type X on alkaline solutions seem to be due to a surface charge on the uppermost monolayer rather than to the presence of dipole molecules within the film. A theory is given for the potential distribution produced by these surface charges and it is shown that with potential gradients of the order of 3×10^6 v./cm. over distances of a few Ångström units the contact potentials can increase at a linear rate of 70 mv. per layer only up to films of a thickness of a few hundred layers.

SCHENECTADY, NEW YORK RECEIVED FEBRUARY 11, 1938

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Trisodium Tricyanmelamine Trihydrate

BY J. L. HOARD

Introduction

Tricyanmelamine or cyanuric tricyanamide, $C_3N_3(NCNH)_3$, belongs to an interesting group of closely related and quite stable compounds which are discussed by Franklin[1] under the heading of ammono polycarbonic acids. Tricyanmelamine is soluble in water, yielding a highly conducting, strongly acid solution; both acid and normal salts are readily prepared. The normal sodium salt, $Na_3C_6N_9 \cdot 3H_2O$, crystallizes from aqueous solution as brilliant, colorless, hexagonal needles with well-defined faces not at all affected by long exposure to the atmosphere. Water of crystallization, indeed, is not lost below 160°. The sodium salt is formed, moreover, by the spontaneous polymerization in aqueous solution of sodium dicyanimide, NaC_2N_3.

The stability and high symmetry of crystals of trisodium tricyanmelamine trihydrate single it out as an appropriate representative for X-ray study of this interesting class of compounds. The crystal structure of this salt and the information obtained therefrom about the structure of the anion are discussed in this paper.

Determination of the Structure

The crystals used in this investigation were obtained from the late Professor E. C. Franklin of Stanford University.[2] A Laue photograph taken with the X-rays passing through a basal section of one of the hexagonal needles, the incident beam being accurately normal to (00·1), showed the six-fold axis and six planes of symmetry of the point-group D_6^h. The character of the face development observed on the ends of a number of the hexagonal needles was, however, in every case only trigonal. D_3^h is indicated unambiguously as the true point-group since it is the only one which can satisfy simultaneously these symmetry conditions.

Oscillation and rotation photographs about the needle axis were prepared using $CuK\alpha$ and $MoK\alpha$ radiation. Layer line spacings lead to $c_0 = 6.56$ Å., equatorial reflections to $a_0 = 10.23$ Å., these values being accurate to within about 0.1%. It was possible, indeed, to index all reflections appearing upon rotation and oscillation photographs upon the basis of this unit, reflections in the equator being observed for values of $2 \sin \theta$ as high as about 1.96 when $CuK\alpha$ was the radiation employed.

The further observation that no reflection of the type $\{mm \cdot l\}$, l odd, appears leads to the unique selection of $D_{3h}^4 - C\bar{6}2c$ as the correct space-group with a high degree of probability. The structure of $Na_3C_6N_9 \cdot 3H_2O$ is then to be based upon the hexagonal unit with $a_0 = 10.23$ Å., $c_0 = 6.56$ Å., containing $2Na_3C_6N_9 \cdot 3H_2O$, space-group $D_{3h}^4 - C\bar{6}2c$.

Chemical evidence indicates that the tricyanmelamine ion, $C_3N_3(NCN)_3^{3-}$, is isoelectronic with the cyanuric triazide molecule. D_{3h}^4 affords positions[3] for carbon and nitrogen atoms which permit of the existence of such anions in the unit cell. The two anions may be considered as centered at positions $2(b)$: $0,0,1/4$; $0,0,3/4$, with a minimum molecular symmetry (C_3^h) consisting in a three-fold axis with a reflection plane perpendicular to it. Structurally speaking, there are two sets of carbon and three sets of nitrogen atoms, each of these be-

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(1) Franklin, "Nitrogen System of Compounds," Am. Chem. Soc. Monograph, Reinhold Publishing Corp., New York, N. Y., 1935, pp. 101–107.

(2) Crystals of this substance were given also by Professor Franklin to Professor Linus Pauling and Dr. J. H. Sturdivant of the California Institute of Technology, and the early stages of the X-ray investigation, leading to an approximate sketch of the correct structure, were duplicated in its essentials by us. Upon discovery of this duplication, Professor Pauling and Dr. Sturdivant very kindly relinquished their claim to the problem.

