

**PARA-
AMINOBENZONITRILE
AND ITS DERIVATIVES;
DISSERTATION**

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Para-aminobenzonitrile and Its Derivatives; Dissertation by Louis Elsberg Wise

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LOUIS ELSBERG WISE

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Para-Aminobenzonitrile and Its Derivatives.

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY.

BY

LOUIS ELSBERG WISE, B.A.,

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TO MY MOTHER AND FATHER.

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ORGANIC CHEMICAL LABORATORIES,
HAYMEYER HALL, COLUMBIA UNIVERSITY,
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HISTORICAL INTRODUCTION.

The literature on the nitrile and amide of *p*-aminobenzoic acid presents little more than a number of analogies between the method of preparing these compounds, and the synthesis of their *o*- and *m*-isomers. Very few of their derivatives have been described, and in the earlier work on the *p*-nitrile, there have been such wide discrepancies between the results of different investigators, that compilers have found it impossible to definitely state the fusion point, one of the physical constants which should characterize this compound.

In 1864, Beilstein and Reichenbach,¹ while investigating the position isomerism in the aromatic series, prepared "nitrodracylamid," a substance which they reduced with ammonium sulphide. This reduction product, obtained by them in the form of large yellow crystals carrying water of crystallization, and liquefying between 178° and 179°, could be saponified with potassium hydroxide to the corresponding aminobenzoic acid, and was thus identified as *p*-aminoamide.

Four years later, in a preliminary paper, Engler,² first mentioned the *p*-nitro and *p*-aminobenzonitriles, and several derivatives, which were described in more detail by the same author in 1869.³ This chemist prepared the *p*-nitrobenzonitrile by heating together equimolecular parts of anhydrous phosphoric acid and nitrobenzamide, and distilling the product, an oil which soon solidified in the neck of the retort. The nitro-nitrile was recrystallized once from alcohol.

This mode of preparation and the properties of the compound were very nearly akin to those of the "nitrobenzonitrile" (the *m*-derivative), but its boiling and melting points were both higher. The latter is given by Engler as 139° C. By heating the substance in a sealed tube with concentrated hydrochloric acid, he obtained *p*-nitrobenzoic acid.

Para-nitrobenzonitrile dissolved in ten times its weight of a concentrated solution of ammonium sulphide with evolution of heat. On cooling, a crystalline mass was de-

posited, which after several recrystallizations gave yellow, star-shaped clusters of the para-aminobenzthiamide, or keeping the author's nomenclature, the "hydrosulphide of para-amidobenzonitrile."

Engler furthermore reduced para-nitrobenzonitrile to the para-amidobenzonitrile. He dissolved the nitro compound in absolute alcohol, and added zinc and concentrated hydrochloric acid. The reaction was vigorous and if carried too far yielded the benzylamine. In his description, he states that he left the substance in contact with the reducing agents for eighteen hours. At the end of this time he made alkaline with caustic soda and concentrated the solution. After most of the alcohol had evaporated, a light oil separated, which solidified on cooling. This solid deposit was washed with water, and recrystallized from alcohol. It melted at 74° C. On analysis it was identified as para-aminobenzonitrile, which was readily soluble in alcohol and ether, and difficultly soluble in hot water. It formed long, colorless needles, which were soft to the touch, and which sublimed above their melting point. The same investigator also prepared and described the hydrochloride and chlorplatinate of the para-aminobenzonitrile.

In 1874, Fricke,⁴ in a research which in no way refers to the work of Engler, prepared para-nitrobenzamide from the nitrobenzoylchloride and ammonia, and by distillation with phosphorus pentoxide, obtained the same nitro-nitrile in the form of colorless leaflets, which he found difficultly soluble in cold water and alcohol, readily soluble in hot alcohol, chloroform, and acetic acid, and the melting point of which he records as 147° C. From this he readily obtained para-amidobenzonitrile⁵ by means of tin and glacial acetic acid. This amino derivative crystallized in small colorless needles, which liquefied at 110° C. and whose other properties agreed with those already mentioned. He also described the hydrochloride, as well as the salts of nitric and sulphuric acid.

In 1875, Griess,⁶ prepared a base by treating para-uraminobenzoic acid with phosphoric anhydride. During the reaction carbon dioxide was evolved, and water eliminated.