In this series of 2:1 complexes it is desirable to avoid the use of ethanol as a solvent. Chloroform or petroleum ether is more satisfactory for the isolation of the unstable complexes.

The 2,4,7-trinitrofluorenone complex has been reported previously[8b] but its analysis did not correspond to any simple molar ratio. This conclusion was reached on the basis of several nitrogen analyses at different laboratories, all of which checked but all of which we have found subsequently to be in error. The carbon and hydrogen analyses showed the complex to be a 1:1 combination. *Anal.* Calcd. for $C_{30}H_{17}N_3O_7$: C, 67.8; H, 3.2. Found: C, 68.1; H, 3.5.

3,4-Benzfluorene, III.—An attempted reduction of 3,4-benzfluorenone with phosphorus and iodine in acetic acid resulted in the almost complete recovery of the ketone. It was then successfully reduced by the Huang-Minlon[16] modification of the Wolff-Kishner reaction. A solution of 0.317 g. of the ketone, 0.5 cc. of 85% hydrazine hydrate, 0.4 g. of sodium hydroxide and 25 cc. of ethylene glycol was refluxed for two hours. During this time the yellow solid became red and gradually went into solution; then all the red color disappeared leaving a clear yellow solution. At the end of the two hours, the condenser was removed and the contents boiled in the open until the temperature in the flask was 200°. The condenser was replaced and the solution refluxed two hours, cooled and poured into ice and hydrochloric acid. The precipitate was dried and crystallized from ethanol. The first crop (0.19 g.) separated as nearly colorless plates tinged with a pink color, m.p. 122.6–124.0°. The second crop (0.05 g.) had about the same melting point. On recrystallization of the first crop from benzene–alcohol a small amount of insoluble material was noted and separated. This melted at 241.5–244.0° and was probably the hydrazone of the benzfluorenone. The soluble fraction gave pure 3,4-benzfluorene, m.p. 126.8–127.4°.[17]

The known mono-picrate[17] was obtained from ethanol as fine red needles, m.p. 131.4–132.2°.

The trinitrobenzene complex was obtained from benzene–alcohol as orange-yellow crystals, m.p. 154.2–155.2°. *Anal.* Calcd. for $C_{23}H_{15}N_3O_6$: C, 64.3; H, 3.5. Found: C, 64.5; H, 3.5.

The trinitrofluorenone complex separated from benzene-alcohol as fine, light red needles, m.p. 191.8–192.8°. *Anal.* Calcd. for $C_{30}H_{17}N_3O_7$: C, 68.8; H, 3.2. Found: C, 67.6; H, 2.9.

2-Phenylnaphthalene and its complex with 2 moles of trinitrobenzene has been described previously[8] as has the complex with trinitrofluorenone.[8b]

Summary

The physical properties and ultraviolet absorption spectra of the three benzfluorenes and the three benzfluorenones were determined and significant features discussed. The molecular complexes formed between these compounds and various polynitro compounds were prepared and studied. In nearly all respects the behavior of 1,2- and 2,3-benzfluorene was similar but 3,4-benzfluorene differed from its isomers. It is proposed that the differences stem from the possibility of hydrogen overlap in the 3,4-benzfluorene molecule which may cause it to assume a less planar structure than its isomers.

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[16] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[17] Cook, Dansi, Hewett, Iball, Mayneord and Roe, *J. Chem. Soc.*, 1319 (1935), give the melting point of the hydrocarbon as 124–125° and the melting point of its picrate as 130–131°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

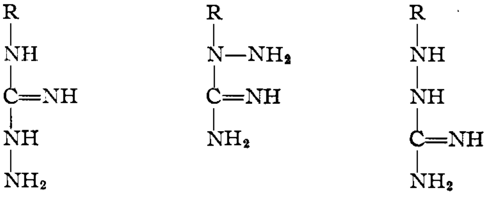
Isomerism of Sulfanilylaminoguanidines[1]

BY ALBERT H. GREER,[1a] DENNIS L. KERTESZ[2] AND G. B. L. SMITH[3]

