Typical spectrometer patterns of the 5.5 Å. region of samples of varying degrees of crystallinity are presented in Fig. 1. The quick quenching to a low temperature of polymer heated above its transition temperature results in a glass-clear sample which gives a low intensity, broad diffraction line characteristic of a relatively disordered amorphous structure (Fig. 1a). Extensive crystallinity with increasing opacity is developed by lengthening the residence time of the polymer at temperatures between 190° and the transition temperature. The increase in crystallinity is accompanied by a splitting of the broad amorphous line into two strong and relatively sharp lines with less intense lines at the side (Figs. 1b, c, d).

The influence of molecular weight on the development of crystallinity was investigated by studying the effect of the various thermal treatments noted in Fig. 1 on samples with molecular weights of 50,000, 75,000 and 100,000, respectively. For a given heat treatment, the degree of crystallinity developed varied inversely with molecular weight.

Fiber diagrams were obtained from highly crystallized and oriented fibers prepared by the hot drawing of the polymer. The fiber patterns varied with degree of orientation. Arcs which developed on slight orientation split in two at the equator as the extent of orientation was increased and finally, in the most oriented sample, sharp spots were formed. The spacings and relative intensities of these spots were in exact correspondence with the 5.5 Å. region lines observed in the spectrometer curves of the most crystalline sample.

Measurement of the lateral spacings along the row lines of the fiber diagrams and of the lines observed in the Debye–Scherrer patterns gave a series of spacings, beginning with 5.6 Å., which were in the inverse ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$. These ratios, being characteristic of the hexagonal system, suggested that the polymer chains were packed in hexagonal unit cells. One dimension of the unit cell was calculated from these data and found to be 6.5 Å. The repeat distance along the fiber axis was determined to be 35 Å. from measurements of the layer-line separation of the spots. These data established the unit cell to be hexagonal, with the dimensions $A = 6.5$ Å. and $C = 35$ Å.

One structure which accounts for the extraordinarily long fiber spacing of 35 Å. is a spiral chain arranged so that the spiral starts to repeat itself after approximately 14 monomer units. This structure is similar to that which has been assigned to the spiral of polyisobutylene[3] and of Teflon.[4] A planar zig-zag chain such as in polyvinyl chloride or polyethylene is ruled out because it requires a fiber axis spacing of about 5 Å.

On the basis of this assumed structure, the density of the polymer may be calculated using the equation

$$d = \frac{1.65 \times M \times n}{V}$$

where

M = molecular weight of monomer unit = 116.5
n = no. of monomer units per unit cell = 14
V = volume of unit cell = 1290 Å.[3]

The calculated value is 2.10 g./cc, in agreement with the value of 2.12 g./cc. determined experimentally by the flotation method using a solution of *sym*-tetrabromoethane and diethyl phthalate.

Acknowledgments.—The author is grateful to Drs. E. Solomon, I. Fankuchen and D. Harker for their helpful comments and suggestions.

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(3) C. S. Fuller, C. J. Frosch and N. R. Pape, THIS JOURNAL, **62**, 1909 (1940).

(4) R. H. H. Pierce, W. M. D. Bryant and J. F. Whitney, presented at National A. C. S. Meeting, Buffalo, N. Y., March, 1952.

Dissociation Constants of Substituted Ethylenediamines[1]

BY FRED BASOLO, R. KENT MURMANN AND YUN TI CHEN

RECEIVED NOVEMBER 6, 1952

In the course of investigating the stepwise formation constants of numerous metal ammines, it was necessary to determine the acid–base dissociation constants or "hydrolysis" constants of the amines. These dissociation constants have been reported for the N-alkylethylenediamines[2] and this paper gives an account of analogous determinations for several NN′-dialkylethylenediamines and C-substituted ethylenediamines.

Experimental

Reagents.—NN′-diMeen, NN′-diEten, NN′-di-*n*-Pren and NN′-di-*n*-Buen[3] were prepared by the method of Schneider.[4] NN′-di-*i*-Pren was prepared by a modification of the procedure of Zienty,[5] using ethylene dibromide and isopropylamine. One mole of ethylene dibromide was refluxed with five moles of isopropylamine for 24 hours. The mixture became almost solid with crystals. An excess of 20% sodium hydroxide solution was added and the mixture distilled over solid sodium hydroxide. The amine was then distilled over sodium; yield 60%.

