

bis-Benzimidazoles from Dibasic Acids

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Monobasic acids have been shown to condense readily with *o*-phenylenediamine to yield 2-substituted benzimidazoles¹ which serve as useful derivatives. If dibasic acids are used in this reaction the products depend on the mole ratio of the reactants and the experimental conditions. With a 1 to 1 ratio of the dibasic acid and *o*-phenylenediamine or an excess of the dibasic acid the products have been formulated as cyclic diamides, N-substituted amidic acids and N-substituted diamides of the dibasic acids.²

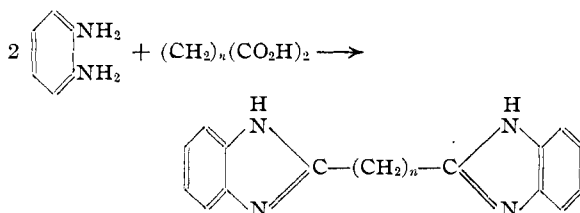
TABLE I
bis-BENZIMIDAZOLES FROM DIBASIC ACIDS

Di-basic acid	Condensation product	Dec. temp., °C.	Yield, %	Analyses, %			
				Calcd.		Found	
				C	H	C	H
Succinic	C ₁₆ H ₁₄ N ₄	325-330	28	73.28	5.34	73.58	5.64
Glutaric	C ₁₇ H ₁₆ N ₄	258-259	50	73.09	5.84	74.12	6.03
Adipic	C ₁₈ H ₁₈ N ₄	259-260	46	74.50	6.25	74.59	6.08
Pimelic	C ₁₉ H ₂₀ N ₄	225-226	62	75.02	6.64	74.62	6.77
Suberic	C ₂₀ H ₂₂ N ₄	263-266	56	75.44	6.96	75.32	7.16
Azelaic	C ₂₁ H ₂₄ N ₄	273-275	63	75.89	7.26	75.52	7.25
Sebacic	C ₂₂ H ₂₆ N ₄	277-279	60	76.27	7.56	75.76	7.55

TABLE II
DIHYDROCHLORIDES OF POLYMETHYLENE-bis-BENZIMIDAZOLES

Acid	Formula	Dec. temp., °C.	Analyses, %					
			Calcd.			Found		
			C	H	Cl	C	H	Cl
Succinic	C ₁₆ H ₁₆ N ₄ Cl ₂	312-315	57.32	4.81	21.16	57.39	5.15	21.22
Glutaric	C ₁₇ H ₁₈ N ₄ Cl ₂	270-273	58.47	5.19	20.31	57.99	5.44	20.25
Adipic	C ₁₈ H ₂₀ N ₄ Cl ₂	305-309	59.58	5.52	19.52	59.23	5.53	19.58
Pimelic	C ₁₉ H ₂₂ N ₄ Cl ₂	270-272	60.60	5.84	18.79	60.83	5.89	18.60
Suberic	C ₂₀ H ₂₄ N ₄ Cl ₂	296-299	61.40	6.15	18.12	61.50	6.23	17.90
Azelaic	C ₂₁ H ₂₆ N ₄ Cl ₂	269-272	62.22	6.46	17.49	62.02	6.52	17.56
Sebacic	C ₂₂ H ₂₈ N ₄ Cl ₂	263-265	63.00	6.73	16.91	63.22	6.87	16.86

In the present work it has been found possible to produce bis-benzimidazoles by heating two moles of *o*-phenylenediamine with one mole of each of the dibasic acids ranging from succinic through sebacic acid. A reaction temperature of 125-135° and 4 *N* hydrochloric acid as a catalyst gave yields ranging from 28 to 63%.



(1) Pool, Harwood and Ralston, *THIS JOURNAL*, **59**, 178 (1937); Brown and Campbell, *J. Chem. Soc.*, 1699 (1937); Bloom and Day, *J. Org. Chem.*, **4**, 14 (1939).

(2) Walther and Pulawski, *J. prakt. Chem.*, **59**, 249 (1899); Meyer, *Ann.*, **327**, 1 (1903); **347**, 17 (1906); Phillips, *J. Chem. Soc.*, 2393 (1928).

The products were white crystalline compounds which melted with decomposition. They readily formed dihydrochlorides.

Experimental

Heptamethylene-bis-benzimidazole.—A mixture of 9.4 g. (0.05 mole) of azelaic acid, 10.8 g. (0.10 mole) of *o*-phenylenediamine and 120 ml. of approximately 4 *N* hydrochloric acid was refluxed in an oil-bath at a temperature of 125-135° with good stirring for seven hours. The reaction mixture was cooled to room temperature and filtered. The filtrate was chilled in an ice-bath and slowly made neutral to litmus by the dropwise addition of a saturated solution of sodium carbonate. The product was collected on a filter, washed with cold water and recrystallized from absolute ethanol. The yield was 10.5 g. The other polymethylene-bis-benzimidazoles were all prepared by the same general procedure. They were white crystalline compounds with high decomposition points (Table I).

Dihydrochlorides.—A mixture of 10.0 g. (0.03 mole) of the dry bis-benzimidazoles and approximately 50 ml. of absolute ethanol was treated with dry hydrogen chloride for two hours. The reaction mixture was cooled in an ice-box overnight whereupon the dihydrochloride separated from solution. The product was collected on a filter, washed with acetone and recrystallized from methanol.