(3) R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institution of Washington, 2d ed., 1931, pp. 159–160.

ing placed in the positions 6(h): $u,v,1/4$; $v-u,\bar{u},1/4$; $\bar{v},u-v,1/4$; $v,u,3/4$; $\bar{u},v-u,3/4$; $u-v,\bar{v},3/4$. It is necessary also to place $6H_2O$ in 6(h) with a sixth set of parameter values, so that the anions and water molecules pack together in the symmetry planes. The only acceptable positions for sodium ions are those of 6(g): $u,u,0$; $0,\bar{u},0$; $\bar{u},0,0$; $u,u,1/2$; $0,\bar{u},1/2$; $\bar{u},0,1/2$, with u about 0.405. Leaving hydrogen out of consideration, this tentative structure has thirteen parameters to be determined from the intensity data.

Whatever the particular values of the parameters, certain regularities are required in the intensities of reflections appearing on photographs taken with the needle axis as the axis of oscillation if the proper positions have been selected for the various kinds of atoms. For arbitrarily chosen values of h and k, the structure factor for $\{hk{\cdot}l\}$, l odd, is independent of the particular value of l; the structure factor for $\{hk{\cdot}l\}$, $l/4$ integral, is independent of the particular value of l; and the structure factor for $\{hk{\cdot}l\}$, $l/4$ half-integral, is independent of the particular value of l. Again the only difference between the structure factor for $\{hk{\cdot}l\}$, $l/4$ integral and that for the corresponding $\{hk{\cdot}l\}$, $l/4$ half integral lies in a change of phase of 180° between sodium and all other atoms so that the average intensities (considering the structure factor alone) of the layer line reflections with $l = 2$ should be comparable with those for $l = 0$ or $l = 4$. Also the layer with $z = 3/4$ is derived from that with $z = 1/4$ by the operation of a two-fold axis lying in the plane $y = 1/2$ and it follows that layer lines with l odd must be much weaker on the average than those with l even (sodium, of course, not contributing anything to the former). The observed intensity pattern is in agreement apparently with the general relationships stated in this paragraph.

Values can be assigned to twelve of the thirteen parameters so that the anions are of approximately the size and shape which would be expected on the basis of existing data, and so that anions and water molecules pack together to give the type of compact layer illustrated in Fig. 1. Each sodium ion, lying on a two-fold axis between the negatively charged layers, can be assigned a parameter value so as to be octahedrally surrounded by four nitrogen and two oxygen atoms at reasonable distances.

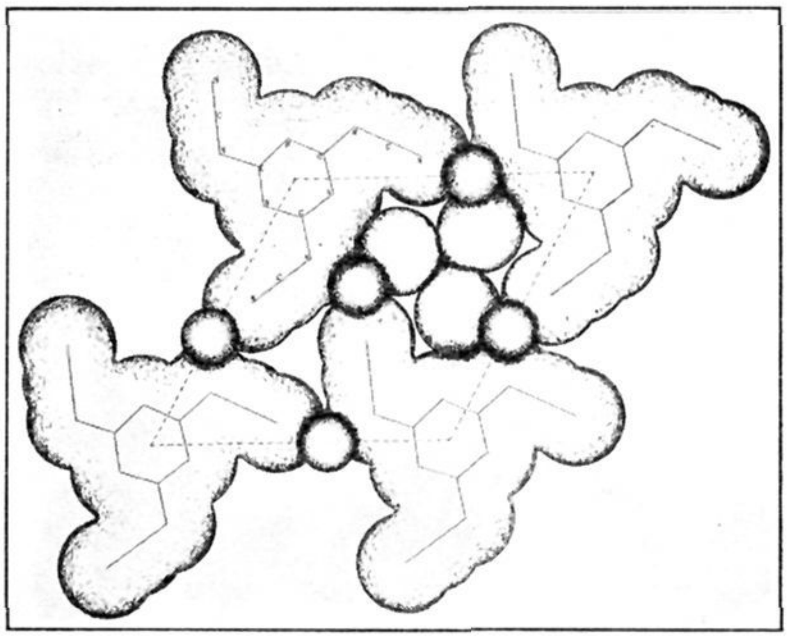

Fig. 1.—A packing diagram of the atomic layer with $z = {}^1/_4$ together with the sodium ions in $z = {}^1/_2$.