A sulfanilylaminoguanidine melting at 208–210° was prepared by Winnek, *et al.*,[4] by condensation of N^4-acetylsulfanilyl chloride with S-methylthiourea or with cyanamide, followed by hydrazinolysis or hydrazination and deacetylation. More recently, Owades[5] has obtained the same sulfanilylaminoguanidine by the catalytic hydrogenation of N^4-acetylsulfanilylnitroguanidine and subsequent deacetylation. Prior to this, Kertesz[6] had prepared another sulfanilylaminoguanidine melting at 298–300° by condensing *p*-nitrobenzenesulfonyl chloride with aminoguanidine, and reducing the product by catalytic hydrogenation. We have now prepared a third sulfanilylaminoguanidine melting at 188–190°.

It is evident that three structural isomers of sulfanilylaminoguanidine are possible, as follows

R = sulfanilyl



1-Sulfanilyl-3-aminoguanidine I

1-Sulfanilyl-1-aminoguanidine II

Sulfanilylamidoguanidine III

The above does not include the tautomeric isomers for which formulas can be written. Isomer I has three tautomers, isomer III has two, and isomer II only one.[4]

The present paper describes the preparation

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[1] Abstracted from parts of the theses submitted by Albert H. Greer (M.S. Chem., 1945) and Dennis L. Kertesz (Ph.D., 1941) to the Graduate Faculty of Polytechnic Institute of Brooklyn.

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[4] Winnek, *et al.*, THIS JOURNAL, **64**, 1682 (1942).

[5] J. Owades, M.S. Thesis, Polytechnic Institute of Brooklyn, 1944.

[6] D. Kertesz, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1941.

