

[CONTRIBUTION NO. 19 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Monoarylguanidines. IV. Benzoselenazoleguanidine^{1,2}

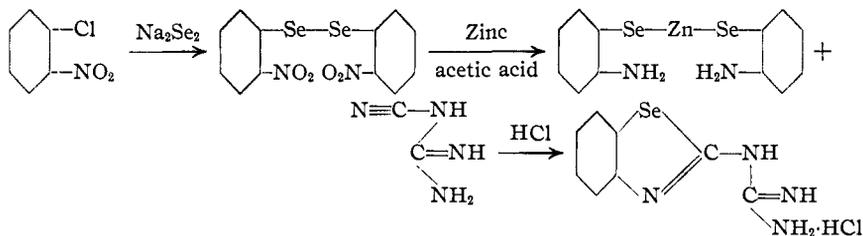
By G. B. L. SMITH, J. P. MIALE AND C. W. MASON³

Introduction

In previous communications^{1b,1c} it has been shown that dicyandiamide reacts with *o*-aminophenol and *o*-aminothiophenol to form benzoxazoleguanidine and benzothiazoleguanidine. Since the analogy existing in organic chemistry between selenium on the one hand, and oxygen and sulfur on the other, is well established for many types of compounds, the preparation of benzoselenazoleguanidine by the analogous reaction of dicyandiamide with *o*-aminoselenophenol should be possible.

This investigation was undertaken in order that the physical, chemical, and pharmacological properties of benzoselenazoleguanidine might be studied and compared with those of the oxy, thio and imide analogs. The present paper describes a further application of the nitrile property of dicyandiamide in its reaction with *o*-aminoselenophenol to form benzoselenazoleguanidine.

Properties of Benzoselenazoleguanidine.—The synthesis of benzoselenazoleguanidine was accomplished through the reaction series



Benzoselenazoleguanidine is a white crystalline solid resembling macroscopically the hydrated needles of benzothiazoleguanidine^{1c} but it is not hydrated. It is only sparingly soluble in water and its aqueous solution is a weak base comparable in strength with the other analogs. This is shown by the potentiometric titration and the fact that the salts of benzoselenazoleguanidine and strong acids may be titrated with a standard solution of sodium hydroxide, using phenolphthalein as indicator.⁴

In another respect the salts are like those of the thio and oxy compounds, the picrate being the least soluble and the hydrochloride the most soluble.

(1) For earlier articles of the series see (a) Smith, *THIS JOURNAL*, **51**, 476 (1929); (b) Smith, Kane, and Mason, *ibid.*, **51**, 2522 (1929); (c) Smith, Mason, and Carroll, *ibid.*, **53**, 4103 (1931).

(2) The substances described were prepared by Mr. Miale and this paper is an abstract of part of the thesis submitted by him in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1932.

(3) Assistant Professor of Chemical Microscopy at Cornell University.

(4) The titration curve will be given in an article on base strength of some arybiguanidines and related compounds soon to be published from this Laboratory.

For the series, the order of solubility of their salts in aqueous solution from most soluble to least soluble is as follows: hydrochloride—thio, seleno, oxy; sulfate—seleno, oxy, thio; nitrate—oxy, thio, seleno; picrate—oxy, seleno, thio; and of the base—thio, oxy, seleno. A comparison of the melting points of the several compounds^{1b,1c} likewise fails to show any strict periodic relationships among them.

