The present note describes the synthesis, physical properties, and standard derivatives, which characterize the diamine molecule II.

EXPERIMENTAL[5]

N,N,N′,N′-Tetramethyl-1,2-propanediamine (II). To 4060 ml. of 90% formic acid in a 12-l. 3-neck round-bottom flask fitted with a condenser, stirrer, and dropping-funnel was slowly added 1334 g. (17.3 moles) of 1,2-propanediamine[6] with thorough mixing. Then somewhat more rapidly was introduced 5960 ml. of a 37% formalin solution. The uniform evolution of bubbles of carbon dioxide from the body of the solution indicated the progress of the reaction. After the early rapid gas liberation had subsided, the flask was heated at a gentle refluxing temperature for 48 hours. While still boiling, the reaction mixture was carefully treated with 1.0 l. of concentrated sulfuric acid to bind the amine as a salt. The excess formaldehyde, formic acid, and water then were distilled off.

When the still pot residue began to froth badly (after 5600 ml. of distillate had been collected), 900 g. of sodium hydroxide (as a warm 50% aqueous solution) was added. About one liter of amine product distilled over. More was obtained by salting it out from the residue with concentrated aqueous potassium hydroxide. The combined amine fractions were dried over potassium hydroxide pellets and distilled from sodium. The yield of N,N,N′,N′-tetramethyl-1,2-propanediamine, b.p. 138–139° at 745 mm. was 1692 g. (76%) of clear colorless liquid with a very strong amine odor. The product was completely miscible with water and organic solvents. It remained a mobile fluid even at −100°. Cooling below this temperature in a liquid nitrogen bath led to a rapid increase in viscosity with ready supercooling to a hard brittle glass. It was not found possible to crystallize this amine.

Other physical properties found include n_D^{25} 1.4230 (Abbe-type refractometer); d_4^{25} 0.7900 (pycnometer); and dielectric constant 2.4 (determined with dielectric constant meter made by Yellow Springs Instrument Co., Yellow Springs, Ohio).

Anal. Calc'd for $C_7H_{18}N_2$: C, 64.56; H, 13.93; N, 21.51; Neut. equiv., 65.1; MR_D, 42.00.[7] Found: C, 64.47; H, 13.75; N, 21.42; Neut. equiv., 65.0; MR_D, 41.98.

II·Dihydrochloride. This compound was obtained by adding dropwise from a hypodermic syringe 5 ml. of diamine II to 15 g. of concentrated hydrochloric acid in a 50-ml. Erlenmeyer flask with shaking and cooling in an ice-bath to remove the high heat of neutralization. The reaction mixture then was concentrated by heating to remove almost all of the water. There resulted a clear colorless viscous resin which set to a glass on cooling to room temperature. Slow crystallization took place over a period of days. A portion of the crystals, removed and washed with a small amount of absolute ethanol, had m.p. 177–179°. Potentiometric titration with base proved the diprotic nature of this compound.

II·Monopicrate.[8] To 10 ml. of a saturated solution of picric acid in anhydrous ethanol was added 1.0 ml. of diamine II. The solution was refluxed for one minute and allowed to cool slowly overnight. The yellow crystalline salt was filtered off and washed well with ethanol. Yield was 0.80 g., m.p. 112–114°.

Anal. Calc'd for $C_{13}H_{21}N_5O_7$: C, 43.45; H, 5.89; N, 19.49. Found: C, 43.75; H, 5.95; N, 19.40.

II·Di(methiodide). To 2.0 ml. of methyl iodide in 10 ml. of methanol in a 25-ml. Erlenmeyer flask cooled in an ice-bath was added dropwise from a hypodermic syringe 1.0 ml. of diamine II. Constant shaking and cooling were required to dissipate the heat of reaction. After addition was complete, the solution was heated to boiling and allowed to cool slowly overnight. Crystallization occurred. The product was filtered off and washed thoroughly with cold methanol. Yield was 2.0 g. (80%), m.p. 222–224° with decomposition and gas evolution. Recrystallization from methanol gave crystals, m.p. 223–225° with decomposition.