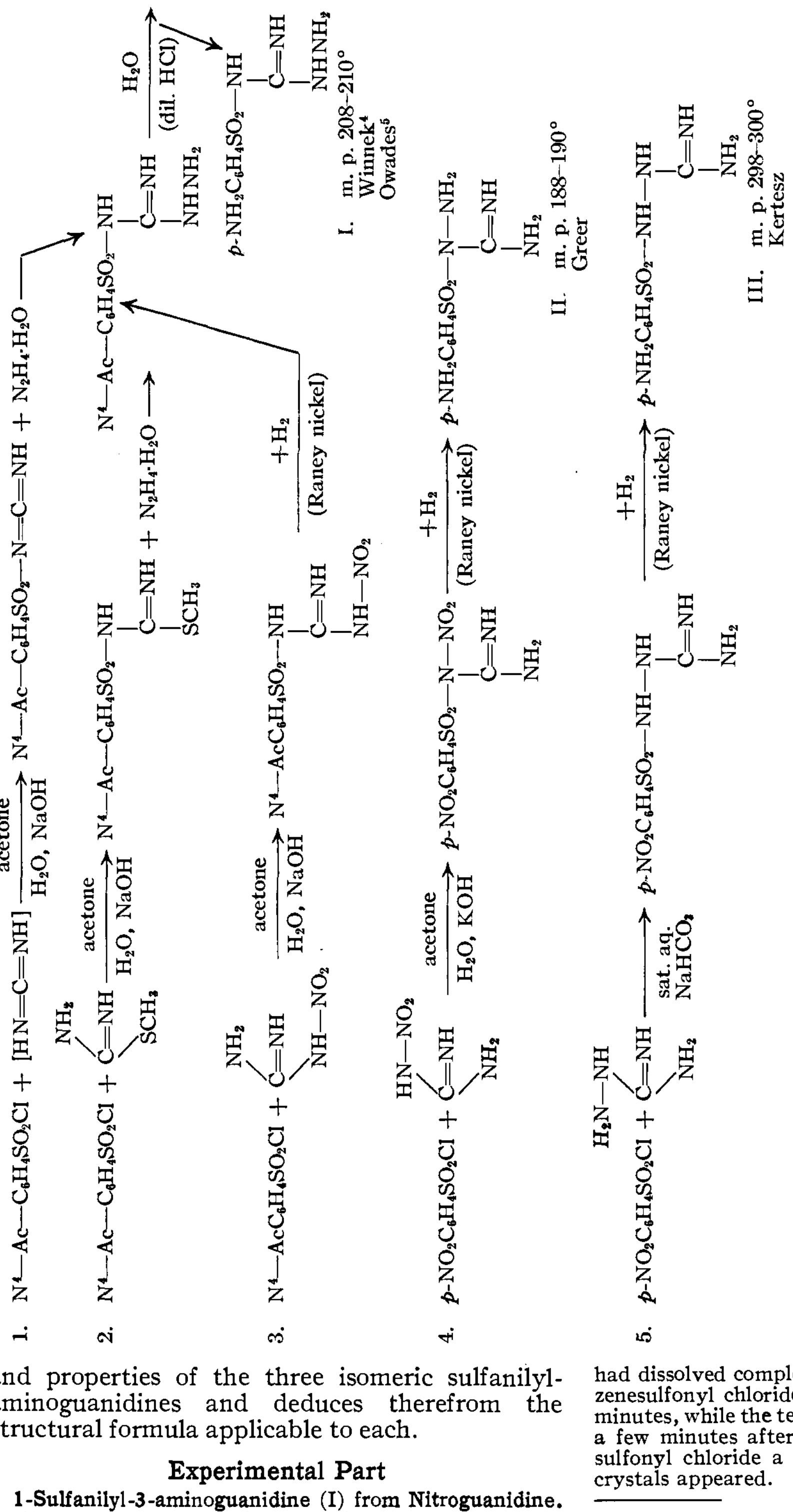

Fig. 1.—Methods of preparation of the sulfanilylaminoguanidines.

and properties of the three isomeric sulfanilylaminoguanidines and deduces therefrom the structural formula applicable to each.

Experimental Part

1-Sulfanilyl-3-aminoguanidine (I) from Nitroguanidine.—Nitroguanidine, 5.2 g. (0.05 mole) was suspended in 60 ml. of acetone, and to this mixture 0.5 g. of potassium hydroxide in 10 ml. of water was added slowly with vigorous stirring. The initial *p*H was approximately 10–11. After the nitroguanidine was dissolved completely, the solution was cooled to 18° and 11 g. (0.05 mole) of N^4-acetylsulfanilyl chloride was added during a period of thirty minutes. The mixture was stirred for three hours at room temperature by which time a voluminous precipitate had formed. Thirty milliliters of water was added, the precipitate was filtered off, washed with cold water and recrystallized from 80% ethanol, to give 2 g. (13%), of colorless crystals, m. p. 195–198°. This 1-N^4-acetylsulfanilyl-3-nitroguanidine (6.0 g., 0.02 mole) in ethanol solution was reduced with hydrogen in the presence of Raney nickel catalyst, the catalyst was removed by filtration, and the 1-N^4-acetyl-sulfanilyl-3-aminoguanidine, obtained by carefully evaporating the solvent, was recrystallized from 70% ethanol; yield, 3.2 g. (57%), m. p. 256–257°. Five grams (0.018 mole) of the acetyl compound was heated for two hours under reflux in a mixture of 30 ml. of ethanol and 5 ml. of 6 *N* hydrochloric acid. On cooling, dilute sodium hydroxide solution was added, I precipitated, was filtered off and recrystallized from ethanol; yield 2.2 g. (53%), m. p. 208–210°.

Isomer I from Aminoguanidine.—Aminoguanidine hydrobromide, 6.2 g. (0.04 mole), was heated in 50 ml. of dry pyridine on a steam-bath. When nearly complete solution had taken place, 9.3 g. (0.04 mole) of N^4-acetylsulfanilyl chloride was added slowly with stirring. After ten additional minutes on the steam-bath, the mixture was cooled for twenty-four hours. A small residue consisting of unreacted aminoguanidine salt was removed by filtration, the filtrate was evaporated to dryness and the residue was recrystallized from a small quantity of 70% ethanol; yield, 1.5 g. (14%), m. p. 256–257°. The material was identical with the intermediate obtained above, and therefore it was not deacetylated.

