by the thermal depolymerization of potato starch. The dextrin comprises approximately 65% of the total dextrin content of the corn seedlings. Since the dextrin belongs to the starch dextrin series, it appears probable that it is a polysaccharide substance used in the respiratory process of the seedlings.

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MONOARYLGUANIDINES. II. BENZOXAZOLEGUANIDINE[1]

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Introduction

Since *o*-aminophenol reacts with organic compounds containing the nitrile group to form benzoxazoles,[4] it was thought that this type reaction might be employed as an additional confirmation of the cyanoguanidine formula of dicyandiamide.[5] Dicyandiamide was first prepared by Beilstein and Geuther,[6] and the present name was given to the compound by Haag.[7] In addition to the Bamberger formula three other possible structural configurations have been suggested.[8] The Bamberger α-cyanoguanidine formula, originally suggested with very little substantial proof, is now generally accepted, and probably the most convincing arguments for the correctness of this formula have been advanced by Hale and Vibrans,[9] who reviewed the literature concerning dicyandiamide and studied the product of the reaction between acetylacetone and dicyandiamide. Blair and Braham[10] believe that this structural configuration explains the formation of biguanide and guanidine salts when dicyandiamide is fused

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[1] This paper was presented at the Columbus meeting of the American Chemical Society, April 30–May 4, 1929.

[2] This paper is constructed from part of the thesis submitted by Mr. Kane in partial fulfilment of the requirements for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1928.

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[4] (a) Skraup, *Ann.*, 419, 75 (1919); (b) Wheeler, *Am. Chem. J.*, **17**, 400 (1895).

[5] Suggested by Bamberger, *Ber.*, **16**, 1074 (1883).

[6] Beilstein and Geuther, *Ann.*, **108**, 99 (1858); **123**, 241 (1862).

[7] Haag, *ibid.*, **122**, 22 (1862).

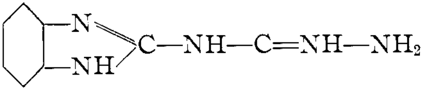
[8] (a) Strecker, "Lehrbuch der Organischen Chemie," 5th ed., p. 637, through Hallwachs, *Ann.*, **153**, 293 (1870); (b) Klason, *J. prakt. Chem.*, [2] **33**, 126 (1886); (c) Pohl, *ibid.*, [2] **77**, 533 (1908).

[9] Hale and Vibrans, This Journal, **40**, 1046 (1918).

[10] Blair and Braham, *ibid.*, **44**, 2342 (1922).

with ammonium salts. On the other hand, Werner and Bell[11] have not accepted this formula and more recently Hart,[12] a student of E. C. Franklin, assumed the Pohl β-cyanoguanidine formula in writing the equation for the reduction of dicyandiazide to dicyandiamide.[13]

In addition to the condensation of *o*-aminophenol with a nitrile group, benzoxazoles may be formed by condensation of *o*-aminophenol with a carboxyl group[14] or with an acid amide,[4a] and benzimidazoles may be prepared by substituting *o*-phenylenediamine for *o*-aminophenol. Ziegelbauer[15] and Pellizzari[16] have prepared a compound which they called *o*-phenylenebiguanide by the interaction of *o*-phenylenediamine and dicyandiamide and Pellizzari assigned the formula

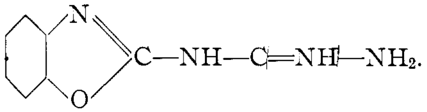


to this compound.[17]

This reaction is of peculiar interest in connection with the present investigation as it also gives simple proof of the presence of the nitrile group in the dicyandiamide molecule.

Reaction between *o*-Aminophenol and Dicyandiamide.—Ammonia is copiously liberated when *o*-aminophenol and dicyandiamide in molecular proportions are fused. When heated under a reflux in an alcoholic solution of hydrochloric acid, they react to form the hydrochloride salt of a new base. This salt may be isolated by crystallization from the alcoholic solution; when dissolved in water and treated with a solution of sodium hydroxide, the free base is obtained. The mother liquor from the original reaction gives ammonia on treatment with an excess of a solution of sodium hydroxide and practically one mole for each mole of reacting substances was obtained. The base was found to have the formula $C_8H_8N_4O{\cdot}H_2O$, and several monobasic salts of $C_8H_8N_4O$ were prepared.

