$$\frac{B}{EB} = 37.5\,\frac{DEB}{TEB}$$

Other relationships between the components of a mixture and the number of ethyl groups and benzene rings it contains are

$$EB + 2DEB + 3TEB = \text{moles ethyl groups}$$
$$B + EB + DEB + TEB = \text{moles benzene rings} = 100$$

These equations define a family of curves expressing the composition of an equilibrated mixture as a function of the ratio of ethyl groups to benzene rings. One such family, chosen because it passes through the experimental points, is plotted in Fig. 1. The vertical distances between the curves at any ratio of ethyl groups to benzene rings are equal to the amounts of each of the four components in the equilibrium product distribution. From this graph, therefore, the equilibrium product composition obtained from any mixture of benzene, ethylbenzene, diethylbenzene and triethylbenzene can be estimated.

Whiting, Indiana

[Contribution from the Chemistry Research Branch, Aeronautical Research Laboratory, Wright Air Development Center]

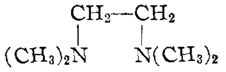
Amines. IV. The Base Strengths of Tetramethylated 1,2-Ethanediamines[1]

By Leonard Spialter and Ross W. Moshier

Received February 27, 1957

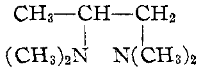
The base strengths of N,N,N′,N′-tetramethyl-1,2-ethanediamine and N,N,N′,N′-tetramethyl-1,2-propanediamine have been experimentally determined. It is shown that apparently anomalous values for the latter are explicable in terms of the inductive effect of the added methyl substituent together with the decrease of effective internal dielectric constant arising from a volume increase in the Kirkwood–Westheimer type of molecular cavity.

In the course of determining the base strengths of N,N,N′,N′-tetramethyl-1,2-ethanediamine (I) and N,N,N′,N′-tetramethyl-1,2-propanediamine (II), both diprotic amines, unusual relations were found between the values for the first and second dissociation steps of the conjugate acids of the two compounds. The data of Rometsch, Marxer and Miescher[2] led them to formulate four dissociaton rules for polyamines. Of these, an important one states that the dissociation interval (the difference between the pK values for consecutive dissociation steps) depends on the length of the chain between the two basic centers involved. Little effect is indicated for any other molecular structure features. It was therefore interesting to observe disagreement with such an assumption for the case of the diamine II compared to diamine I and the work of Rometsch, *et al.*[2]



$(CH_3)_2N{-}CH_2{-}CH_2{-}N(CH_3)_2$

I



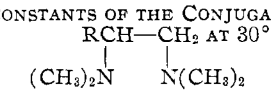
$(CH_3)_2N{-}CH_2{-}CH(CH_3){-}N(CH_3)_2$

II

The base strength data on the two diamines are presented in Table I. The convention adopted here for expressing base strengths, and apparently the preferred one,[3,4] is the use of pK_{ai}, the negative common logarithm of the acidity constant, K_{ai}, for the ith dissociation step of the conjugate acid of the amine base. Thus pK_{a_1} and pK_{a_2}, as applied here, have the same meaning as pK_{AH_2} and pK_{AH}, respectively, used by Carlson, *et al.*,[5] in the description of a diprotic base.

Table I

Acidity Constants of the Conjugate Acids of



$RCH(N(CH_3)_2){-}CH_2N(CH_3)_2$ at 30°

R	pK_{a_1}	pK_{a_2}	ΔpK_a
—H (I)	5.85[a]	8.97[a]	3.12
—CH$_3$ (II)	5.40	9.49	4.09

[a] Rometsch, *et al.*,[2] report 5.7 and 9.1, respectively, for pK_{a_1} and pK_{a_2}.

The data of Table I show an apparent violation of the Rometsch, *et al.*, rule when a hydrogen atom is replaced by a methyl group. Moreover, the result of such a structure change is to increase the ΔpK_a (in contrast to the decrease of this difference when a methylene is interposed in the molecular backbone[2]) and to do this by operating in two directions: lowering pK_{a_1} and raising pK_{a_2}. These peculiar anomalies between two such closely related molecules clearly suggest that the C-methyl substituent in II must be exerting two different specific influences, with one being more important for the first dissociation step and the other for the second.

The greater value for pK_{a_2} in the case of II compared to that of I reflects a substantially increased basicity in the former diamine for coördinating with the first acidic proton. This is undoubtedly attributable to the inductive ($-I$) effect of the additional methyl group whose contribution with respect to decreasing the acidity of acids and increasing the basicity of amines has been previously discussed.[3,6]

Additional experimental verification for the enhancement of base strength in a related tertiary amine as a consequence of the introduction of a β-methyl group is to be found in the work of Gero.[7] This investigator found N,N,N′,N′-tetraethyl-1,2-

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[1] For previous paper in this series see L. Spialter and J. A. Pappalardo, *J. Org. Chem.*, **22**, 840 (1957).