1-Sulfanilyl-1-aminoguanidine (II).—Nitroguanidine, 13.8 g. (0.12 mole), was suspended in 180 ml. of acetone and to this was added 18.6 g. of potassium hydroxide dissolved in 30 ml. of water. After the nitroguanidine had dissolved completely, 30 g. (0.13 mole) of *p*-nitrobenzenesulfonyl chloride[7] was added during a period of thirty minutes, while the temperature was maintained at 18°. In a few minutes after the last addition of *p*-nitrobenzenesulfonyl chloride a voluminous mass of yellowish-white crystals appeared. After the addition of 50 ml. of water,

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[7] The workers in this Laboratory for many years have prepared *p*-nitrobenzenesulfonylchloride and this substance had a melting point of 67°. Recently, this substance was obtained from Eastman Kodak Company and the melting point was 76°, as most frequently given in the literature. Mixed melting point determination of the two materials gave 76°. Therefore we had been dealing formerly with a thermodynamically less stable polymorph.

the mixture was stirred for three hours at room temperature. The mixture was neutralized with glacial acetic acid; the solid material was removed by filtration and washed with small quantities of water, crystallized four times from 70% ethanol and decolorized with charcoal; yield 18 g. (52%), m. p. 202–203° dec. This 1-*p*-nitrobenzenesulfonyl-1-nitroguanidine in ethanol solution was reduced with hydrogen in the presence of Raney nickel catalyst, using chloroplatinic acid as promotor.[8] After removal of the catalyst, the solvent was evaporated under reduced pressure at 40° to give a light orange oil which crystallized on cooling. The product was dissolved in ethanol, decolorized with carbon, and upon the addition of a small quantity of water, white crystals were formed. Recrystallization from 60% ethanol afforded 8.6 g. (60%) of II, m. p. 188–190°.

Sulfanilylamidoguanidine (III).—Aminoguanidine sulfate ($CN_4H_6 \cdot {}^1/_2H_2SO_4$), 4.92 g. (0.04 mole), dissolved in 20 ml. of water, was added to 100 ml. of a saturated solution of sodium bicarbonate (saturated at 45°), to give a solution of *p*H 8.5. *p*-Nitrobenzenesulfonyl chloride, 5 g. (0.023 mole), was added during a period of thirty minutes to the above solution which had been heated to 55°. The *p*-nitrobenzenesulfonyl chloride dissolved in about two hours and the solution was evaporated to dryness under reduced pressure. The residue was extracted with small portions of hot absolute ethanol first by decantation and finally by repeated washings of the solid material on a Büchner funnel. The alcoholic solution was evaporated under reduced pressure to incipient crystallization and then cooled. The nitro compound was filtered, recrystallized from ethanol, washed with ether and dried over phosphoric anhydride; yield 3 g. (50%), m. p. 298–299° dec. Reduction of this compound by hydrogen in the presence of Raney nickel catalyst yielded 1.7 g. (64%) of III, m. p. 298–300° dec., which was recrystallized from ethanol.

X-Ray Diffraction Measurements.—X-Ray diffraction photographs were taken of the three isomers according to methods outlined by Fankuchen[9] and Buerger.[10] These transmission powder diffraction patterns showed that three distinct crystalline compounds have been formed. Single crystal oscillation patterns about all three axes of the three sets of crystals gave different axial lengths and different cell volumes. The molecular weights were calculated from the cell volumes using the equation.

$$\text{Mol. wt.} = \frac{\text{Volume (Å.}^3) \times \text{density}}{n \times 1.65}$$

where n = number of molecules per unit cell. The density of each set of crystals was determined by the flotation method of solid suspended in a liquid of the same density, Table I.

Isomer I.—The symmetries of the single crystal photographs proved that the crystals must have one of the triclinic symmetries. The space group is therefore P1 or P$\bar{1}$ (C_1^1 or C_i^1). The cell dimensions are d(100) = 9.32 Å., b = 9.75 Å., c = 22.20 Å., volume = 1990 (Å.^{3}). The number of molecules per unit cell is 8.