Both *dl*-bn and *m*-bn were prepared by reduction of dimethylglyoxime with platinum and hydrogen in a Parr bomb (80% yield)[6] and also by reduction with Raney nickel–aluminum alloy and aqueous alkali (41% yield).[7] The second method was found to be the most convenient in spite of the low yield because it could be carried out on a larger scale. The *meso* and *racemic* bn's were separated by fractional crystallization of the dihydrochlorides from methyl alcohol. The *racemic* form is about eight times more soluble than the *meso* form at room temperature. The free amines were liberated by the reaction of the calculated amount of sodium methoxide with the dihydrochlorides in absolute alcohol, followed by distillation under reduced pressure.

iso-Bn was prepared by the reduction of α-aminobutyronitrile with lithium aluminum hydride in anhydrous ether. Eighty-four grams of α-aminoisobutyronitrile in 200 ml. of anhydrous ether was added dropwise, over a period of two hours, to a well-stirred slurry of 76 g. of $LiAlH_4$ and 2 l. of

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(1) This investigation was supported by a grant-in-aid from the National Institutes of Health; Grant No. G-3239.

(2) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 2373 (1952).

(3) The diamines discussed here are designated as follows: NN′-diMeen = N,N′-dimethylethylenediamine; NN′-diEten = N,N′-diethylethylenediamine; NN′-di-*n*-Pren = N,N′-di-*n*-propylethylenediamine; NN′-di-*i*-Pren = N,N′-di-*i*-propylethylenediamine; NN′-di-*n*-Buen = N,N′-di-*n*-butylethylenediamine; pn = 1,2-diaminopropane (propylenediamine); *dl*-bn = *rac*-2,3-diaminobutane; *m*-bn = *meso*-2,3-diaminobutane; *iso*-bn = 1,2-diaminoisobutane; TetraMeen = 2,3-diamino-2,3-dimethylbutane; *dl*-stien = *rac*-1,2-diphenylethylenediamine; *m*-stien = *meso*-1,2-diphenylethylenediamine.

(4) P. Schneider, *Ber.*, **28**, 3074 (1895).

(5) F. B. Zienty, THIS JOURNAL, **68**, 1388 (1946).

(6) L. B. Clapp, Ph.D. Thesis, University of Illinois, 1941.

(7) F. H. Dickey, W. Fickett and H. J. Lucas, THIS JOURNAL, **74**, 944 (1952).

anhydrous ether. The mixture was stirred overnight at room temperature and then decomposed by the addition of 50 ml. of water, 40 ml. of 20% sodium hydroxide solution and 150 ml. of water, in that order, with cooling. The solid was removed by filtration and the ether solution dried over anhydrous sodium sulfate. Fractional distillation of this solution gave 30 g. (34%) of *iso*-bn. Another 10–15 g. of the amine was obtained from the solid by digesting it with hot benzene and distilling the extract.

Anal. Calcd. for the dihydrochloride, $C_4H_{12}N_2Cl_2$: Cl, 44.0. Found: Cl, 43.7.

TetraMeen could not be prepared from the reaction of 2,3-dibromo-2,3-dimethylbutane with either aqueous ammonia or liquid ammonia. Likewise it was found that tetramethylsuccinamide reacted with sodium hypobromite in water to give only complex mixtures from which no TetraMeen could be isolated. TetraMeen was finally prepared by the reduction of 2,3-dinitro-2,3-dimethylbutane[8] with zinc and concentrated hydrochloric acid[9] (40% yield). Catalytic reduction with platinum or Raney nickel and hydrogen gave very poor yields of impure product.

The synthesis of *m*-stien involved the condensation of benzaldehyde with liquid ammonia to yield hydrobenzamide which was rearranged to amarine by heating at 130° for five hours.[10] Amarine was acetylated by refluxing with acetic anhydride and sodium acetate for four hours. Hydrolysis of the *meso*-N-benzoyl-N'-acetyl-1,2-diphenylethylenediamine with 50% (by volume) sulfuric acid[11] and treatment with sodium hydroxide gave solid *m*-stien, which was recrystallized several times from water to give a pure product.

rac-Stilbenediamine was prepared by rearranging amarine to isoamarine by heating four moles of amarine with five moles of sodium hydroxide in 150 ml. of water and 800 ml. of diethylene glycol to boiling for one hour. The isoamarine was then acetylated and hydrolyzed as with amarine and pure *dl*-stien was obtained after three crystallizations from high boiling petroleum ether.