[2] R. Rometsch, A. Marxer and K. Miescher, *Helv. Chim. Acta*, **34**, 1611 (1951).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIII, p. 722–750.

[4] D. Davidson, *J. Chem. Ed.*, **32**, 550 (1955).

[5] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, This Journal, **67**, 1334 (1945).

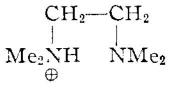
[6] (a) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939); (b) H. C. Brown and co-workers, This Journal, **66**, 435, 846 (1944).

[7] A. Gero, *ibid.*, **76**, 5158 (1954).

ethanediamine to have values of 6.18 and 9.55 for pK_{a_1} and pK_{a_2}, respectively, corresponding to increased basicity at both nitrogen atoms, yet with a ΔpK_a of 3.37 compared to Rometsch's figure of 3.1 for a two-carbon chain diamine.

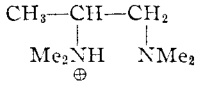
In view of the known marked attenuation of the inductive effect with distance through the chain from the reactive center, it appears reasonable to assume that the nitrogen on the methyl-bearing carbon is the site of the enhanced basicity and that the other half of the molecule with its nitrogen is essentially identical with the second half of I. Any discrepancy from this prediction would be expected to be small and to arise from second-order inductive effect of the C-methyl producing a slight enhancement of basicity for the second nitrogen of II, paralleling the greater effect on pK_{a_2}.

It then becomes indeed surprising to find that, in fact, the order of base strengths for the half-neutralized diamines, as reflected in the pK_{a_1} values, is inverse to that for the free amines. The ampholyte III derived from I is a significantly stronger base than is the ampholyte IV from II. In terms of the Rometsch, *et al.*,[2] dissociation interval, ΔpK_{ij} (the absolute difference between pK_i and pK_j), ΔpK_{21} for II here is 4.1, a substantial departure from the average value of 3.1 for a number of other two-atom chain polyamines, including I. Once the ampholyte has been formed, therefore, a new effect must be called for to explain the anomalous observations.



$$\begin{array}{cc} CH_2 & \text{—}CH_2 \\ | & | \\ Me_2NH & NMe_2 \\ \oplus & \end{array}$$

III



$$\begin{array}{ccc} CH_3\text{—} & CH & \text{—}CH_2 \\ & | & | \\ & Me_2NH & NMe_2 \\ & \oplus & \end{array}$$

IV

Undoubtedly, the source of the peculiar value for pK_{a_1} lies in C-methyl's introducing one or more significant effects other than purely inductive (or possibly hyperconjugative, which, however, would be expected to operate electronically in the same direction as does induction). Reasonable sources of such other influences could be the long range polar or direct, and the short range or steric effects. The likely cause of the observed anomaly seems to lie with long range polar effects.

Electrostatic contributions to the dissociation of dibasic acids have been elegantly treated by Kirkwood and Westheimer.[8] However, the treatment has apparently never been applied to the diamines or the conjugate acids thereof. In these latter systems, we find that the species of concern are either neutral or positively charged cations whereas the carboxylic acid system involves neutral and negatively charged molecules. Nevertheless, the equations and concepts of Kirkwood and Westheimer should remain directly applicable. Calculations on charge separation in the two diamine molecules were determined for the cases of both spherical and ellipsoidal cavity models using the corresponding diprotic acid formulas.

The Spherical Model.—The equation of Kirkwood and Westheimer for the spherical cavity[8a] was changed slightly[9] to the form

$$\sqrt{x}D_E = \frac{e^2(2(1 - \cos\theta))^{-1/2}}{2.303\ bkT(\Delta pK - \log\sigma)} \qquad (1)$$

where

x = (r/b)
r = distance in Å. between each charge center and center of sphere
b = radius of molecular spherical cavity in Å.
e = electronic electrostatic charge
k = Boltzmann constant
ΔpK = $pK_{a2} - pK_{a1}$
σ = statistical factor of 4 for symmetrical bis-tertiary amines
θ = angle between radius vectors from center of molecule to charge centers; here, 180°
D_E = effective dielectric constant of the cavity
T = temperature, °K.