Isomer II.—The symmetries of the single crystal photographs proved that the crystals must have one of the monoclinic symmetries. The space group is therefore Pm or P2 (C_s^1 or C_2^1). The crystals are elongated with blunt edges and the intermediate refractive index is along the length of the needle axis. The acute bisectrix makes an angle of 14° with the main face of the crystal. The cell dimensions are a = 7.43 Å., b (needle axis) = 5.54 Å., c sine beta = 12.30 Å., volume = 506 (Å.^{3}). The number of molecules per unit cell is 2.

Isomer III.—The symmetries of the single crystal photographs proved that the crystal must have one of the orthorhombic symmetries. The needle crystals had straight extinction and its cross-section contains an angle of 77°. Reflections of the type 0*kl* occur only when *l* is even and reflections of the type *hk*0 occur only when *h* is even. The space group is therefore Pcma or Pc-a (D_{2h}^9 or C_{2v}^8). The cell dimensions are a = 7.85 Å., b = 10.00 Å., c = 24.65 Å., volume = 1934 (Å.)^3. The number of molecules per unit cell is 8.

Discussion

Three sulfanilylaminoguanidines, with the empirical and molecular formula, $C_7H_{11}O_2N_5S$, as shown, respectively, by analyses and X-ray molecular weight determination, have been prepared. That these are indeed three different compounds is demonstrated uniquely by mixed melting points and properties (Table I).

TABLE I

PROPERTIES OF THE THREE ISOMERS

Isomer			I	II	III
M. p.			208–210°[a]	188–190°[a]	298–300° dec.[a]
Density at 20°			1.55	1.52	1.57
Crystal system			Triclinic	Monoclinic	Orthorhombic
Molecules/unit cell			8	2	8
Unit cell vol., cu. Å.			1990	506	1934
Space group			P1 or P$\bar{1}$ C_1^1 or C_i^1	Pm or P2 C_s^1 or C_2^1	Pcma or Pc-a D_{2h}^9 or C_{2v}^8
Molecular weight[b]			232.5	231	230
Hydrazine titration			Quant.	Trace	Negative
Analyses, %[d,e]	Calcd.	C	36.67	36.67	36.67
		H	4.83	4.83	4.83
		S	13.98	13.98	13.98
	Found	C	36.78	37.27	36.60
		H	4.77	4.68	4.77
		S	13.00	13.55	13.40
		N	12.08[c]		

[a] Mixed m. p.: I + II, 130°; I + III, 180°; II + III 250–253°; I + II + III, 245–250°. [b] Calcd. 229. [c] Hydrazine nitrogen. [d] 1-*p*-Nitrobenzenesulfonyl-1-nitroguanidine, $C_7H_7O_6N_5S$; Calcd.: C, 29.06; H, 2.43. Found: C, 28.85; H, 2.59. [e] *p*-Nitrobenzenesulfonylamidoguanidine, $C_7H_9O_4N_5S$: Calcd.: C, 32.42; H, 3.49; S, 12.36; N (total nitrogen) (Dumas), 27.01. Found: C, 32.30; H, 3.40; S, 11.00; N, 26.44.

The structural formula (*vide supra*) applicable to each substance can be deduced from the methods of synthesis. The method of Winnek, *et al.*,[4] can give a compound to which only formula I is applicable. The condensation of N^4-acetylsulfanilyl chloride with either amino- or nitroguanidine gives Winnek's compound and therefore formula I is applicable to the product of these con-

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[8] Lieber and Smith, THIS JOURNAL, **58**, 2170 (1936).

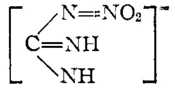
[9] Fankuchen, "Physical Methods of Organic Chemistry," 1st ed., Chapter 14, Interscience Publ., New York, N. Y., 1945, p. 585.

