Identification of the Isomeric Phenylenediamines[1]

FRANK J. WELCHER, Indiana University, and JOHN A. BUEHLER, Anderson College

Reagents which are capable of reacting with organic compounds to form ring structures are frequently of great value in organic analysis (1). Many cations react with bifunctional organic compounds to form highly colored chelate complexes, provided the two functional groups are so located in the molecule as to permit the formation of stable 5- or 6-membered rings. As a rule these complexes are highly colored. Similarly, organic reagents may react with organic compounds to form ring structures which are colored, and thus permit the identification of the latter. These reactions possess the advantage in organic analysis that they reveal the presence of two reactive groups, and in addition they may also show their relative positions in the molecule. Further, steric configurations may be indicated.

A typical illustration of the use of inorganic cations for the identification of an organic compound is the characterization of anthranilic acid by means of various inorganic salts as proposed by Moses (5). When various classification tests have shown an unknown to be one of the three isomeric aminobenzoic acids, the o-isomer (anthranilic acid) is readily recognized by simply treating it with a solution of a cupric, nickel, or ferric salt. Only in anthanilic acid are the amino and carboxyl groups joined to the benzene ring in such a manner that a stable chelate ring can result. Unfortunately, the p- and m-isomers cannot be detected in this manner.

It is believed that by a careful selection of generally well-known reactions various isomeric compounds can be differentiated. In recent work carried out in this laboratory it became necessary to identify quickly the three isomeric phenylenediamines. A number of reactions were studied as a possible means of accomplishing this purpose. Those most suitable are:

(1) Acetylacetone.—Acetylacetone reacts in an acid solution with o-phenylenediamine to yield the intensely colored purple compound, 2,4-dimethyl-1,5-benzodiazepine, which contains a 7-member ring. (6, 7, 8, 9.) This reaction is very sensitive and is not given by the m- and p-isomers.

(2) The LaRosa Reaction.—When magnesium hydroxide is precipitated in the presence of the oxidation products of p-phenylenediamine, a violet-colored precipitate is formed (3). The o- and m-isomers do not give a similar test.

(3) The Lauth Reaction.—When p-aminodimethylaniline is treated in an acid solution with hydrogen sulfide and ferric chloride, the thiazine dye, methylene blue, is formed (4). p-Phenylenediamine reacts similarly to give a clear blue solution. The o- and

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m-isomers do not yield a blue color, but the former gives a reddish brown color and the latter a pale yellow color.

If the above reactions are applied to a small crystal of the phenylenediamine or the dihydrochloride on a spot plate, or in a test tube, it is possible in a minute or two to determine the positions of the two amino groups. With the acetylacetone reaction, a purple color indicates the o-isomer, since the m- and p-isomers do not react. In the absence of any color, the compound is shown to be either the m- or p-isomer. Then by applying the Lauth reaction, the p-isomer is indicated by the formation of a beautiful blue color and the m-compound by a very pale yellow color. Actually the Lauth reaction can be used to differentiate all three isomers, since the o-isomer gives a reddish brown color, the m-isomer a pale yellow, and the p-isomer a blue color; but this series of reactions is not as satisfactory as the combination of the two tests, especially if the amines are not pure. The tests are summarized in the following chart:

Reaction	o-Phenylene-diamine	m-Phenylene-diamine	p-Phenylene-diamine
Acetylacetone	Purple Solution	Colorless Solution	Colorless Solution
LaRosa	Greenish-yellow Precipitate	Orange-yellow Precipitate	Deep violet Precipitate
Lauth	Brownish-red Solution	Pale yellow Solution	Deep-blue Solution

The above reactions may be used to detect small quantities of the amines when the latter are present as impurities. For example, less than 1 per cent of o-phenylenediamine as an impurity can be detected in samples of the m- or p-isomers by the acetylacetone reaction. Similarly, 1 per cent of p-phenylenediamine can be detected in the presence of the other isomers by using the Lauth reaction if blanks are run simultaneously. The pure blue of the p-isomer is not obtained when o- and m-phenylenediamine are present, but the colors obtained with pure samples of the latter are significantly changed in the presence of small amounts of p-phenylenediamine. Small quantities of the three amines can also be detected in the presence of inert impurities.

Experimental

Acetylacetone Test.—Place a few crystals of the diamine to be tested on a spot plate and add 0.2 ml. of distilled water, one drop of 6 N HCl, and 2 drops of a 1 per cent aqueous solution of acetylacetone.

o-Phenylenediamine gives a purple colored solution.

m- and p-Phenylenediamines do not give a color reaction.

LaRosa Test.—Place a few crystals of the diamine to be tested on a spot plate, and then add 0.2 ml. of distilled water, one drop 6 N HCl, one drop of a $FeCl_3$ solution which contains 0.25 mg. of $FeCl_3$ per ml., 3 drops

of 6 N KOH, and two drops of a magnesium nitrate solution that contains 100 mg. of magnesium ion per ml.

o-Phenylenediamine gives a pale greenish-yellow precipitate.

m-Phenylenediamine gives a pale yellow-orange precipitate.

p-Phenylenediamine gives a deep violet colored precipitate.

Lauth Test.—Place a few crystals of the diamine on a spot plate, and add 0.2 ml. of distilled water, one drop of 6 N HCl, 0.2 ml. of a saturated aqueous solution of hydrogen sulfide, and one drop of a $FeCl_3$ solution which contains 2.5 mg. of $FeCl_3$ per ml.

o-Phenylenediamine gives a brownish-red solution.

m-Phenylenediamine gives a yellow solution.

p-Phenylenediamine gives a deep violet-blue solution.

Summary

A simple procedure for the identification of the three isomeric phenylenediamines is described.

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