Anal. Calc'd for $C_9H_{24}I_2N_2$: C, 26.10; H, 5.84. Found: C, 26.20; H, 5.80.

II·Di(methyl-p-toluenesulfonate). This derivative was prepared by a procedure identical with that described above for the dimethiodide except for the use of 2.0 ml. of methyl *p*-toluenesulfonate instead of the iodide. The yield was 2.4 g. (80%) of the di(methotosylate), m.p. 225–228°. Recrystallization from methanol gave m.p. 228–229° with a little decomposition since the fused material, after crystallization, had m.p. 223–225°.

Anal. Calc'd for $C_{23}H_{38}N_2O_6S_2$: C, 54.95; H, 7.62. Found: C, 55.11; H, 7.45.

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(5) Analyses were performed by Oakwold Laboratories, Alexandria, Virginia. Melting points were corrected values taken on a Kofler micro hot-stage.

(6) The diamine was the Matheson, Coleman, and Bell technical grade propylenediamine. A representative sample subjected to analysis by fractional distillation indicated 96% purity, b.p. 119–120°. The 1,2-propanediamine forms no azeotrope with water, according to ***Synthetic Organic Chemicals Catalog***, Carbide and Carbon Chemicals Corporation, New York, N. Y., 1945, 12th ed., p. 75.

(7) Values for atomic refractivities (sodium D-line) were those of A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 898.

(8) One of the referees called our attention to a paper by E. Rothstein, *J. Chem. Soc.*, 1560 (1940), which reports in a small footnote the isolation of a compound presumed to be the bis-quaternary ammonium picrate of the diamine described in the present note. This purported "N,N,N,-N′,N′,N′-hexamethylpropylenediammonium picrate" was obtained by extended heating of trimethyl-β-chloropropylammonium chloride with potassium hydroxide and then adding picrate ions. The nature of the reaction conditions, lack of structure proof, and the reported m.p. 315–316° make us feel that Rothstein's compound may be tetramethylammonium picrate which fits the analytical data better and has been described as melting at 312–313°, W. Lossen, *Ann.*, **181**, 364 (1876); 318–320°, M. Kohn and F. Grauer, *Monatsh.*, **34**, 1751 (1913); 313°, P. Walden, H. Uhlich, and G. Busch, *Z. physik. Chem.*, **A123**, 429 (1926).

Amines. II.[1] The Preparation and Reduction of Benzo[*c*]cinnoline

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An unreported preparation and catalytic reduction product of benzo[*c*]cinnoline have been found. Benzo[*c*]cinnoline (I) also referred to in the literature as 2,2′-azodiphenyl, dibenzopyridazine, phen-

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(1) For previous paper in this series, see R. W. Moshier and L. Spialter, *J Org. Chem.*, **21**, 1050 (1956).

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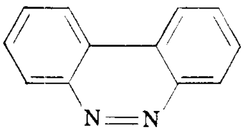
azone, diphenazone, diphenylenazone, 3,4-benzocinnoline, and 5,6-naphthisodiazine has been prepared by the reduction of 2,2′-dinitrobiphenyl: electrochemically,[2] chemically with sodium amalgam and methanol,[3] lithium aluminum hydride,[4] ferrous oxide,[5] or iron[6] and catalytically by hydrogenation with platinum oxide[7] or Raney nickel.[8]

The hydrogenation of either I or benzo[*c*]cinnoline oxide (II) with a platinum oxide catalyst reportedly resulted only in the obtaining of I, although there was evidence[7] that hydrazobiphenyl (III) formed and was readily oxidized to I. The hydrogenation of 2,2′-dinitrobiphenyl at an unspecified but presumably lower temperature and lower pressure in the presence of Raney nickel[8] also gave I. In no case was it reported that the catalytic hydrogenation of I yields 2,2′-diaminobiphenyl.