The boiling points or melting points of the final purified amines shown in Table I are in good agreement with the values reported in the literature.

TABLE I

NN'-DI-ALKYLETHYLENEDIAMINES ($RNHCH_2CH_2NHR$)

R	B.p., °C.
Me	118–119[4]
Et	148–150[4]
n-Pr	186–188[a]
i-Pr	171–171.5
n-Bu	111–113 (10 mm.)[a]

C-SUBSTITUTED ETHYLENEDIAMINES ($NH_2CRR'CR''R'''NH_2$)

Amine	B.p., °C.	M.p., °C.
pn	118–119[b]	
dl-bn	44–45 (25 mm.)[7]	
m-bn	46–48 (25 mm.)[7]	
iso-bn	36–38 (15 mm.)[11]	
TetraMeen	147–148[9]	97–98[9]
dl-stien		80–82[10]
m-stien		119–120[10]

[a] J. A. King and F. H. McMillan, THIS JOURNAL, **68**, 1774 (1946). [b] Beilstein, "Organische Chemie," Band IV, p. 257.

Preparation of Solutions and Titrations.—The amines were diluted with water until they were 1.5 to 5 molar and then standardized against standard acid by means of conductometric and *p*H titrations. Because of the low solubility of NN'-di-*n*-Buen, *dl*-stien, and *m*-stien, they were dissolved in 15, 50 and 50% by volume dioxane–water solutions, respectively. The primary standard for all acid–base titrations was a sample of 99.96% potassium hydrogen phthalate obtained from the Bureau of Standards.

The constant ionic strength nitric acid solution containing barium nitrate was made in the same manner as previously described.[2] All measurements were made in the presence of 0.05 *M* $Ba(NO_3)_2$ and 0.50 *M* KNO_3 except *dl*- and *m*-stien which were titrated against a standard perchloric acid solution containing 0.005 *M* $Ba(ClO_4)_2$ in 50% dioxane–water. The solutions were maintained at constant temperature by means of a constant temperature bath at 25 ± 0.1° and by an intimate mixture of ice and water at 0 ± 0.1°. A Beckman *p*H meter model G was standardized against Beckman standard buffers at a *p*H of 4.00 and 7.00 before each run. With solutions containing 50% dioxane, a calibration curve was made to correct for the change in activity coefficient of the hydrogen ion in a solvent of different dielectric constant. No such correction was necessary for the NN'-di-*n*-Buen because the final solutions contained less than 1% of dioxane.

With each amine, one complete titration curve was made and a series of constant values obtained for pK_1 and pK_2. In each case either another titration was made or two separate solutions were made one of which fell in the first dissociation constant range and the other in the second dissociation range. The constants were checked by measuring the respective *p*H's. The constants calculated from these solutions agreed with those obtained from the titration within ±0.01 *pK* unit.

The dissociation constants at 0 and 25° along with the heats of neutralization are summarized in Tables II and III. A graphic representation of these *pK* values is shown in Figs. 1 and 2.

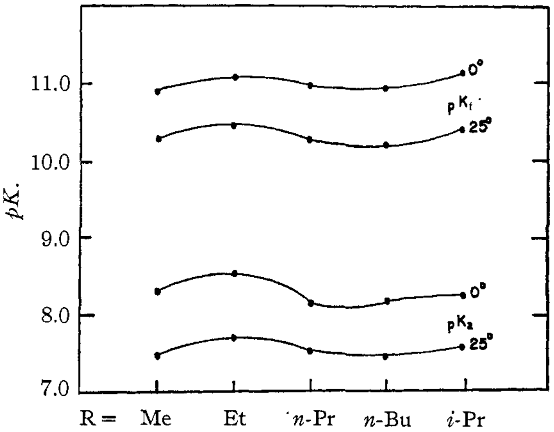

Fig. 1.—Dissociation constants of N,N'-dialkylethylenediamines, $RNHCH_2CH_2NHR$.