That the structure illustrated for this substance in Fig. 1 is essentially correct is shown by a comparison of calculated and observed intensities, which are exhibited in Table I. (All planes in each layer line which might give recordable reflections in the camera are included.) The following formula was employed for calculation

$$I = \text{Constant} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot \left[1 - \left(\frac{\sin \mu}{\sin 2\theta}\right)^2\right]^{-1/2} \cdot |S|^2$$

The parameter values of Fig. 1 are as follows

$C_I : u = 0.145, v = 0.094;$
$C_{II} : u = 0.385, v = 0.135;$
$N_I : u = 0.055, v = 0.154;$
$N_{II} : u = 0.300, v = 0.198;$
$N_{III} : u = 0.463, v = 0.077;$
$O : u = 0.282, v = 0.485;$
$Na : u = 0.405$

The f-values of Pauling and Sherman[4] are employed throughout this paper. The crystal used (with CuKα) was a needle of nearly regular hexagonal cross section, about 0.1 mm. in average diameter. No correction is included for extinction, for the rather small absorption of the crystals for X-rays, or for the decrease in intensity arising from thermal vibrations in the crystal; the omission of the temperature factor requires that, with increasing sin θ/λ, the observed intensities fall off more rapidly than those calculated.

Observed intensities were estimated by comparison of Kα and Kβ reflections appearing on photographs of widely differing times of exposure, making use also of an intensity scale prepared for the purpose. The $\{h0{\cdot}0\}$ intensities were estimated with great care, the others only moderately so.

It is seen that the agreement between calculated and observed intensities (Table I) is at least quali-

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(4) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

TABLE I

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF X-RAY REFLECTION[a]

{*hk*·0}	Intensity Calcd.	Intensity Obsd.	{*hk*·1}	Intensity Calcd.	Intensity Obsd.	{*hk*·2}	Intensity Calcd.	Intensity Obsd.
01·0	190	180	01·1	4	0	01·2	770	600
11·0	200	128	11·1	0	0	11·2	460	250
02·0	150	90	02·1	230	90	02·2	160	90
12·0	43	32	12·1	105	90	12·2	145	100
03·0	18	16	03·1	115	90	03·2	310	200
22·0	13	8	22·1	0	0	22·2	95	12
13·0	180	150	13·1	250	128	13·2	185	50
04·0	20	24	04·1	4	2	04·2	1	1
23·0	43	16	23·1	3	3	23·2	42	16
14·0	12	8	14·1	7	4	14·2	24	2
05·0	11	4	05·1	4	3	05·2	230	90
33·0	95	24	33·1	0	0	33·2	2	1
24·0	160	64	24·1	8	4	24·2	6	1
15·0	19	8	15·1	12	2	15·2	2	0
06·0	20	10	06·1	7	1	06·2	1	0
34·0	75	24	34·1	7	1	34·2	6	1
25·0	44	16	25·1	26	3	25·2	25	3
16·0	5	3	16·1	12	3	16·2	65	6
44·0	58	8	44·1	0	0	44·2	35	12
07·0	5	2	07·1	6	0	07·2	40	6
35·0	32	8	35·1	2	1	35·2	1	0
26·0	1	1	26·1	16	4	26·2	30	3
17·0	6	2	17·1	1	0	17·2	8	2
45·0	20	6	45·1	4	0	45·2	8	6
36·0	13	2	36·1	32	2	36·2	55	12
08·0	4	0	08·1	2	0	08·2	4	0
27·0	1	1	27·1	3	1	27·2	9	5
18·0	40	6	18·1	4	1	18·2	4	0
55·0	27	6	55·1	0	0	55·2	50	8
46·0	17	2	46·1	4	1	46·2	6	2
37·0	10	2	37·1	4	0	37·2	8	0
09·0	7	1	09·1	1	0	09·2	4	0
28·0	1	0	28·1	1	0	28·2	11	1
19·0	7	2	19·1	1	0	19·2	2	0
56·0	1	0	56·1	2	0	56·2	4	0
47·0	4	3	47·1	2	0	47·2	10	0
38·0	9	1	38·1	4	0	38·2	2	0
0·10·0	21	3	0·10·1	1	0	0·10·2	3	0
29·0	15	2	29·1	3	0	29·2	2	0
66·0	7	2	66·1	0	0	66·2	2	0
57·0	4	1	57·1	4	0	57·2	4	0
1·10·0	2	0	1·10·1	1	0	1·10·2	1	0
48·0	1	1	48·1	2	0	48·2	2	0
39·0	1	0	39·1	1	0			
0·11·0	1	0	0·11·1	1	0			
2·10·0	1	0	2·10·1	2	0			
67·0	3	1						
58·0	1	0						

