the expected dithiobiuret (IV). These were crystallized from ethanol. The results of these experiments are tabulated in Table III.

(II) Reduction of 3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines (V) by Ethanolic Ammoniacal Hydrogen Sulfide. The dithiazolidines were dissolved in hot ethanolic ammoniacal hydrogen sulfide solution, and a stream of hydrogen sulfide was passed through the solution for 3 h. The clear solution on dilution with water or acidification afforded the related dithiobiurets. These were crystallized from ethanol (Table III).

The identity of each product was established by mixture melting point technique with the authentic sample obtained by conventional reduction of the isodithiobiurets described in Table III and by identical IR spectra.

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Synthesis of Some Bromine-Containing 2,4-Diaminotriazines

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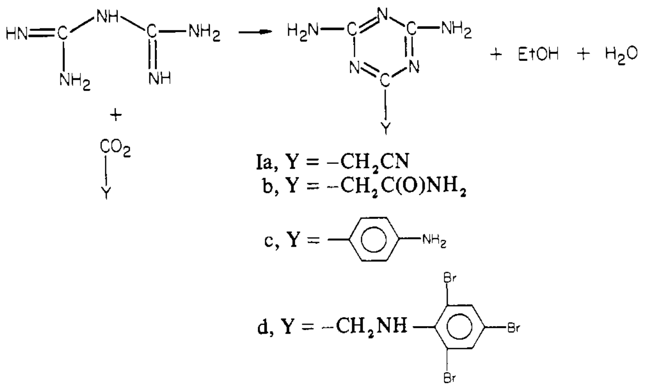
2,4-Diamino-1,3,5-triazines substituted in the 6-position with cyanomethyl (Ia), carbamoylmethyl (Ib), and 4-aminophenyl (Ic) groups were prepared by the reaction of the appropriate esters with biguanide and brominated in aqueous media to the dibromides IIa–c. The triazine Id, substituted in the 6-position with a 2,4,6-tribromoanilinomethyl group, was prepared by the reaction of biguanide with ethyl *N*-(2,4,6-tribromophenyl)glycinate (IV). The latter was prepared by the bromination of ethyl *N*-phenylglycinate in a mixture of water and acetic acid. *N*-(2,4,6-Tribromophenyl)glycinamide (V) was prepared by the reaction of IV with alcoholic ammonia. 2,4-Bis[bis(hydroxymethyl)amino]-6-(3,5-dibromo-4′-aminophenyl)-1,3,5-triazine (III) and 2,4-bis[bis(hydroxymethyl)amino]-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (VI) were prepared by the reaction of IIc and Id, respectively, with aqueous formaldehyde. Some infrared data on the compounds are presented.

While investigating flame retardants for cotton textiles, I prepared some new 2,4-diaminotriazines with groups containing bromine.

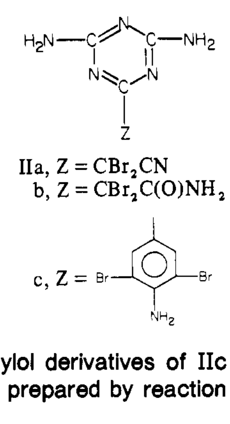
Chance and Timpa reported an example of a brominated diaminotriazine (*1*). They prepared 2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine (DABPT) by the reaction of ethyl γ-tribromobutyrate with biguanide. Ostrogovich reported an analogue of DABPT, 2,4-diamino-6-tribromomethyl-1,3,5-triazine, prepared by direct bromination of 2,4-diamino-6-methyl-1,3,5-triazine (*4*).

In this investigation compounds Ia–d were prepared by the reaction of biguanide with the appropriate ester YCO_2Et, as described by Thurston for compounds Ia (*7a*) and Ic (*7b*).

The ester required for Id, ethyl *N*-(2,4,6-tribromophenyl)glycinate (IV), was prepared by the reaction of ethyl *N*-phenylglycinate with bromine in a mixture of water and acetic acid. IV reacted with ammonia in ethanol solution to form *N*-(2,4,6-tribromophenyl)glycinamide (V). IV hydrolyzed readily in hydrochloric acid to the corresponding acid *N*-(2,4,6-tribromophenyl)glycine, a compound reported in the literature (*5*).



Compounds Ia–c were then allowed to react with bromine in aqueous media to form diaminotriazines IIa–c.