The spherical radius, b, was estimated, as was done by Kirkwood and Westheimer, by the application of Traube's rule[10] for the uncharged molecule in aqueous solution. The partial molar volume of N,N,N′,N′-tetramethyl-1,2-ethanediamine (I) in water is then 124.4 cm.³, corresponding to a molecular volume of 20.63×10^{-23} cm.³ and a radius of 3.67 Å. for the molecule considered as a sphere. The analogous quantities for the propanediamine homolog (II) are 140.5 cm.³, 23.30×10^{-23} cm.³ and 3.82 Å., respectively. The ΔpK values used were 3.12 for I and 3.57 for diamine II. The latter is obtained if one corrects pK_{a_2} of II for the inductive effect of the added methyl group; *i.e.*, assume that pK_{a_2} of II would have been 8.79, the same as that of I in the absence of the inductive effect, while pK_{a_1} remains uninfluenced. The statistical factor is also changed to 2 for II. The resultant calculated data are presented in Table II.

TABLE II

VALUES OF KIRKWOOD–WESTHEIMER PARAMETERS

Spherical model	N,N,N′,N′-Tetramethyl-1,2-ethanediamine	N,N,N′,N′-Tetramethyl-1,2-propanediamine
$\sqrt{x}D_E$	12.95	9.60
$\sqrt{x}$ [a]	0.647	0.609
r	2.37 Å.	2.33 Å.
Charge separation[b]	4.74 Å.	4.66 Å.
D_E	20.0	15.8
Ellipsoidal model		
$D_E\ (\lambda_0^3 - \lambda_0)^{-1/3}$	12.97	9.59
λ_0 [c]	1.727	1.806
Charge separation, R	4.86 Å.	4.78 Å.
D_E	19.1	15.4

[a] Interpolated from Table II, ref. 8a, p. 511. Note typographical error in that table's caption which should read $\sqrt{x}D_E(x)$. [b] Separation between charge centers is $2r$ because $\theta = 180°$. [c] Interpolated from Table II, ref. 8b, p. 515.

The Ellipsoidal Model.—The equation for the ellipsoidal cavity applicable to diamines was modified[9] to the form

$$D_E\ (\lambda_0^3 - \lambda_0)^{-1/3} = \frac{e^2}{2.303kT(\Delta pK - \log\sigma)}\left(\frac{\pi}{6V}\right)^{1/3}$$

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[8] (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938); (c) F. H. Westheimer and M. W. Shookhoff, THIS JOURNAL, **61**, 555 (1939).

(9) The basic equations for the spherical (ref. 8a, p. 511) and the ellipsoidal cavity (ref. 8b, p. 515) use the defined quantity $\Delta pK = \log(K_1/\sigma K_2)$ (ref. 8c, p. 555), where σ is a statistical factor. In the interests of uniformity of nomenclature and current practice, we prefer to use $\log(K_1/\sigma K_2) = (\Delta pK - \log\sigma)$.

(10) J. Traube, *Saml. chem. chem-tech. Vorträge*, **4**, 255 (1899).

where

V = molecular vol. (computed from Traube's rule)

λ_0 = confocal elliptical coördinate (ratio of sum of focal distances of a point on surface of an ellipsoid of revolution to the interfocal distance, R), obeys relation $\lambda_0^3 - \lambda_0 = 6V/\pi R^3$ for such an ellipsoid, where V is the volume and other quantities have been defined above.

The charge separation distances for both diamines by whatever model is used fall within the region of 4.66 to 4.86 Å. These suggest similar backbone and steric configurations for these molecules so that the difference in ΔpK values, aside from an added inductive effect in II, is a result of a 25% decrease in effective cavity dielectric constant for the larger molecule.

The charge separation distances also fall within the limits for the theoretical H to H distance for a di-acidified ethylenediamine skeleton defined by the extended chain value of 5.10 Å. and by the free rotation value of 3.94 Å.[11] Structural parameters used in these latter calculations were as follows: $r_{\mathrm{N-H}} = 1.03$ Å.[12], $r_{\mathrm{C-N}} = 1.47$ Å.,[13] $r_{\mathrm{C-C}} = 1.54$ Å.,[13] with all bond angles assumed to have the tetrahedral value of 109°28′.

The exceedingly good results obtained from the Kirkwood–Westheimer calculations may well be fortuitous, but the agreement is heartening.

Contributions from steric factors imposed by the added methyl group in II might play a role by increasing the energy in the conformation with "*trans*" dimethylamino groups so that the preferred orientation is skewed, resulting in a smaller value for the charge separation. However, scale molecular models of either the Fisher–Hirschfelder–Taylor or Stuart–Briegleb type would not suggest large contributions from this source.

Experimental

N,N,N′,N′-Tetramethyl-1,2-ethanediamine (I).—This diamine was prepared by a procedure analogous to that used for the propane homolog II[14] and in comparable yield. For the basicity measurements, a fraction was taken boiling at 119.4–119.5° at 724 mm. (lit.[15] b.p. 120° at 760 mm.), with $n^{18}\mathrm{D}$ 1.4196 (lit. $n^{20}\alpha$ 1.4180, $n^{20}\beta$ 1.4298[16]). The freezing point, previously unreported, was −55.1°, as determined from cooling curves.