The yields were 90-95%. The dihydrochlorides described in Table II were all white crystalline compounds whose solubility and decomposition points exhibited an alternation similar to the solubility and melting points of the corresponding dibasic acids.

The two dibasic acids, oxalic and malonic, react with *o*-phenylenediamine in different fashions. Oxalic acid formed 2,3-dihydroxyquinoxaline (dec. 351-355°) in agreement with the observation of Phillips.² Its structure was established by conversion to the known 2,3-dichloroquinoxaline³ (m. p. 150°) by means of phosphorus pentachloride. Malonic acid, when heated with two moles of *o*-phenylenediamine produced an 80% yield of a crystalline white powder which decomposed at 345-349°.

Anal. Calcd. for C₉H₈O₂N₂: C, 61.36; H, 4.55; N, 15.89. Found: C, 61.38; H, 4.74; N, 16.04.

This product was insoluble in dilute acids and organic solvents. It was hydrolyzed by 25% alkali to *o*-phenylenediamine. Its analysis, decomposition point and insolubility in solvents show that this compound differs from any

(3) Bergstrom and Ogg, *THIS JOURNAL*, **53**, 249 (1931).

previously prepared^{1,2} using different ratios of reactants and suggest that it is some type of a substituted polyamide.

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The Discharge of Zinc Ions at the Dropping Mercury Cathode. A Test of the Ilkovic Equation

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The use of the polarograph in this Laboratory for the determination of zinc in plant materials and fertilizers has required an examination of the relation between limiting current and concentration of zinc over a wider concentration range than usual. Lingane and Kolthoff¹ have tested the same relationship over the range 10^{-4} – 10^{-2} molar for four metal ions depositing from 0.1 *M* potassium chloride. On the other hand, a five-fold concentration range is about all that is usually covered in most of the reported methods of polarographic analysis.

The basal solution used here has the composition 0.1 *M* ammonium chloride, 0.02 *M* potassium thiocyanate and 0.0002% methyl red. Like the solution proposed by Stout, *et al.*,² it enables zinc to be determined in the presence of nickel, and any data available about it are of more practical value to those concerned with the determination of zinc than these obtained for potassium chloride solutions, in which zinc and nickel are not resolved.

With this mixed basal solution in the electrolysis cell, the anode potential proved to be equal (to within a few millivolts) to that of the saturated calomel electrode, so that cathode potentials, when referred to the S. C. E. as zero, may be taken as equal to the applied potentials. The deposition potential was found to be -1.02 volts. The temperature coefficient of the limiting current was determined between the temperatures 18 and 28°, the current increasing by 1.72% of its value at 20° for a rise of 1°. All other measurements were conducted at a temperature of $20 \pm 0.15^\circ$ and at a potential of -1.20 volts, limiting current conditions having then been reached. From the table it will be seen that the relation between current and zinc concentration is linear (to within about $\pm 1.5\%$) over a one hundred-fold concentration range.

(1) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

(2) P. R. Stout, J. Levy and L. C. Williams, *Coll. Czech. Chem. Comm.*, **10**, 129 (1938).

Ilkovic³ has shown that the value of i/C can be calculated from the diffusion coefficient, the mass of mercury (m) flowing per second from the cathode, and the drop time (t). Values of the two latter were determined and are given in the table, while the diffusion coefficient was calculated from the ionic mobility at infinite dilution, assuming a value of 47.8 at 20° for the latter. On substituting these values in the Ilkovic equation, it is found that $i/C = 4.67$ microamperes per millimole per liter, which is 9% lower than the observed value of 5.10.

TABLE I
RELATION BETWEEN CONCENTRATION OF ZINC AND
LIMITING CURRENT

$m = 1.392$ mg./sec., $t = 3.61$ sec., $m^2/t^{3/2} = 1.545$ mg.²/sec.^{-1/2}.

<i>C</i> , millimoles/ liter	<i>i</i> , microamp.	<i>i/C</i> microamp./ mmole/liter
0.0500	0.252	5.04
.250	1.016	5.06
.500	2.54	5.08
1.00	5.18	5.18
5.00	25.7	5.14

Mean 5.10

The agreement is good enough to support the view that the mechanism of this particular discharge process is substantially the same as that pictured by Ilkovic. At the same time, the combined errors involved in the measurements of i/C , m and t probably do not exceed 3%, so that the discrepancy cannot be disregarded. Lingane and Kolthoff obtained a similar result for the discharge of zinc from 0.1 *M* potassium chloride, the observed limiting current exceeding the calculated by 5%. They suggested this might be due to the occurrence of the complex ion $ZnCl^+$. If, as here, the electrolyte contains potassium thiocyanate, the tendency toward complex formation may well be greater. Hence, in view of the difficulty of knowing what value to assign to the diffusion coefficient, it is of more interest to combine the four experimentally determined quantities in the form of the ratio $i/Cm^{2/3}t^{1/6}$. The value of this ratio at any one temperature should then be a constant independent of the type of capillary, and should characterize any one particular discharge process. For the data just presented at 20°, it has the value 3.31, or 3.56 at 25°, allowing for a temperature coefficient of 1.48%. This represents the difference between the observed temperature coefficient of the limit-

(3) D. Ilkovic, *ibid.*, **6**, 498 (1934).