substances, many or all of which are liable to be present with the protein, especially in vegetable extracts, may be quite enough to cause a strong Molisch reaction.

The evidence of a carbohydrate group in the protein molecule which Molisch's reaction affords cannot, therefore, be accepted as conclusive, other evidence which shows that more than insignificant quantities of carbohydrate are present being also necessary.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 77.]

p-AMINOBENZONITRILE.¹

BY MARSTON TAYLOR BOGERT AND LOTHAIK KOHNSTAMM.

Received March 9, 1903.

INTRODUCTORY.

IN the last edition of Beilstein's "Handbuch," Vol. II, p. 1273, three widely separated melting-points are recorded for *p*-aminobenzonitrile, namely, 74°, as reported by Engler;² 110°, reported by Fricke;³ and 86°, reported by Griess.⁴ In the recent German edition of "Roscoe and Schorlemmer," and in Richter's "Lexikon," the preference is given to the figure 110°—why, we do not know, unless it is due to the usual inclination on the part of compilers of reference works to give the preference to the highest figure. As the matter is not cleared up in the recently issued supplement to "Beilstein" (Vol. II), and as we have not been able to discover anything in the literature which would further enlighten us, it seemed of interest to investigate the subject, and to determine if possible which of these widely divergent melting-points (if any, indeed, were correct) represented the real melting-point of *p*-aminobenzonitrile, especially as a further study of this nitrile and its derivatives was contemplated.

The results obtained show quite clearly that the melting-point of 86°, as given by Griess,⁵ is substantially correct. We have repeated the work of Engler, Fricke and Griess, and have also prepared the nitrile by a fourth method. The products obtained

¹ Read before the New York Section at its meeting May 20, 1902.

² *Ztschr. Chem.* (1868), p. 613; *Ann. Chem.* (Liebig), **149**, 297 (1869).

³ *Ber. d. chem. Ges.*, **7**, 1321 (1874).

⁴ *Ibid.*, **8**, 861 (1875).

⁵ *Loc. cit.*

by the various methods were identical in all respects, and melted sharply at 85.5°-86° (corr.). A few derivatives of the aminonitrile were also prepared.

EXPERIMENTAL.

p-Nitrobenzonitrile.—This was prepared from *p*-nitraniline by the Sandmeyer reaction, in a manner entirely analogous to that already described by Bogert and Hand¹ for the ortho compound, carbon tetrachloride being used to extract the crude nitrile from the accompanying mineral cyanides, and further purification being accomplished by crystallization from dilute acetic acid. The crystals thus obtained melted sharply at 147° (uncorr.). Fricke² and Hantzsch and Schultze³ give the melting-point as 147°, while Sandmeyer⁴ reports it as 146°. It will be noted that the melting-point of this nitrile is the same as that of the *p*-nitraniline from which it was prepared. We did not find the yield of nitrile to be nearly so large as in the case of the ortho compound. This is perhaps due to the formation of diazoamino⁵ and biphenyl⁶ compounds. The method recommended by Pinnow and Müller⁷ was also tried, but the yield was still less satisfactory. By the action of concentrated sulphuric acid, this nitrile may be changed to *p*-nitrobenzamide, melting-point 200° (uncorr.), as already observed by Claus.⁸

Reduction of p-Nitrobenzonitrile by Engler's Method.—Five grams of *p*-nitrobenzonitrile were dissolved in 100 cc. absolute alcohol, 12 cc. hydrochloric acid (sp. gr. 1.2) added, and the reduction accomplished by the use of 8 grams of granulated zinc, the mixture being allowed to stand for two days with frequent shaking. It was then filtered and the alcohol removed from the filtrate by distillation under diminished pressure. From the residual solution, on cooling, there separated a mass of fine needles, which were washed thoroughly with cold water (to remove zinc salts) and added to a mixture of cracked ice and ether

¹ This Journal, **24**, 1035 (1902).

² *Loc. cit.*

³ *Ber. d. chem. Ges.*, **28**, 666 (1895).

⁴ *Ibid.*, **18**, 1492 (1885).

⁵ Schraube and Schmidt: *Ber. d. chem. Ges.*, **27**, 520 (1894).

⁶ Niementowski: *Ibid.*, **34**, 3325 (1901).