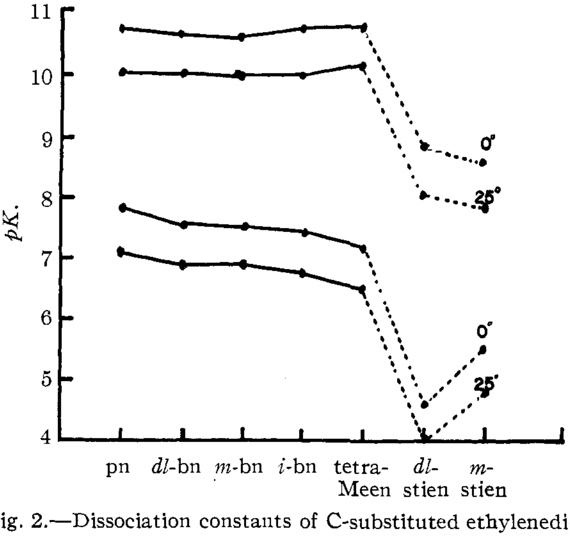

Fig. 2.—Dissociation constants of C-substituted ethylenediamines: —, water; - - -, 50% dioxane–water.

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[8] L. W. Siegle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

[9] J. Bewad, *Ber.*, **39**, 1233 (1906).

[10] I. Lifschitz and J. G. Bos, *Rec. trav. chim.*, **59**, 173 (1940); O. F. Williams, Ph.D. Thesis, University of Illinois (1952).

[11] W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.*, **I**, 843 (1935).

Results

The acid–base dissociation constants of the N,N′-dialkylethylenediamines are nearly the same from methyl to *n*-butyl with a slight rise in pK_1 and pK_2 with NN′-di-Eten. This same maximum was noted previously for pK_2 of the N-alkylethylenediamine series[2] at N-ethylethylenediamine, although it was not found in pK_1. As is the case in the N-alkylethylenediamine series, NN′-di-*i*-Pren is a stronger base than NN′-di-*n*-Pren. It is likewise noteworthy that although the pK_2 values of the N,N′-dialkylethylenediamines are similar to the pK_2 values of the N-alkylethylenediamines, these are not the same.

TABLE II

DISSOCIATION CONSTANTS AND HEATS OF NEUTRALIZATION OF N,N′-DIALKYLETHYLENEDIAMINES

Amine	pK_1 0°	pK_1 25°	pK_2 0°	pK_2 25°	ΔH, kcal. ΔH_1	ΔH, kcal. ΔH_2
NN′-diMeen[a]	8.30	7.47	10.89	10.29	−12.4	− 8.9
NN′-diEten	8.53	7.70	11.06	10.46	−12.4	− 8.9
NN′-di-*n*-Pren	8.14	7.53	10.97	10.27	− 9.1	−10.4
NN′-di-*n*-Buen	8.18	7.46	10.93	10.19	−10.7	−11.0
NN′-di-*i*-Pren	8.26	7.59	11.12	10.40	−10.0	−10.7

[a] 7.28, 10.06 (No specific temperature was given). Irving, Paper No. 4, "A Discussion on Coördination Chemistry," Butterwick Research Laboratories, I.C.I., Sept. 21–2, 1950.

TABLE III

DISSOCIATION CONSTANTS AND HEATS OF NEUTRALIZATION OF C-SUBSTITUTED ETHYLENEDIAMINES

Amine	pK_1 0°	pK_1 25°	pK_2 0°	pK_2 25°	ΔH, kcal. ΔH_1	ΔH, kcal. ΔH_2
pn[a]	7.81	7.13	10.76	10.00	−10.1	−11.3
dl-bn	7.60	6.91	10.69	10.00	−10.3	−10.3
m-bn	7.55	6.92	10.63	9.97	− 9.4	− 9.8
iso-bn	7.41	6.79	10.74	10.00	− 9.2	−11.0
TetraMeen	7.18	6.56	10.73	10.13	− 9.2	− 8.9
dl-stien (50% dioxane)	4.60	3.95	8.85	8.09	− 9.7	−11.3
m-stien (50% dioxane)	5.55	4.78	8.59	7.85	−11.6	−11.0

[a] 7.00, 9.78 (30°, 0.5 KNO_3). Carlson, McReynolds and Verhoek, THIS JOURNAL, **67**, 1334 (1945).

Substitution of methyl groups in the carbons of an ethylenediamine skeleton only slightly decreases the base strength of the amine. However, substitution of phenyl groups, as in stilbenediamine, appears to decrease the base strength but it must be remembered that much of this decrease may be due to a change in solvent. Little difference was noted between *dl*-bn and *m*-bn although the former was slightly more basic, while pK_1 of *dl*-stien is slightly larger than that for *m*-stien and the reverse is true for their pK_2 values.

The heats of neutralization are in the range of −9 to −12 kcal. which is slightly higher than that found for the N-alkylethylenediamines.

