4,4'-(Diphenylmethane)bisoxamic acid chloride (I). To 99.3 g. (0.78 mole) of oxalyl chloride was added 10.0 g. (0.037 mole) of 4,4'-diaminodiphenylmethane dihydrochloride in one portion with stirring. The heterogeneous mixture was heated at reflux with stirring for 12 hr. in a dry atmosphere. After removal of the excess oxalyl chloride at reduced pressure with gentle heating, the residual solid was dissolved in about 3 l. of dry, ethanol-free chloroform. The almost clear solution was filtered to remove some fine particles of unchanged dihydrochloride and evaporated on the steam bath to about 500 ml. At this concentration a large amount of yellow, crystalline solid was present. After cooling to room temperature, the yellow needles were filtered off in a dry-box under a dry nitrogen atmosphere, weight 9.9 g. (71%), m.p. 165–167° (dec.).

Anal. Calcd. for $C_{17}H_{12}O_4N_2Cl_2$: C, 53.85; H, 3.19; O, 16.88; N, 7.39; Cl, 18.70. Found: C, 52.65, 52.64; H, 3.08, 3.17; O, 17.0, 16.8; N, 7.16, 7.13; Cl, 19.7, 20.0.

Diethyl 4,4'-(diphenylmethane)bisoxamic acid. To 73.7 g. (0.505 mole) of diethyl oxalate warmed to about 30° was added 10.0 g. (0.0505 mole) of 4,4'-diaminodiphenylmethane with stirring. The solution was heated under reflux for 1.5 hr., then allowed to cool to room temperature. The solid was filtered and dried in a vacuum oven at 20 mm. pressure and 60°. The weight of tan colored product was 17.6 g. (88%), m.p. 150–153°. Recrystallization from ethanol gave colorless needles, m.p. 153–153.5°.

Anal. Calcd. for $C_{21}H_{22}O_4N_2$: C, 63.3; H, 5.60; N, 7.05; O, 24.1. Found: C, 63.28, 63.35; H, 5.83, 5.77; N, 6.94, 6.96; O, 23.9, 24.0.

The diethyl ester was also obtained by using chloroform containing ethanol as recrystallizing medium for 4,4'-(diphenylmethane)bis-oxamic acid chloride. It was obtained as colorless needles (from *n*-hexane/chloroform) in 91% yield, m.p. 152–152.5°. The infrared absorption spectra and mixed melting point of these two samples showed them to be identical.

N-Ethyloximidic acid chloride (II; R = C_2H_5). To 158.4 g. (1.25 mole) of oxalyl chloride protected from the atmosphere by calcium chloride tubes was added 5.0 g. (0.061 mole) of ethylamine hydrochloride with stirring. The mixture was heated at reflux for 50 hr., then the excess oxalyl chloride was removed at reduced pressure. The solid residue was dissolved in a chloroform/*n*-hexane (3/1) mixture and the chloroform boiled off leaving a small amount (100 mg.) of tan crystals, m.p. >220° which showed a negative silver nitrate test. This is believed to be *N,N'*-diethyltetraketo-piperazine.

After filtration of this high melting solid the brown filtrate was evaporated to about 80 ml. and allowed to cool in a dry-box. A large amount of tan needles formed which were filtered. These were dried in a vacuum desiccator and the dry weight was 8.0 g. (77%). It was recrystallized from *n*-hexane giving tan needles, m.p. ~85–90°. It showed an immediate positive silver nitrate test and the infrared spectrum was consistent with the structure proposed.

Anal. Calcd. for $C_5H_5O_4NCl_2$: C, 31.88; H, 2.23; N, 6.20; Cl, 31.38. Found: C, 32.1, 32.5; H, 2.71, 2.84; N, 6.25, 6.03; Cl, 28.2, 27.5.

The di-*N*-methylanilide was prepared by adding a large excess of *N*-methylaniline to a chloroform solution of the acid chloride. This had a melting point of 118.5–119.5°. Two crystallizations from aqueous ethanol gave colorless crystals, m.p. 132–133°.

Anal. Calcd. for $C_{20}H_{21}O_4N_3$: C, 65.38; H, 5.76; O, 17.4; N, 11.44. Found: C, 65.32, 65.32; H, 5.81, 5.76; O, 17.4, 17.6; N, 11.23, 11.25.