[10] Buerger, "X-Ray Crystallography," 1st ed., John Wiley & Sons, Inc., New York, N. Y., 1942.

densations. Reduction of the condensation product of *p*-nitrobenzenesulfonyl chloride with nitroguanidine gives a different compound and therefore cannot have formula I. The mode of synthesis of this second compound precludes formula III and therefore formula II is applicable. Reduction of the condensation product of *p*-nitrobenzenesulfonyl chloride with aminoguanidine gives still a third compound and hence it is represented by formula III.

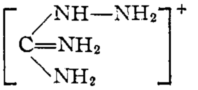
Further evidence for the correctness of the assignment of structural formulas to the three compounds is furnished by two chemical reactions. (1) Determination of hydrazine nitrogen according to the Jamieson method as developed by Smith and Wheat[11] gave a quantitative result in the case of I. For II a slight qualitative reaction was observed which may be attributed to contamination with I. With III no reaction was observed, even when subjected to drastic hydrolytic conditions. (2) When the N^4-acetyl or *p*-nitro intermediates of the three isomers were treated with acidic solution of benzaldehyde only I and II formed benzylidene derivatives. Pellizzari and Cuneo[12] separated two alkylaminoguanidines analogous in structures to II and III by the formation of a benzylidene derivative which formed only with the alkylaminoguanidine corresponding to structure II. It is seen that I and II have a free amino group attached to a nitrogen atom and part of a hydrazine group. In III, however, only an =NH group is present.

The formation of a particular isomer depends upon the *p*H of the medium in which the condensation is effected and also upon the properties of (1) the benzenesulfonyl chloride employed and (2) the compound with which this substance is condensed. When *p*-nitrobenzenesulfonyl chloride is condensed with nitroguanidine, 1-*p*-nitrobenzenesulfonyl-1-nitroguanidine is formed while N^4-acetylsulfanilyl chloride gives 1-N^4-acetylsulfanilyl-3-aminoguanidine. Here the inductive effect of the para-substituent group on the benzene ring may be the determining factor. On the other hand, hydrogen bonding of the nitro group and the (=NH) group may protect the 1- and 2-nitrogen atoms. Further study should prove of interest. The condensation in each case is effected in a very strong alkaline medium (*p*H above 10) and under such conditions the predominating ionic species of nitroguanidine is probably the secondary anion[13]



$$\left[\begin{array}{l}\ \ \diagup N{=}NO_2 \\ C{=}NH \\ \ \ \diagdown NH\end{array}\right]^-$$

Aminoguanidine is a moderately strong to strong base. In weakly acidic or weakly alkaline solution the primary aminoguanidonium ion is the predominating species present



$$\left[\begin{array}{l}\ \ \diagup NH{-}NH_2 \\ C{=}NH_2 \\ \ \ \diagdown NH_2\end{array}\right]^+$$

The nitrogen atoms connected to the carbon atom are blocked by the stability of the aminoguanidonium ion but in this medium the fourth nitrogen is available for condensation. This condensation has been effected only in a saturated solution of sodium bicarbonate. It has also been found that when N^4-acetylsulfanilyl chloride and aminoguanidine are allowed to react in pyridine, condensation is on the 1- or 2-nitrogen atoms resulting in the formation of 1-N^4-acetylsulfanilyl-3-aminoguanidine.

Acknowledgment.—The authors are indebted to Dr. I. Fankuchen of the Polytechnic Institute of Brooklyn for his assistance in the X-ray analysis of this study.

Summary

The three possible structural isomers of sulfanilylaminoguanidine have been prepared. Mixed melting point determinations, characteristic chemical and physical properties, and X-ray diffraction studies have demonstrated conclusively that these are three distinct compounds. On the basis of their modes of formation formulas have been assigned to each compound. The reasons for the formation of each isomer have been discussed.

BROOKLYN, N. Y. RECEIVED[14] APRIL 16, 1949

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[11] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).

[12] Pellizzari and Cuneo, *Gazz. chim. ital.*, **24**, I, 222 (1894).

[13] Hahn, Pribyl, Lieber, Caldwell and Smith, THIS JOURNAL, **66** 1223 (1944).

[14] Original manuscript received December 6, 1946.