Experimental

Materials.—The zinc salt of *o*-aminoselenophenol was prepared by reducing *o*-dinitrodiphenyl diselenide with zinc in a solution of glacial acetic acid.⁵ *o*-Dinitrodiphenyl diselenide was prepared by the method of Bogert and Anderson⁵ as modified by Bogert and Stull,⁶ which consisted of the interaction of sodium diselenide⁷ with *o*-nitrochlorobenzene.⁸

Benzoselenazoguanidine Hydrochloride.—Dicyandiamide (approx. 2 g.) and zinc *o*-aminoselenophenol (approx. 2 g.) were dissolved in 200 ml. of water and heated to boiling under a reflux. A dilute solution of hydrochloric acid was added slowly in very slight excess and the heating was continued for about three hours. There was a slight odor of hydrogen selenide and a small amount of elementary selenium separated. The solution was then filtered and decolorized with Norit, and after making strongly acid with hydrochloric acid (50 ml. of solution and 5 ml. of concd. hydrochloric acid), was allowed to stand for twelve hours. The hydrochloride separated as a white microcrystalline precipitate, which was filtered, washed with alcohol and dried.

Benzoselenazoguanidine (Base).—One gram of benzoselenazoguanidine hydrochloride was dissolved in 20 ml. of hot water and a slight excess of a 20% solution of sodium hydroxide was added. The base separated immediately and was filtered, washed with cold water and dried.

Benzoselenazoguanidine Sulfate, Nitrate and Picrate.—The sulfate, nitrate and picrate were obtained by adding a solution of the respective acid to a solution of benzoselenazoguanidine hydrochloride obtained as described above and in each case an immediate precipitation of the salt resulted. The substances were filtered, washed with cold water and dried. The nitrate and sulfate were white microcrystalline solids and the picrate was yellow. Analytical and other data concerning benzoselenazoguanidine and its salts are given in Table I.

Microscopical Studies

Benzoselenazoguanidine.—As prepared macroscopically there is no evidence of decomposition and coarse prisms, roughened by transverse striations, but otherwise transparent, are observed. When recrystallized from aqueous alcohol either thin plates and skeletal leaflets, or, if cooled very slowly, tabular crystals, rectangular or with terminal angles of about 140°, are formed. These crystals are biaxial and have their axial plane lengthwise, with the acute bisectrix inclined to the principal pinacoidal faces; they are in all probability monoclinic. Double refraction is strong, positive (+), with $2V$ about 30° and $r > v$ very strong. Refractive indices of the pinacoidal views are: vibrations crosswise, 1.780 (± 0.005);

(5) Bogert and Anderson, *Proc. Nat. Acad. Sci.*, **11**, 217 (1925).

(6) Bogert and Stull, *THIS JOURNAL*, **49**, 2011 (1927).

(7) Sodium selenide was purchased from Eimer and Amend.

(8) Purchased from the Eastman Kodak Company.

TABLE I
ANALYTICAL AND OTHER DATA OF BENZOSELENAZOLEGUANIDINE AND ITS SALTS

Compound	M. p., °C.	Calcd.	Analyses, %			Soly. at 20° g./100 g. of H ₂ O	Solubility in non- aqueous solvents
			Found	Found	Found		
Base	193-200	C	40.13	40.08	39.94	0.0134	Insol. CS ₂ , CHCl ₃ , Bz; sol. EtOH, Et ₂ O, acetone
		H	3.34	3.38	3.68		
Nitrate	193-198	C	31.77	31.89		0.0388	Insol. Et ₂ O, Bz, CS ₂ , CHCl ₃ ; sl. sol. EtOH; sol. acetone
		H	3.00	3.26			
		HNO ₃	20.84	20.74			
Hydrochloride	247-249	C	34.81	34.83		1.9114	Insol. CHCl ₃ , Bz; sl. sol. CS ₂ , EtOH, Et ₂ O; sol. acetone
		H	3.29	3.26			
		N	20.30	19.36			
Sulfate	287-289	C	33.29	32.89		0.3891	Insol. Et ₂ O, Bz, CS ₂ , CHCl ₃ ; sl. sol. EtOH, ace- tone
		H	2.95	3.42			
		Se	27.47	27.63	27.50		
Picrate	267-270	C	35.88	35.86		0.0316	Insol. Et ₂ O, CS ₂ , CHCl ₃ ; sl. sol. EtOH, Bz, ace- tone
		H	2.36	2.59			
		N	20.90	20.99			

lengthwise, 1.640 (± 0.005); crystals on edge exhibit another value for vibrations crosswise, 1.9 (est.). From the melt spherulites of fine leaflets are obtained and there is no evidence of decomposition before melting.