THE PIONEERING RESEARCH DIVISION
TEXTILE FIBERS DEPT.
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON 98, DEL.

(6) C. Eberhardt and A. Welter, *Ber.*, **27**, 1811 (1894).

Acid Dissociation Constants and Copper Chelate Stability Constants of *N*-Aralkyl-ethylenediamines

A. E. FROST[1] AND A. A. CARLSON

Although the proton and copper(II) complexes of ethylenediamine and its *N*-alkyl-derivatives have been reported,[2-6] no such data is available for the *N*-aralkylethylenediamines.

N-alkylation of ammonia[4] leads to an increase in basicity or to stronger proton complexes. Since increased basicity generally produces increased complex stability in a given series of ligands enhanced stability of metal-amine complexes is expected. This reasoning holds true in the case of primary amines but not in the case of secondary or tertiary amines wherein the increased basicity due to *N*-alkyl substitution is simultaneously accompanied by an increase in steric interference and lower stability.[3] The same behavior exists in the *N*-alkylethylenediamines which form weaker metal complexes than does ethylenediamine. The observed order of complex stability:ethylenediamine > *N*-methylethylenediamine > *N*-ethylethylenediamine > *N*-isopropylethylenediamine is the reverse of the order of pK_a values (Table II). The effect of steric interference, absent in the proton complexes, becomes more pronounced as R increases in size. It, therefore, became of interest to examine the effect of *N*-monoaralkyl substitution on the proton and copper complexing ability of ethylenediamine.

The acid dissociation constants of the dihydrochlorides of *N*-benzylethylenediamine, *N*-(β-phenethyl)ethylenediamine and *N*-(p-methylbenzyl)ethylenediamine, together with the stability constants of their copper(II) complexes at 25° in 0.1*M* KCl have been determined and are reported here.

EXPERIMENTAL

Reagents. The *N*-aralkylethylenediamines were prepared by direct condensation of the appropriate aralkyl chloride with ethylenediamine in a five to one molar ratio at 85–90° for 4 to 6 hr. The products were liberated from their hydrochloride salts by adding a slight excess of 30% sodium hydroxide solution to the hot reaction mixture and stirring for 1 hr. The aqueous phase was removed and the remaining organic phases dried with solid KOH followed by metallic

(1) Now at Chas. Pfizer & Co., Inc., Brooklyn 6, N. Y.

(2) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(3) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 2373 (1952).

(4) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 2931 (1952).

(5) D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc. (London)*, **215**, A, 417 (1952).

(6) H. Irving and M. Griffiths, *J. Chem. Soc.*, 213 (1954).

TABLE I

N-ARALKYLETHYLENEDIAMINES AND THEIR DIHYDROCHLORIDE SALTS

	Diamines	Dihydrochlorides	N		Cl	
	B.P., °C.	M.P., °C.	Calcd.	Found	Calcd.	Found
Benzyl-	111–113 (5 mm.)[7]	260 (dec.)	12.6	12.3	31.8	31.8
β-Phenethyl-	136–140 (12 mm.)[8]	240–260 (dec.)	11.8	11.6	30.0	29.7
p-Methylbenzyl-	107–110 (1 mm.)	>250 (dec.)	11.8	11.2	30.0	29.1

sodium to remove the final traces of water. Fractional distillation over sodium gave the products as colorless oils.

The dihydrochloride salts were prepared in the conventional manner and purified by recrystallization from aqueous ethanol.

Apparatus and Procedure. The titration assembly and procedure were essentially the same as that described by Chaberek and Martell.[9] The diamine dihydrochlorides were used at a concentration of about 1×10^{-3} mole of ligand per run. For the determination of copper complex stability constants a two to one molar ratio of ligand to copper(II) was used.

Acid Dissociation Constants. The consecutive dissociation constants of the acids conjugate to the diamines were calculated from potentiometric titration data of the free ligands by the algebraic method.[9]

Stability of the Copper-Diamine Complexes. The stability constants of the copper-diamine complexes (1-2) were calculated from the 1-2 titration curves by the method of Bjerrum.[10] From the plot of ñ (the degree of formation of the complex) versus pB (the negative logarithm of the ligand concentration), the values of log K_1 and log K_2 were read at ñ values of 1.5 and 0.5 respectively. In the titration of N-(p-methylbenzyl)ethylenediamine with copper(II), precipitation of a deep violet crystalline solid occurred at pH 5.9 even at ligand concentrations of 5×10^{-4} (2.5×10^{-4} mole copper(II)). However, a sufficient number of points was obtained to permit calculation of log K_1 and log K_2. The plots of ñ versus pB exhibited a definite inflection indicative of a greater tendency for complex formation with the first ligand molecule than with the second.