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$\Delta^{5,7}$-Steroids. XV.[1] $\Delta^{3,5,7}$-Cholestatriene-3-ol Acetate

BY SEYMOUR BERNSTEIN, MILTON HELLER AND JAMES H. WILLIAMS

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In the previous paper of this series, there was described the preparation of $\Delta^{3,5,7}$-cholestatriene-3-ol acetate by the treatment of $\Delta^{4,7}$-cholestadiene-3-one with acetic anhydride and pyridine. The physical constants [m.p. 101.5–103°; $\lambda_{\max}^{\text{abs. alc.}}$ 302.5–303, 315 and 330.5 mμ, ε17900, 22600, and 16200, respectively; $[\alpha]^{25}\text{D}$ −147° (chloroform)] of this preparation were strikingly different than those reported by Dauben and co-workers,[2] who prepared this enol acetate from $\Delta^{4,6}$-cholestadiene-3-one with acetic anhydride and acetyl chloride. In view of the reported conversion of $\Delta^{4,6,22}$-ergostatriene-3-one with acetic anhydride and acetyl chloride to $\Delta^{2,4,6,22}$-ergostatetraene-3-ol acetate (64% yield),[3] it was proposed[1] that the California preparation may have consisted of mixed crystals of $\Delta^{2,4,6}$- and $\Delta^{3,5,7}$-cholestatriene-3-ol acetates.

We now wish to report that, in our hands, treatment of the $\Delta^{4,6}$-3-ketone with acetic anhydride and acetyl chloride gave $\Delta^{3,5,7}$-cholestatriene-3-ol acetate (27% yield), identical in *all* respects with the compound prepared from the $\Delta^{4,7}$-3-ketone. A spectral analysis of the initial mother liquors obtained on the recrystallization of the enol acetate indicated the presence of only starting material (?), and no $\Delta^{3,5,7}$- or $\Delta^{2,4,6}$-enol acetates. This may be accounted for by incomplete reaction, or by unintentional hydrolysis of any enol acetate present. Whether or not a $\Delta^{4,6}$-3-ketone under these conditions gives rise to a mixture of enol acetates remains unsolved.

To substantiate further this method of preparing a $\Delta^{3,5,7}$-enol acetate from a $\Delta^{4,6}$-3-ketone, $\Delta^{4,6}$-androstadiene-17β-ol-3-one benzoate was transformed into $\Delta^{3,5,7}$-androstatriene-3,17β-diol-3-acetate-17-benzoate.

Finally, mention should be made of a pertinent optical rotational analysis. It is known that if C-17 "vicinal action" is absent, a compound with an "ergosterol" side chain will have a specific rotation of about 20° ($\Delta[M]\text{D}$ 78°) *more negative* than the corresponding "cholesterol" compound.[4] An examination of the rotations of the four compounds compiled in Table I reveals gross irregularities which unequivocally indicate "vicinal action." These anomalies may be explainable by the suggestion of Barton and Cox[5] of a possible qualitative correlation between anomalies and the ultraviolet absorption spectra of the compounds.

TABLE I

ROTATIONAL ANALYSIS

Compound	$[\alpha]\text{D}$ ($CHCl_3$)	$\Delta[\alpha]\text{D}$
$\Delta^{4,7}$-Cholestadiene-3-one	+33°[a]	...
$\Delta^{4,7,22}$-Ergostatriene-3-one	−12[a]	45°
$\Delta^{3,5,7}$-Cholestatriene-3-ol acetate	−147,[a] −145[b]	...
$\Delta^{3,5,7,22}$-Ergostatetraene-3-ol acetate	−144[a]	0

[a] See ref. 1. [b] This work.

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[1] Paper XIV, R. Antonucci, S. Bernstein, M. Heller and J. H. Williams, *J. Org. Chem.*, **17**, 1446 (1952).

[2] W. G. Dauben, J. F. Eastham and R. A. Micheli, THIS JOURNAL, **73**, 4496 (1951); m.p. 91–93°, $\lambda_{\max}^{\text{alc.}}$ 305, 316 and 330 mμ, ϵ_{316} 20,000; $[\alpha]^{25}\text{D}$ −69° (chloroform).

[3] I. M. Heilbron, T. Kennedy, F. S. Spring and G. Swain, *J. Chem. Soc.*, 869 (1938).

[4] S. Bernstein, W. J. Kauzmann and E. S. Wallis, *J. Org. Chem.*, **6**, 319 (1941).

[5] D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, 783 (1948).