Benzoselenazoleguanidine Hydrochloride.—Prisms with numerous lengthwise striations and inclusions are observed in the original sample of the material. On recrystallization from water well-formed prisms (110), of orthorhombic symmetry, with basal (001) and macro (100), pinacoidal faces also prominent are observed. All views give parallel extinction; $Bx_a = C$; axial plane $\perp b$; $2V$ is large, $r > v$, and double refraction negative (-). Refractive indices are $\alpha = 1.580$ (± 0.005); $\beta = 1.785$ (± 0.005); $\gamma = 2.0 +$ (est.). $X = c$, $Y = b$, $Z = a$. From a fused melt there are obtained monoclinic prisms with clinopinacoid, analogous in form to those similarly obtained from benzothiazoleguanidine hydrochloride. They show an extinction angle of about 15° , strong positive (+) double refraction, and Bx_a nearly \perp to (001).

Benzoselenazoleguanidine Sulfate.—The substance appears as thin rectangular plates, usually nearly square, and as platy rosetts. The crystals are uniaxial, optically positive (+) and belong to the tetragonal system. Refractive indices are, $\omega 1.615$ (± 0.005), $\epsilon 1.83 \pm 0.1$.

Benzoselenazoleguanidine Nitrate.—Either as originally prepared or as recrystallized from water, thin prisms are observed. The crystals are of monoclinic symmetry, elongated // c with clinopinacoidal faces prominent; the angle β is about 75° . Views showing parallel extinction have

refractive indices of 1.480 (± 0.005) for vibrations lengthwise and 1.87 (± 0.1) for vibrations crosswise. Views showing oblique extinction have refractive indices of 1.460 (± 0.005) for vibrations 18° to their elongation and 1.81 (± 0.01) for vibrations \perp to this direction. $2V$ is about 60° , and double refraction is negative ($-$). The axial plane is $// b$, with Bx_a visible in end views.

Benzoselenazoleguanidine Picrate.—Yellow needles with faint if any pleochroism appear in recrystallization from water. Extinction is either parallel or about 18° . Refractive indices are: vibration crosswise, *ca.* 1.9; vibrations lengthwise, 1.495 (± 0.005). The crystals are probably monoclinic.

Summary

The benzazoleguanidine series has been extended by the preparation of benzoselenazoleguanidine through the reaction between dicyandiamide and *o*-aminoselenophenol. The base, nitrate, hydrochloride, sulfate and picrate have been isolated and certain physical, chemical and crystallographical properties of these substances have been observed.

BROOKLYN, NEW YORK

RECEIVED MAY 15, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies of Conjugated Systems. XIV. The Preparation and Properties of 1-Phenyl-4-aminobutadiene and 1-Phenyl-4-anilidobutadiene

BY IRVING E. MUSKAT AND LOREN B. GRIMSLEY

The characteristic properties and addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. One of the objects of this investigation was to throw some light on the mechanism of substitution and directive influence in the aromatic series. Some of the addition reactions of butadiene, phenylbutadiene, carboxybutadiene, chloro- and bromobutadiene have already been studied and a theory has been developed¹ which explains these addition reactions without recourse to any special hypothesis of conjugation. In this paper we shall present the results of an investigation on the preparation and properties of aminobutadiene derivatives.

The aminobutadiene derivatives are the aliphatic analogs of the aromatic amines, such as aniline, diphenylamine and α -naphthylamine. Since the aromatic amines are among the most reactive as well as among the most important of aromatic compounds, a study of the aminobutadiene derivatives may not only throw some light on the reactions of aromatic

(1) Muskat and Northrup, *THIS JOURNAL*, **52**, 4043 (1930).