form, in agreement with Hantzsch's views of tautomeric equilibrium.

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