[a] Temperature factor not included.

tatively satisfactory in general, and for the most part is satisfactory in detail. The agreement is better for {*hk*·0} than it is for {*hk*·1} or {*hk*·2} reflections, for which the sine terms are relatively more important.

The parameter values used above were not, naturally, the only set employed for calculating intensities. In particular, if each anion be rotated through about thirty degrees so as to make anion–anion contacts between terminal nitrogen atoms of side chains about the three-fold axis at 2/3, 1/3, *z*, another, quite distinct grouping arises. The packing relations turn out to be rather unsatisfactory, and intensity comparisons to be completely unsatisfactory for this case.

The results contained in Table I are good enough to make it quite sure that the parameter values used for calculation cannot be far from the true ones. Variations of several thousandths in some of the individual values are certainly not improbable. It does not seem feasible to determine the positions accurately enough to give interatomic distances, for instance, the C–N separation in the cyanuric ring, to within 0.01 or 0.02 Å., in spite of the fact that excellent quantitative data can be obtained readily for crystals of this substance. A Fourier analysis of the data designed to achieve such accuracy is not feasible since no significant projection of the structure contains a center of symmetry. Neither can the laborious method of trial and error be employed profitably to achieve high accuracy in the parameter determinations since: (1) the *f*-values used for carbon and nitrogen are only very approximate even for idealized atoms of spherical symmetry, whereas in the present case over 70% of the electrons of the anion are used for bond formation with presumably a considerable concentration of scattering material in specific regions: (2) the temperature factor must be expected to show a marked dependence upon the orientation of the incident beam with respect to the crystallographic axes as well as upon the angle of scattering. Both of these factors are unpredictable at present.

Discussion of the Structure

A drawing of an atomic layer with $z = 1/4$ together with a superimposed layer of sodium ions in $z = 1/2$ is shown in Fig. 1. The parameter values employed lead to the interatomic distances given in Table II. Of these, the first five refer to separations of adjacent pairs of atoms within the anion, the next four to the packing relations of oxygen within an atomic layer, the following three to the coördination of nitrogen and oxygen about sodium, and the last two values give the closest distances of approach of two atoms (nitrogen) in neighboring anions.

It is profitable to compare this structure with that found for cyanuric triazide.[5] Although not identical in detail, these two studies of cyanuric triazide agree in assigning to the molecule a size and shape generally quite similar to that found for

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[5] E. W. Hughes, *J. Chem. Phys.*, **3**, 1 (1935); **3**, 650 (1935); I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935); *J. Chem. Phys.*, **3**, 241 (1935).

TABLE II

INTERATOMIC DISTANCES IN TRISODIUM TRICYANMELAMINE TRIHYDRATE

Atom	Neighbor	Separation, Å.
C_I	N_I	1.34
C_I	N_I	1.35
C_I	N_{II}	1.40
N_{II}	C_{II}	1.32
C_{II}	N_{III}	1.21
O	O	2.87
O	N_I	3.00
O	N_{II}	3.03
O	N_{III}	3.16
Na	O	2.44
Na	N_{II}	2.46
Na	N_{III}	2.49
N_{II}	N_{III}	3.34
N_{III}	N_{III}	3.55

the tricyanmelamine ion. The linear cyanamide groups in the side chains of $C_3N_3(NCN)_3^{\equiv}$ are, as expected, somewhat longer than the azide groups of $C_3N_3(N_3)_3$.