Crystalline methylol derivatives of IIc and Id, III and VI, respectively, were prepared by reaction with aqueous formaldehyde. Elemental analyses showed that the products were both tetramethylol derivatives.

Compounds Ib,d, IIa–c, III, IV, V, and VI are new compounds.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses (C, H, N, Br) in agreement with theoretical values were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Biguanide was prepared fresh by refluxing anhydrous biguanide sulfate in a methanol solution of freshly prepared sodium methylate (*6*). The biguanide was used in solution as prepared for all of the reactions. Because sodium sulfate formed in the preparation did not interfere with subsequent reactions, it was not necessary to separate if from the biguanide. Ethyl malonyl chloride was prepared from diethyl malonate by the monopotassium salt of the half ester (*2, 3*) and converted to ethyl malonamate with anhydrous ammonia in ice-cold ether.

2,4-Diamino-6-carbamoylmethyl-1,3,5-triazine (Ib). Ethyl malonamate (34.7 g, 0.26 mol) and methanol (100 mL) were placed in a flask equipped with a dropping funnel, a stirrer, and a soda lime trap (to exclude CO_2). The flask was cooled to ~15 °C in an ice–water bath. Freshly prepared biguanide (26.3 g, 0.26 mol, in 250 mL of methanol) was added, with stirring, over 35 min at 15–20 °C. A white precipitate began to form within 8–9 min. The mixture was allowed to stir overnight at room temperature. It was then cooled to 15 °C, and the white precipitate was filtered, washed with cold water to remove sodium sulfate, and finally washed with cold methanol. A crude yield of 32.7 g (76%) was obtained. A pure sample recrystallized from water had a melting point of 295–296 °C (decomp) when placed in a preheated bath at 295 °C. The IR spectrum showed absorption bands at 3472 and 3412 (s, NH), 1650 (s, C=O), 1584–1537 (s, multiple absorption, diaminotriazine), and 825 (s, diaminotriazine) cm^{-1}.

2,4-Diamino-6-(dibromocyanomethyl)-1,3,5-triazine (IIa). Ia (15.0 g, 0.1 mol) and 250 mL of water were placed in a flask equipped with a reflux condenser, a stirrer, and a dropping funnel. Bromine (32.0 g, 0.2 mol) was added dropwise to the resulting slurry with vigorous stirring over 20 min. The mixture was stirred at room temperature for 1.5 h and then placed in a refrigerator overnight. The light-gray precipitate was filtered and washed with cold water. A crude yield of 26 g (83%) was obtained. A pure sample was obtained by dissolving 3 g of IIa in 5 mL of dimethylformamide, filtering, and pouring the solution into 75 mL of water. The resulting precipitate was washed with cold water and finally with cold methanol. The grayish crystals had a melting point of 238–240 °C (decomp) when placed in a bath preheated to 238 °C. The IR spectrum showed absorption bands at 3500 (s, NH), 3430 (s, NH), 3330 (s, NH), 1630 (s, NH), 1580–1460 (s, multiple absorption, diaminotriazine), 820 (m, diaminotriazine), 640 (w, CBr), 625 (w, CBr), and 565 (s, CBr) cm^{-1}.

2,4-Diamino-6-(dibromocarbamoylmethyl)-1,3,5-triazine (IIb). Ib (16.4 g, 0.1 mol) and 250 mL of water were placed in a flask equipped with a reflux condenser, a stirrer, and a dropping funnel. Bromine (32.0 g, 0.2 mol) was added dropwise over 2.5 h. The temperature reached a maximum of only 30 °C during the addition. The reaction mixture was cooled in ice water, and crystals were filtered. They were washed with ice water, and then with cold methanol. The cream-colored crystals weighed 11.9 g. A second crop of crystals (13.2 g) was obtained by adjusting the pH of the filtrate to 7.1 by adding 29% ammonium hydroxide (25.7 g, 0.44 mol). The total yield of crude IIb was 25.1 g (78%). A purer sample of white crystals was obtained by recrystallization from water. The melting point was 219–220 °C (decomp) when a sample was placed in a bath preheated to ~215 °C. The IR spectrum showed absorption bands at 3475 (m, HN), 3350 (m, NH), 725 (s, C=O), 1575–1465 (v, multiple absorption, diaminotriazine), 810 (m, diaminotriazine), 800 (s, diaminotriazine), 705 (m, CBr), 635 (m, CBr), and 604 (m, CBr) cm^{-1}.