⁷ *Ibid.*, **28**, 149 (1895).

⁸ *J. prakt. Chem.* (2), **51**, 399 (1895).

in a separatory funnel. Caustic alkali was then run in to alkaline reaction and the solution repeatedly extracted with ether. The ether extracts were combined, the ether distilled off, and the liquid residue placed over sulphuric acid *in vacuo*, where it soon solidified in a crystalline mass. On recrystallization from water, long white needles were obtained, melting-point 85.5° - 86° .

Engler gives the melting-point of his product as 74° , and it is, therefore, quite evident that his material could not have been pure *p*-aminobenzonitrile. In his purification of the crude aminonitrile he evaporated the alkaline solution of the free base until an oil separated upon the surface which solidified on cooling, and then recrystallized this until it showed a melting-point of 74° . That some saponification occurred in this evaporation of the alkaline solution seems more than likely, and Engler admits that the mother-liquors contained the sodium salt of what was apparently *p*-aminobenzoic acid. His product was probably a mixture, in spite of the fact that the percentage composition as ascertained by analysis corresponded with that calculated for *p*-aminobenzonitrile.

Reduction of p-Nitrobenzonitrile by Fricke's Method.—We have found it more convenient, in carrying out this process, to use alcohol, although Fricke does not mention this in his description of the method. Five grams of the nitronitrile were dissolved in 100 cc. of absolute alcohol and reduced with 10 cc. of glacial acetic acid and 10 grams of granulated tin, adding a few drops of platinic chloride to start the reaction. Several days were required for complete reduction. The tin was then precipitated by hydrogen sulphide, the filtrate neutralized with sodium carbonate and evaporated to dryness, the residue extracted with ether, and the ethereal extracts evaporated *in vacuo*. The crystals thus obtained were recrystallized from water, then appearing as long white needles, melting-point 85.5° - 86° , and identical with the reduction-product from Engler's method. Fricke reports the melting-point of his product as 110° . From his method of purifying the crude material (which is not given in the article quoted, but appears in his dissertation)¹ it is difficult to determine the particular compound or mixture which he had in hand. It seems manifest, however, that his product was not pure *p*-aminobenzonitrile as he believed.

¹ Inaugural Dissertation Göttingen, 1874. "Ueber Nitro- and Amido-Benzonitrile."

Preparation of p-aminobenzonitrile by Griess's Method.—Twenty grams of *p*-uraminobenzoic acid was distilled with phosphorus pentoxide, and the impure *p*-aminobenzonitrile thus produced was purified by recrystallization from water, until the melting-point remained constant at 85.5°-86°, the purified substance being identical in all respects with the *p*-aminobenzonitrile already described. Our results, therefore, agree entirely with those of Griess.

Reduction of p-Nitrobenzonitrile by Stannous Chloride and Hydrochloric Acid.—The reduction of the nitronitrile in this case was carried out exactly as outlined by Bogert and Hand¹ for the ortho compound. The crude aminonitrile, crystallized from water, formed long white needles, melting at 85.5°-86°, and identical with the *p*-aminobenzonitrile obtained by the other methods. In this reduction, care must be taken to make sure that the reaction is complete, as the tendency to separate intermediate reduction products (azoxy-, hydroxylamino-derivatives, etc.) appears to be greater than with the orthonitronitrile.

Some of the pure material, obtained by this latter method, was analyzed with the following results:

	Calculated for $C_7H_6N_2$.	Found.				
		I.	II.	III.	IV.	V.
Carbon.....	71.18	71.11	71.33			
Hydrogen	5.09	5.19	5.18			
Nitrogen	23.72			23.88	23.53	23.70

Properties of p-Aminobenzonitrile.—Long white or colorless prisms, or compact glassy tablets. Large crystals may be obtained from a mixture of chloroform and petroleum ether, by careful evaporation. The melting-point is 85.5°-86° (corr.), and is not changed by further crystallization. It is very difficultly soluble in petroleum solvents, cold or hot; difficultly soluble in cold water, moderately soluble in hot; difficultly soluble in cold carbon bisulphide or carbon tetrachloride, slightly soluble in the same at their boiling-points; apparently insoluble in cold oil of turpentine, but dissolves readily on boiling; very easily soluble in methyl alcohol, ethyl alcohol, isoamyl alcohol, ether, ethyl acetate, ethyl nitrate, benzene, chloroform, acetone, or glacial acetic acid; apparently insoluble in concentrated hydrochloric acid, difficultly soluble in

¹ *Loc. cit.*

dilute; unattacked by cold concentrated caustic soda, but decomposed by it on boiling.