The "packing" distance between nitrogen atoms of two neighboring molecules is about 3.15 Å. on the average in cyanuric triazide, to be compared with about 3.34 Å. (in the same layer) in sodium tricyanmelamine. (Half this value, 1.67 Å., was used in drawing the envelopes of the anions in Fig. 1.) In the latter case, however, the nitrogen atoms carry a negative charge. The separation of adjacent negative layers is $c_0/2$ or 3.28 Å.; the smallest value of the N–N separation between these layers is 3.55 Å. (Table II).

Each sodium ion is surrounded by two oxygen and four nitrogen atoms at the corners of a distorted octahedron. The Na–O distance, 2.44 Å., is about that which has been found repeatedly for coördination number six. Na–N separations of 2.46 and 2.49 Å. are slightly smaller than might have been anticipated. This may be correlated with the favorable orientation of the anions with respect to sodium, resulting in regions of high electron density (unshared electron pairs) on the nitrogen atoms being directed toward sodium ions.

The relationships of water molecules to each other and to nitrogen atoms (all of which presumably carry some negative charge) are not such as to indicate the presence of definite hydrogen bridges or bonds within the structure. The packing relations are, nevertheless, consistent with the idea that there is an appreciable stabilizing contribution to the energy of the crystal arising from electrostatic interactions of water molecules with each other and with nitrogen.

The more detailed investigation given by Knaggs[5] to cyanuric triazide seems to require that the cyanuric ring contain two unequal C–N distances of 1.31 and 1.38 Å., corresponding essentially to alternate double and single bonds. On the other hand, the theoretical treatment of Pauling and Sturdivant[6] shows that the rather unusual stability of a compound of this type can be understood in terms of a large stabilizing energy arising from resonance among a number of nearly equivalent valence bond structures. If the C–N separations in the ring are appreciably different, the most important case of this resonance is expected to be largely inhibited. Values of 1.34 or 1.35 Å., assigned to the C–N distance in the present work, are close to the expected average, but the accuracy of the parameter determinations cannot be considered adequate to furnish real evidence with regard to the problem stated. To give these interatomic distances to within 0.01 Å., an accuracy will usually be required equivalent to fixing several individual parameters to rather better than 0.001.

Careful Fourier analyses of the X-ray data from several appropriate compounds containing the cyanuric ring are needed in order that such detailed conclusions can be accepted with complete confidence.

It is of interest to note that tricyanmelamine itself crystallizes from aqueous solution as the trihydrate, comparable in stability with the sodium salt. The hydrated acid may contain layers very nearly identical, except for the addition of protons, with the negative layers of Fig. 1. It is planned to investigate the structure of this compound in this Laboratory in the hope that the superposition of layers will prove to be such that an illuminating Fourier analysis will be possible.

It seems probable that the triammonate of sodium tricyanmelamine, $Na_3C_6N_9{\cdot}3NH_3$, is isomorphous with the trihydrate. The packing relations exhibited by water molecules toward each other and toward nitrogen atoms should be satisfactory also for ammonia.

Thanks are due to Professor Linus Pauling and Dr. J. H. Sturdivant for their kindness in relinquishing their claim to this problem. I have had also the benefit of helpful discussions with Professor Pauling. I am indebted to Dr. J. Sherman for some of the intensity calculations.

Summary

It is deduced from X-ray data that trisodium

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(6) Pauling and Sturdivant, *Proc. Nat. Acad. Sci.*, **23**, 615 (1937).

tricyanmelamine trihydrate possesses a hexagonal unit of structure with $a_0 = 10.23$ Å., $c_0 = 5.56$ Å., containing $2Na_3C_6N_9 \cdot 3H_2O$, space-group $D^4_{3h} - C\bar{6}2c$. The tricyanmelamine ions pack together with water molecules in symmetry planes to form atomic layers which are equally spaced perpendicular to the hexagonal axis. These negatively charged layers are bound together by sodium ions (Fig. 1) each of which is octahedrally surrounded by four nitrogen and two oxygen atoms at distances agreeing with the sums of the respective ionic radii. Packing relations within this structure and the stereochemistry of the anion are compared with the corresponding data for cyanuric triazide. The stabilities of both anion and crystal are reflected in the compact and generally satisfactory nature of the structure.