The following evidence is offered as proof that this substance is benzoxazoleguanidine,



(1) The base does not give reactions characteristic of the phenylhydroxy or phenylamino

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[11] Werner and Bell, *J. Chem. Soc.*, **117**, 1133 (1920); **121**, 1790 (1922).

[12] Hart, This Journal, **50**, 1922 (1928).

[13] Attention is called to the possibility of an intramolecular rearrangement to the Bamberger formula in this reaction.

[14] Ladenburg, *Ber.*, **9**, 1524 (1876).

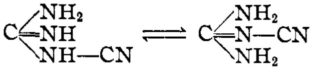
[15] Ziegelbauer, *Monatsh.*, **17**, 653 (1896).

[16] Pellizzari, *Gazz. chim. ital.*, I, **51**, 89, 140 (1921); see *C. A.*, **15**, 3076, 3078 (1921).

[17] The authors of this paper prefer to call the substance benzimidazoleguanidine. The preparation has been repeated in this Laboratory and a new sulfate, $C_8H_9N_5{\cdot}H_2SO_4{\cdot}2H_2O$ has been prepared; H. A. Roth, "Thesis," Polytechnic Institute of Brooklyn, 1928.

groups. (2) A diacetyl derivative has been prepared.[18] (3) A quaternary methyl iodide derivative has been prepared.[19]

This reaction between *o*-aminophenol and dicyandiamide to form benzoxazoleguanidine gives direct positive evidence of the presence of the nitrile group in the dicyandiamide molecule. It also confirms the conclusion of Pellizzari regarding the structure of *o*-phenylenebiguanide (benzimidazolguanidine). All these results may be explained by assuming either the Bamberger or the Pohl formula. It is indeed highly probable that dicyandiamide is a tautomeric compound and, therefore, an equilibrium product which may be represented by the following



$$\mathrm{C}\begin{array}{l}\diagup \mathrm{NH_2}\\ =\mathrm{NH}\\ \diagdown \mathrm{NH{-}CN}\end{array} \rightleftharpoons \mathrm{C}\begin{array}{l}\diagup \mathrm{NH_2}\\ =\mathrm{N{-}CN}\\ \diagdown \mathrm{NH_2}\end{array}$$

The facts here presented are entirely consistent with this view.

Experimental

Crude Benzoxazoleguanidine Hydrochloride.—One hundred grams of *o*-aminophenol[20] was dissolved in a mixture of 100 cc. of concentrated hydrochloric acid and 100 cc. of 95% alcohol and heated to boiling under a reflux for fifteen minutes. Eighty grams of dicyandiamide[21] was added and the heating was continued for two hours. On cooling crystals formed which were separated by filtration and a second crop was secured by concentration of the mother liquor to half volume. The product thus obtained was dark in color and was used for the subsequent preparation of the base; yield, 130 g.

Ammonia Produced in the Reaction.—An aliquot portion of the mother liquor from the above reaction was treated with a concentrated solution of sodium hydroxide and the liberated ammonia was distilled into an excess of standard acid. The ammonia was determined in the usual manner and 91% of the theoretical (corresponding to 1 mole of NH_3 for each mole of dicyandiamide and *o*-aminophenol) was recovered.

Benzoxazoleguanidine Monohydrate (Base).—Fifty grams of crude benzoxazoleguanidine hydrochloride was dissolved in 300 cc. of boiling water and 13 g. of potassium hydroxide dissolved in 50 cc. of water was added. The base precipitated immediately and after cooling was filtered, washed with cold water and dried; yield, 45 g. This procedure gives a product somewhat yellow in color, but purification may be effected by dissolving in hot water, treating with vegetable charcoal and recrystallizing, or by dissolving in alcohol and pouring into a large volume of cold water.