Through the kindness of Dr. Austin Flint Rogers, of the Department of Mineralogy of Columbia University, the following crystallographic data are appended:

Monoclinic system. $a : b : c = 1.7475 : 1 : 1.4573$. $\beta = 47^\circ 50'$.

Forms: a (100), b (010), c (001), m (110), r ($\bar{1}01$).

		Observed.	Calculated.
mm'	(110 : $\bar{1}10$) (6)	$75^\circ 20'$	
ac	(100 : 001) (6)	$47^\circ 50'$	
cr	(001 : $\bar{1}01$) (3)	$54^\circ 32'$	
am	(100 : 110) (8)	$52^\circ 24'$	$52^\circ 20'$
cm	(001 : 110) (6)	$65^\circ 42'$	$65^\circ 47'$

Crystals rhomboidal in shape, tabular parallel to c ; often quite elongate in the direction of the b axis. Faces c and m dominant; a , b and r , subordinate, the two latter faces usually rounded.

Cleavage a perfect, b less so. The figure given above is an orthographic projection, with (010) as the plane of projection.

Chloride of p-Aminobenzonitrile.—This was prepared by dissolving the nitrile in dry ether and passing in dry hydrochloric acid gas. It separated immediately as a white crystalline precipitate. The determination of hydrochloric acid in this salt invariably gave low results, even when freshly precipitated, washed with absolute ether, and dried *in vacuo* over sulphuric acid.

p-Acetaminobenzonitrile.—The aminonitrile was boiled with acetic anhydride for a few hours and the crude product crystallized from water. Fine white needles, melting-point 200° . Percentage of nitrogen found by analysis, 17.52; required for $\text{CH}_3\text{CONHC}_6\text{H}_4\text{CN}$, 17.50.

p-Propionaminobenzonitrile.—This was prepared by heating the aminonitrile for several hours with propionic anhydride, and crystallizing the crude product from water. It forms crystals melting at 169°. Percentage of nitrogen found by analysis, 16.09; calculated for $C_2H_5CONHC_6H_4CN$, 16.06.

p-Aminobenzamide.—The aminonitrile was warmed for some time at 50° with alkaline hydrogen dioxide solution. On cooling, white crystals separated, melting-point 178°-179°. Not sufficient of the material was prepared for further purification, so that the melting-point as given is probably low. Reichenbach and Beilstein¹ report the melting-point of *p*-aminobenzamide as 178°-179°, but Remsen and Reed² give the corrected melting-point as 182.9°.

p-Aminobenzthiamide, $H_2NCSC_6H_4CN$.—The aminonitrile was dissolved in alcohol, the solution saturated at 0° with dry ammonia and dry hydrogen sulphide, and then heated in a sealed tube at 100° for several hours. The crystals obtained, when purified and dried, showed a melting-point of 172°. Engler³ gives the melting-point of *p*-aminobenzthiamide as 170°.

The study of *p*-aminobenzonitrile and of its derivatives is being continued.

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UNIVERSITY, March, 1903.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE MOLECULAR REARRANGEMENT OF THIOCYAN-
ACETANILIDES INTO LABILE PSEUDOTHIOHY-
DANTOINS; AND ON THE MOLECULAR
REARRANGEMENT OF THE LAT-
TER INTO STABLE
ISOMERS.

BY TREAT BALDWIN JOHNSON.

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[SECOND PAPER.]

In a previous paper from this laboratory by Wheeler and Johnson,⁴ it was shown that a thiocyanacetanilide is capable of a

¹ *Ann. Chem.* (Liebig), **132**, 137 (1864).

² *Am. Chem. J.*, **21**, 281 (1899).

³ *Ztschr. phys. Chem.*, 1868, p. 613; *Ann. Chem.* (Liebig), **149**, 297 (1869).

⁴ *Am. Chem. J.*, **28**, 121 (1902).