ITHACA, N. Y. RECEIVED MARCH 10, 1938

[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Certain Halogen and Nitro Derivatives of 3-Anilino-5-phenylisoxazole and Pyrazole

BY DAVID E. WORRALL

It was shown in a previous communication[1] that the substances obtained from phenylpropiol thioanilide by interaction with hydroxylamine and hydrazine react easily with bromine and nitric acid. Since 3,5-diphenylisoxazole does not react even with fuming nitric acid,[2] it was assumed that substitution took place solely in the aniline group, an assumption that since has been found untenable by comparison with a derivative of known structure.

The thioamide obtained from *p*-bromophenyl isothiocyanate forms an isoxazole isomeric and not identical with that resulting from the action of bromine on anilinophenylisoxazole. Furthermore, it was discovered that 2,4-dibromoaniline as well as benzoic acid could be isolated from the oxidation products of the tribromo derivative of anilinophenylpyrazole. Substitution must start with the isoxazole (or pyrazole) ring and at position four as it is otherwise stripped of hydrogen, subsequently involving the aniline group. Consequently, the substances previously reported as 3-*p*-bromoanilino-5-phenylisoxazole and 3-(2,4,-6-tribromoanilino)-5-phenylpyrazole actually are 3-anilino-4-bromo-5-phenylisoxazole and 3-(2,4-dibromoanilino)-4-bromo-5-phenylpyrazole. It follows that similar changes should be made with the nitro derivatives. The compounds previously listed as 3-(2,4-dinitroanilino)-5-phenylisoxazole and 3-(2,4,6-trinitroanilino)-5-phenylpyrazole should be recorded as 3-(4-nitroanilino)-4-nitro-5-phenylisoxazole and 3-(2,4-dinitroanilino)-4-nitro-5-phenylpyrazole.

Experimental

Phenylpropiol Thio-4-bromoanilide.—This substance was prepared using the customary technique[1] from 0.2 gram mole of *p*-bromophenyl isothiocyanate. The product, thoroughly washed with cold alcohol, amounted to about 50 g. A small portion was crystallized from benzene, separating as bright yellow needles, melting with decomposition at 132–133°. No polymer formation was observed. *Anal.* Calcd. for $C_{15}H_{10}NSBr$: Br, 25.3. Found: Br, 25.6.

3-(4-Bromoanilino)-5-phenylisoxazole.—Ten grams of the crude was added in small lots to a boiling alcoholic solution containing an excess of hydroxylamine. The precipitate thrown out by an equal volume of water was crystallized first from ethylene chlorohydrin, then twice from alcohol; final yield, 2.4 g. of colorless flat needles melting at 180–181°. *Anal.* Calcd. for $C_{15}H_{11}ON_2Br$: Br, 25.4. Found: Br, 25.5.

3-(2,4-Dibromoanilino)-4-bromo-5-phenylisoxazole was obtained by bromination in chloroform of the monobromide. The same substance resulted when the isomeric monobromo derivative and the original non-bromine containing isoxazole were mixed with an excess of bromine. An insoluble substance formed in all cases which blackened and lost hydrogen bromide on contact with wet solvents, but which dissolved in boiling alcohol with only a transitory color, separating out almost immediately as colorless, hair-like crystals, m. p. 176°. *Anal.* Calcd. for $C_{15}H_9ON_2Br_3$: Br, 50.8. Found: Br, 50.7.

3-(2-Chloro-4-bromoanilino)-4-chloro-5-phenylisoxazole was prepared by the chlorination of the bromo derivative. It was isolated from alcohol in the form of small needles, m. p. 163°. *Anal.* Calcd. for $C_{15}H_9ON_2BrCl_2$: Cl, 18.5. Found: Cl, 18.6.

3-(4-Bromoanilino)-4-nitro-5-phenylisoxazole.—By nitration slender yellow needles were obtained, sparingly soluble in alcohol, m. p. 163–164°. *Anal.* Calcd. for $C_{15}H_{10}O_3N_3Br$: Br, 22.2. Found: Br, 21.8.

3-(4-Nitroanilino)-4-bromo-5-phenylisoxazole.—Nitration of the nuclear brominated isoxazole produced this isomer which separated from glacial acetic acid as small

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[1] Worrall, THIS JOURNAL, **59**, 933 (1937).

[2] Wislicenus, *Ann.*, **308**, 249 (1899).