The marked base weakening effect of the aralkyl substituents on the acid dissociation constants of ethylenediamine compared to the base strengthening effect of alkyl substituents[3,4] is evident from a comparison of the data in Table II.

The inductive effect of the phenyl group, previously pointed out by Wepster,[11] appears to be responsible for the considerable increase in acid strength observed, as resonance interactions between the phenyl groups and nitrogen are prohibited by the intervening alkylene bridges.

Although the pK_{H_2B} values increase slightly in the expected order, the increase on going from the benzyl- to the phenethyl derivative is not as great as anticipated in view of the known marked attenuation of the inductive effect with increasing distance from the reaction center. This effect is prominent in the monoamines wherein pK_{HB} increases approximately 0.5 pK unit in going from benzylamine (pK_{HB} 9.37) to phenethylamine (pK_{HB} 9.83).[12] The strong inductive effect of the aralkyl group on the pK_{HB} values of the alkylamines is also evident.

The lower basicity of the donor nitrogens is reflected in the lower log K_1 and log K_2 values of the copper complexes. In addition, steric effects at least with respect to log K_2, undoubtedly contribute to the lower stability values observed. The steric effect on log K_2 can be attributed to the interference of the donor groups of the two ligands. The nature of the steric effects, if such are operative on log K_1, are not known. The overall effect of the N-aralkyl groups appears to be approximately equal to that of the bulky N-isopropyl substituent.[6]

THE DOW CHEMICAL COMPANY
EASTERN RESEARCH LABORATORY
FRAMINGHAM, MASS.

(11) B. M. Wepster, *Rec. trav. chim.*, **71**, 1171 (1952).

(12) H. C. Brown, D. H. McDaniel, and O. Hafliger, "Determination of Organic Structures by Physical Methods," Edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., N. Y., Ch. 14 (1955).

TABLE II

ACID DISSOCIATION CONSTANTS AND COPPER COMPLEX STABILITY CONSTANTS OF N-SUBSTITUTED ETHYLENEDIAMINES $RNHCH_2CH_2NH_2$

R	$pK_{H_2B}^{+2}$	pK_{HB}^{+}	ΔpK	Log K_1	Log K_2	Log K_1/K_2
Benzyl-	6.48	9.41	2.93	9.12	7.56	1.56
p-Methyl- benzyl-	6.51	9.41	2.90	9.23	7.57	1.66
β-Phenethyl-	6.59	9.44	2.85	9.11	7.38	1.73
H—[6]	7.47	10.18	2.71	10.76	9.37	1.43
CH₃—[3,6]	7.56	10.40	2.84	10.55	8.56	1.99
C₂H₅—[3,6]	7.63	10.56	2.93	10.19	8.38	1.81
i-C₃H₇—[3,5]	7.70	10.62	2.92	9.07	7.45	1.62

(7) J. Van Alphen, *Rec. trav. chim.*, **54**, 595 (1935).

(8) A. Funke and J. P. Fourneau, *Bull. soc. Chim.*, **9**, 805 (1942).

(9) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

(10) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen (1941).

Anomalous Optical Rotatory Dispersion in the Morphine Series

J. M. BOBBITT,[1a] ULRICH WEISS,[1b] AND
DIMITRA D. HANESSIAN[1c]

The study of the optical rotatory dispersion of organic compounds is an old idea[2,3] which has been extensively developed in recent years by Djerassi

(1) (a) Department of Chemistry of the University of Connecticut; (b) National Institute of Arthritis and Metabolic Diseases, National Institutes of Health; (c) Department of Chemistry of the Ohio State University.

(2) T. M. Lowry, *Optical Rotatory Power*, Longmans Green, London, 1935.

(3) P. A. Levene and A. Rothen in H. Gilman, *Organic Chemistry*, Vol. II, John Wiley and Sons, New York, 1938, p. 1779.