2,4-Diamino-6-(3,5-dibromo-4'-aminophenyl)-1,3,5-triazine (IIc). Ic (10.0 g, 0.05 mol), 150 mL of concentrated hydrochloric acid, and 450 mL of water were placed in a flask equipped with a reflux condenser, at stirrer, and a dropping funnel. Ic was dissolved by heating the stirred mixture to 65 °C on a water bath. Bromine (16.5 g, 0.1 mol) was added dropwise over 10 min. A precipitate began to form as soon as the bromine addition was begun. Heating and stirring at 65 °C was continued for 3 h. The mixture was cooled to room temperature and allowed to stand overnight. After the mixture was cooled in ice water, the crystals were filtered, slurried with cold acetone, and filtered again. The pale-yellow crystals weighed 17.3 g. They were placed in distilled water (450 mL) and adjusted with good stirring to pH 7.8 with concentrated ammonium hydroxide to neutralize any amine hydrochloride salts that may have been present. The resulting thick slurry was filtered, and the precipitate was washed with water and pressed as dry as possible on the filter. After being air dried the cream-colored crystals weighed 15.5 g, a crude yield of 88% of IIc. A pure sample was obtained by dissolving 1.5 g in DMF (5.0 g) a 125 °C. While the solution was kept hot, water (1.2 g) was added dropwise with stirring until a slight turbidity appeared. The white crystals that separated upon cooling were filtered and washed with a DMF/H_2O mixture. They were finally washed with ethanol and dried at 110 °C. The melting point was 289 °C (decomp) when placed in a bath preheated to 289 °C. The IR spectrum showed absorption bands at 3475 (s, NH), 3420 (w, NH), 3315 (s, NH), 1660 (w, NH), 1620 (s, NH), 1810 (s, diaminotriazine), 610 (m, CBr), and 580 (w, CBr) cm^{-1}.

2,4-Bis[bis(hydroxymethyl)amino]-6-(3,5-dibromo-4'-aminophenyl)-1,3,5-triazine(III). IIc (8.0 g, 0.022 mol) and 37% aqueous formaldehyde (110 g) were placed in a flask and adjusted to pH 7.8 by the addition of 5% NaOH (0.7 g). The mixture was refluxed for 20 min. The clear solution was cooled to room temperature and allowed to stand for 3–4 h. The white precipitate obtained was filtered and washed with 25 mL of 37% formaldehyde. It was then slurried with 100 mL of water, filtered, and washed again with 50 mL of water. After being thoroughly air dried, it weighed 8.4 g (89% yield). The crystalline compound had a melting point of 165–166 °C (decomp) when placed in a bath preheated to 165 °C. The IR spectrum had absorption bands at 3335 (s, OH), 1615 (w, NH), 640 (w, CBr), and 600 (w, CBr) cm^{-1}. All bands between 3315 and 3475 cm^{-1} attributed to NH for IIc disappeared for methylolated IIc, except for a weak shoulder at 3420 cm^{-1}.

Ethyl N-(2,4,6-Tribromophenyl)glycinate (IV). Ethyl *N*-phenylglycinate (20.0 g, 0.11 mol), water (500 mL), and acetic acid (100 mL) were placed in a 1-L flask equipped with a reflux condenser, a stirrer, and a dropping funnel. Bromine (52.7 g, 0.33 mol) dissolved in acetic acid (100 mL) was added dropwise with good stirring over 2 h. At first, a viscous material formed and adhered to the walls of the flask. Eventually it solidified. The solid was scraped off the walls as the bromine addition progressed. The mixture was stirred for an additional 2 h. At this point the bromine color had disappeared. The mixture was cooled in ice water. The crude pale-gray crystals were filtered and recrystallized from 500 mL of boiling methanol. The yield was 31.4 g (68.5%) of white needles (mp 81–82 °C). The IR spectrum showed absorption bands at 3320 (w, NH), 1750 (s, C=O), 577 (w, CBr), 555 (w, CBr), and a broad band centered at 528 (w, CBr) cm^{-1}.

IV was readily hydrolyzed to the corresponding acid, *N*-(2,4,6-tribromophenyl)glycine, by refluxing for ~3 h in concentrated hydrochloric acid. The white crystalline product had a melting point of 202–203.5 °C (decomp) (lit. mp 200 °C) (*5*).