Upon reduction of 2,2′-dinitrobiphenyl with zinc and alkali a 55% yield of I has now been isolated. When I was catalytically hydrogenated with Raney nickel, it had been expected that III would be formed. Consequently, the hydrogenation product was recovered under an atmosphere of nitrogen to avoid possible oxidation of III to I which occurs readily in air.[2,7] Contrary to our expectation, only 2,2′-diaminobiphenyl was obtained. Its infrared spectrum was identical with those of authentic samples of 2,2′-diaminobiphenyl obtained both by chemical[9,10] and by catalytic[7,11] reductions of 2,2′-dinitrobiphenyl. Melting points of the mixtures of reduction product and the authentic samples were undepressed.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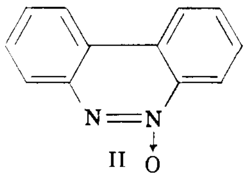
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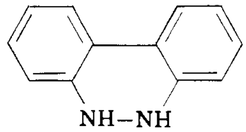
III

EXPERIMENTAL[12]

Benzo[*c*]*cinnoline.* In a 200-ml. 3-neck r.b. flask fitted with a reflux condenser, stirrer, and thermometer, 10 g. (0.041 mole) of 2,2′-dinitrobiphenyl, 133.4 ml. of absolute ethanol, and 13.4 ml. of an aqueous solution containing 10 g. of sodium hydroxide were heated on a water-bath. When the temperature of the mixture reached 70–80°, 30 g. of granular (30 mesh) zinc was added gradually over a period of $^1/_2$ hour. Heating with stirring at 70–80° was continued for an additional $^1/_2$ hour. The hot mixture was filtered through a Büchner funnel to remove the zinc oxide. The yellow crystalline material which precipitated from the cooled filtrate, was filtered and washed with absolute ethanol. The combined filtrate and wash solution were boiled with the zinc oxide residue and filtered while hot. From the cooled filtrate a second crop of yellow crystals was obtained. The combined yellow crystals of benzo[*c*]cinnoline (I), after recrystallization from absolute ethanol, weighed 4.1 g., yield 55.4%, m.p. 156–158°.

Anal. Calc'd for $C_{12}H_8N_2$: C, 79.98; H, 4.48; N, 15.55. Found: C, 79.87; H, 4.58; N, 15.79.

Reduction of benzo[*c*]*cinnoline to 2,2′-diaminobiphenyl.* A teaspoonful of commercial aqueous Raney nickel paste was washed by decanting with three 50-ml. portions of 95% ethanol. Benzo[*c*]cinnoline (0.53 g., 0.0030 mole) dissolved in 10 ml. of absolute ethanol and 10 ml. of an ethanolic suspension of Raney nickel was hydrogenated with shaking at 34–37° in a glass-lined bomb. The vapor-free space was 65 ml. and the pressure dropped from 98 to 70 p.s.i. The ethanolic solution was filtered and concentrated to 8 ml. in an atmosphere of nitrogen. The white colorless crystals of 2,2′-diaminobiphenyl (V) which separated upon cooling weighed 0.35 g., yield 86%, m.p. 77.5–78.5°.

Preparation of 2,2′-diaminobiphenyl from 2,2′-dinitrobiphenyl (IV) *by two different routes:* (*a*). By reduction with tin and hydrochloric acid[10] as described by Macrae and Tucker.[9]

(*b*). By hydrogenation with a platinum oxide catalyst[11] according to the procedure of Ross, Kahan, and Leach.[7]

Anal. Calc'd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: (a) C, 78.24; H, 6.57; N, 15.38. (b) C, 78.25; H, 6.73; N, 15.44.

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[9] T. F. Macrae and S. H. Tucker, *J. Chem. Soc.*, 1520 (1933).

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[12] The melting points are uncorrected. The analyses were performed by Oakwold Laboratories, Alexandria, Virginia.

The Preparation of Diformylmethylamine

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and Richard A. Ogg, Jr.

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In the course of investigations of the nuclear magnetic resonance spectra of N-substituted amides in this laboratory, diformylmethylamine was synthesized. This compound, which has not been previously reported, was prepared by the reaction of acetic anhydride with N-methylformamide in accordance with the following equation.