Benzoxazoleguanidine monohydrate forms glistening pearly very pale yellow platelets. It is very soluble in alcohol and sparingly soluble in water. Molecular weight determinations of the dehydrated base in acetone by elevation of the boiling point yielded results varying from 170–180. Neither alcoholic nor aqueous solutions of the base gave

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[18] The fact that a triacetyl derivative could not be prepared may be attributable to steric hindrance due to the electronegative character of the benzoxazole ring. The electronegative character of this compound is demonstrated by its low activity as an accelerator of vulcanization of rubber; Smith and Wise, *Ind. Eng. Chem.*, **20**, 298 (1928).

[19] This reaction is characteristic of benzoxazoles; Fischer, *J. prakt. Chem.*, [2] **73**, 436 (1906).

[20] Practical grade, obtained from the Eastman Kodak Co.

[21] Obtained from the American Cyanamide Co.

any coloration with a solution of ferric chloride, showing thereby the absence of the phenylhydroxy group. Also, an aqueous suspension of lead dioxide in acetic acid gave no color reaction with solutions of benzoxazoleguanidine, indicating the absence of a primary amino group attached to the benzene nucleus. *o*-Aminophenol gave positive color reactions in each case.

Salts of Benzoxazoleguanidine.—Benzoxazoleguanidine nitrate, sulfate, hydrochloride and picrate were prepared by dissolving 10 g. of the base in the least possible amount of boiling water and treating immediately with a slight excess of the respective acid. The salts are all sparingly soluble in water and crystallized when the solutions were cooled. The salts of the strong acids hydrolyzed in aqueous solution and could be titrated with a standard alkali using phenolphthalein as indicator. Analyses recorded with the exception of the nitrate are all gravimetric determinations by standard methods. The analytical and other data for the base and salts are given in the accompanying table.

TABLE I

ANALYTICAL AND OTHER DATA

Compound	Analyses, % Calcd.		Found	Solubility G./100 g. of H_2O	M. p., °C.
Base				0.0303— 15°	182–184
(Monohydrate)	C,	49.40	49.47, 49.30	.0383— 20°	
	H,	5.19	5.19, 5.19	.0821— 30°	
	N,	28.88	29.20, 28.90	.1608— 50°	
	H_2O,	9.30	9.70, 9.80	.3740— 70°	
				1.5677— 90°	
				2.7524—100°	
Hydrochloride	HCl,	17.09	17.10, 17.19	1.6160—20.5°	254–255
Sulfate	H_2SO_4,	21.67	22.03, 22.08	0.0918—20.5°	280–281
Nitrate	HNO_3,	26.35	26.34, 26.34	.2405—20.5°	219–220
Picrate	N,	24.10	23.81, 23.90	.0184—20.5°	247–248

Diacetylbenzoxazoleguanidine.—Three grams of benzoxazoleguanidine, dissolved in alcohol, was heated with 15 g. of acetic anhydride for forty minutes. The solution was cooled and then poured into cold water and diacetylbenzoxazoleguanidine precipitated; m. p. 209–210°.

Anal. Subs., 0.5000, 0.5000: 7.81, 7.70 cc. of 1.0 N HCl. Calcd.: N, 21.54. Found: N, 21.87, 21.54.

Iodide of Quaternary Methylbenzoxazoleguanidine.—Benzoxazoleguanidine was heated with an excess of methyl iodide under a reflux for four hours. Alcohol was added to form a clear solution and the heating was continued for three hours. The solution was cooled and poured into ether and a crystalline product precipitated; m. p. 192–194°.

Anal. Subs. 0.5000, 0.5000: 15.64, 15.52 cc. of 0.1 N $AgNO_3$. Calcd.: I, 39.90. Found: I, 39.7, 39.4.

Microscopical Notes

Base (Monohydrate).—Recrystallized from hot water, by cooling, or from alcohol by dilution with water, the base gave thin, lath-shaped forms, single or in forked and curving clusters; ends jagged, or rarely oblique, with angles of about 70 or 56°; double refraction strong, with parallel extinction and positive elongation edgewise and flatwise. The index of refraction for vibrations crosswise of the crystals is 1.635; lengthwise of the crystals, 1.495. The axial plane is apparently parallel to the elongation.