***N*-(2,4,6-Tribromophenyl)glycinamide (*V*).** IV (7.5 g, 0.018 mol) and absolute ethanol (300 mL) were placed in a flask and warmed slightly to dissolve all of the crystals. Then the solution was saturated with anhydrous ammonia while the flask was cooled in ice water. White needles separated after the clear solution stood at room temperature for 3 days. The mixture was cooled in ice water, and the crystals were filtered and washed with a small amount of cold ethanol. A second crop of crystals (1.1 g) was obtained by evaporating the filtrate to a volume of 35 mL and cooling in ice water. The total yield was 6.1 g (89%), mp 185–185.5 °C. The IR spectrum showed absorption bands at 3450 (s, NH), 3300 (s, NH), 1674 (s, C═O), 670 (m, CBr), 603 (w, CBr), and 560 (s, CBr) cm^{-1}.

2,4-Diamino-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (Id). Freshly prepared biguanide (6.1 g, 0.06 mol) in methanol (700 mL) was placed in a flask equipped with a stirrer and a soda lime trap to exclude CO_2. IV (25.0 g, 0.06 mol) was added all at once through a powder funnel. After the solution was stirred for 10 min at room temperature, a white precipitate began to form. After being stirred for 7.5 h, the mixture was allowed to stand overnight. The crystals were filtered and washed with fresh methanol. They were then slurried with water (250 mL), filtered again, and washed with methanol. A crude yield of 21.9 g (81%) was obtained. It was recrystallized by dissolving 21.8 g in 80 mL of hot DMF (125 °C) and then adding 9 mL of water dropwise. When the solution cooled, white crystals separated. A second crop of crystals was obtained from the filtrate. The total recovery was 15.5 g, a yield of 57% based on the theoretical yield of 27.2 g. An analytical sample with a melting point of 250–251 °C was obtained by recrystallizing again from hot DMF and finally washing with cold methanol. The IR spectrum showed absorption bands at 3470 and 3450 (s, doublet, NH), 3320 and 3300 (m, doublet, NH), 1655 and 1633 (s, doublet, NH), 605 (w, CBr), 582 (w, CBr), and 535 (s, CBr) cm^{-1}.

2,4-Bis[bis(hydroxymethyl)amino]-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (VI). Id (25.0 g, 0.055 mol) and 37% aqueous formaldehyde (250 mL) were placed in a 500-mL flask and adjusted to pH 9.2 by the addition of 10 drops of 25% NaOH. It was refluxed for 10 min with stirring. During the reflux period, 4 drops more of 25% NaOH were added. After the solution was cooled to room temperature, the pH was readjusted to 9.1 by adding 4 drops more of 25% NaOH. A white precipitate formed as the mixture cooled. After several hours the mixture was cooled in ice water and diluted with ice water to a volume of ~600 mL to complete precipitation. It was filtered, and the precipitate was slurried with cold water, filtered again, and washed on the filter with more cold water. After being thoroughly air dried, the white crystals weighed 30.3 g (96% yield, mp 137-138 °C (decomp). The IR spectrum showed a broad absorption band at 3320 (s, OH), and bands at 665 (w, CBr), 640 (w, CBr), and 620 (w, CBr) cm^{-1}. All of the bands attributed to NH for Id disappeared for methylolated Id.

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Preparation and Chromogenic Properties of Semicarbazones Containing the Ferroin Group

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The syntheses of a series of semicarbazones containing the ferroin group and their chromogenic reactions with iron, copper, cobalt, and nickel ions are described.

In search of new reagents for spectrophotometric determinations of trace metal ions, eleven semicarbazones, all containing the ferroin group $-\mathrm{N}{=}\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}{=}\mathrm{N}-$, were prepared and tested for chromogenic properties in reactions with iron(II), copper(I), cobalt(II), and nickel(II). Four of these (*1–4*) have already been synthesized, but none has been evaluated previously as a chromogenic reagent. The semicarbazones are identified in Table I.

Experimental Section

A mixture of 0.006 mol each of semicarbazide hydrochloride and aldehyde or ketone was treated with 7 mL of 1 M sodium acetate. After heating 30 min on the steam bath, the mixture was cooled, and the precipitate removed by filtration and crystallized from the solvent indicated in Table I.

To test for chromogenic properties as a function of pH, we prepared 0.01 M solutions of the semicarbazones in ethanol and added them to 0.002 M test metal ion solutions, adjusted to known pH values with appropriate buffers. The iron(II) and copper(I) oxidation states were attained by addition of ascorbic acid as reductant. All other reagents, standard solutions, and

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