Recrystallized from 95% alcohol by evaporation, the crystals are the same phase as above, for they may grow directly on them, with no optical discontinuity; six-sided plates, in coffin shapes or in obtuse-ended forms, are common, together with elongated trapezoidal plates. The angles and optical orientation of these crystals indicate that they are identical with those obtained by recrystallization from water, but with somewhat different "habit." Their plane of symmetry corresponds to the transverse plane of the long lath-shaped forms. The six-sided plates show symmetrical extinction flatwise and edgewise in one position. The other edge view exhibits oblique extinction, about 38°, and since the axial plane is inclined to the plane of the plates in a similar direction, the crystals may be assigned to the monoclinic system. The refractive index for vibrations crosswise of the coffin-shaped forms is 1.495; lengthwise, 1.635. The double refraction is probably positive. When heated dry, the crystals become opaque and melt. The melt supercools markedly but eventually crystallizes. Probably dehydration is not complete by melting without continued heating, since the crystals of the hydrate may grow into the melt.

Hydrochloride.—Recrystallized from hot water by cooling, lath-shaped forms, single or clustered, appear first; some show ends obliquely truncated (60°). Their double refraction is strong, with an extinction of about 25° to the long direction of the plates and nearly parallel to their oblique ends. The axial plane is nearly perpendicular to these end faces and corresponds to the lower refractive index (1.490) for this view of the crystals; the other refractive index is about 1.61. 2 V is large, $r < v$, and the crystals are probably negative. They probably belong to the triclinic system. As crystallization proceeds further, other more complex crystals make their appearance as rhomb-shaped plates, generally rounded, and often with the acute angles truncated. They are not single crystals, but are lamellar aggregates or twins. Their polarization colors are anomalous, and they do not extinguish but change hue when rotated between crossed nicols. Their interference figures are very distinctive and indicative of their composite nature; nearly straight dark bars appear alternately in the two 45° positions, but do not rotate.

Sulfate.—When recrystallized from hot water by cooling, the compound forms radiating clusters of strongly curving delicate plates, and opaque mossy rosets. Crystals formed more slowly are lath-shaped, but with poorly defined end faces. They show oblique extinction, the maximum angle being 25°. Their double refraction is strong, with only positive elongation observed.

Recrystallized from sulfuric acid (about 10%), trichiten rosets appear, and on further concentration, rhomb-shaped plates. Laminated growths are frequent. The trichiten rosets are probably identical with the phase described above, but the rhomb-shaped plates, separating from more concentrated acid, are probably the acid salt. By varying the acid concentration in the drop, either phase can be made to grow at the expense of the other. The acid sulfate crystallizes in tablets with obtusely pointed ends, the terminal angles being about 130°. Actually they are monoclinic prisms flattened in the direction of the C axis, the plane of symmetry being crosswise of the longer tablets and parallel to the acute diagonal of the shorter, rhomb-shaped ones. Multiple lamellar twinning in the basal plane is common but does not appear to alter the symmetry of the crystals as a whole. Birefringence is strong, positive, with 2 V large and $r < v$, or else inclined dispersion. Interference figures show only one of the optic axes, which lie in the plane of symmetry of the crystals with the acute bisectrix inclined to the basal plane of the tablets. The crystals may be assigned to the monoclinic system.

Nitrate.—It recrystallizes from hot water in sheaves and rosets of tiny rounded platelets, strongly birefringent.

Picrate.—Recrystallized from hot water, it gives fine thin blade-like and leafy crystals, strongly birefringent, pleochroic in two shades of yellow. The faces and angles are not well defined.

Summary

The reaction between *o*-aminophenol and dicyandiamide results in the formation of benzoxazoleguanidine. This reaction gives direct proof of the presence of the nitrile group in the dicyandiamide molecule. The properties of a number of derivatives of benzoxazoleguanidine are described.

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