N,N,N′,N′-Tetramethyl-1,2-propanediamine (II).—The preparation and properties of this compound have been published elsewhere.[14]

Base Strengths.—For the determination of pK_{ai} values, aqueous solutions, about 10^{-2} M in diamine and 0.5 M in sodium perchlorate, were potentiometrically titrated at 30° with 0.1 N aqueous perchloric acid, using glass and saturated calomel electrodes with a Beckman model G pH-meter. The sodium perchlorate, added to swamp out effects from changing ionic strength, was reagent grade material further purified by recrystallization from water. It gave a neutral aqueous solution. The diamines and aqueous perchlorate solutions were each separately saturated with argon gas bubbled in for at least one half hour to displace carbon dioxide and prevent its influencing the titration. The argon, obtained from a high pressure cylinder, was purified and dried by passage through towers of soda-lime and anhydrous magnesium perchlorate.

The pK_{ai} values were determined from graphical interpolation on the titration curve plot for the pH at the half-neutralization point between each equivalent step. At least two independent titrations were performed on each diamine. The titration curves were clear and the equivalence points sharp so no difficulty was experienced in the determinations.

WRIGHT–PATTERSON AIR FORCE BASE, OHIO

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[11] Computed from the formula of H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[12] This was taken from the work on ammonium halides wherein the neutron diffraction value of H. A. Levy and S. W. Peterson, *Phys. Rev.*, **86**, 766 (1952) and the nuclear magnetic resonance data of H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 643 (1954) and of R. Bersohn and H. S. Gutowsky, *ibid.*, **22**, 651 (1954), all agree within 0.01 Å. See also Table VI in H. A. Levy and S. W. Peterson, THIS JOURNAL, **75**, 1536 (1953).

[13] Concordant values were taken from electron diffraction data on simple aliphatic amines listed in the compilation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[14] R. W. Moshier and L. Spialter, *J. Org. Chem.*, **21**, 1050 (1956).

[15] G. F. Grail, L. E. Tenenbaum, A. V. Tolstoouhov, C. J. Duca, J. F. Reinhard, F. E. Anderson and J. V. Scudi, THIS JOURNAL, **74**, 1313 (1952).

[16] H. T. Clarke, *J. Chem. Soc.*, **101**, 1788 (1912).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

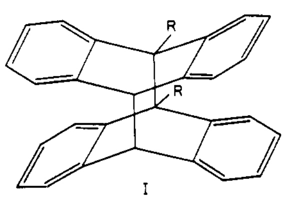
The Acid-catalyzed Dissociation of Bis-9-anthraldehyde[1]

BY FREDERICK D. GREENE, SANTIAGO ROBLEDO OCAMPO AND LOUIS A. KAMINSKI[2]

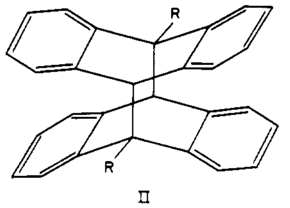
RECEIVED JULY 2, 1957

The photodimer of 9-anthraldehyde (I, R = CHO, bis-9-anthraldehyde) has been shown to undergo facile acid-catalyzed cleavage to 9-anthraldehyde in benzene solution. The cleavage reaction shows great sensitivity to the strength of the acid catalyst, exhibiting the following relative rate sequence at 25°: trifluoroacetic acid, 10^5; trichloroacetic acid, 10^4; dichloroacetic acid, 10^2; monochloroacetic acid, 0.45. The order in stoichiometric acid concentration is a function of the acid strength: trifluoroacetic acid, 2.44; trichloroacetic acid, 2.06; dichloroacetic acid, 1.96; monochloroacetic acid, 1.47. The isotope effect, $k_{\mathrm{cH}}/k_{\mathrm{cD}}$, for dichloroacetic acid and dichloroacetic acid-*d* is 1.1. The driving force for the cleavage reaction is attributed to the electrostatic repulsion between the carbonyl carbon atoms arising from coördination of acid moieties with the oxygen atoms of the formyl groups (V).

Sunlight effects the conversion of a wide variety of anthracene derivatives to dimeric structures in which the two anthracene units are bonded together at the 9,9′- and 10,10′-positions. For the dimerization of a 9-substituted compound, two such structures are possible, I and II. Structure I has been established for the photodimers derived from the 9-



I



II

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[1] Presented before the Organic Division of the 131st Meeting of the American Chemical Society in Miami, Florida, April, 1957.

[2] Cabot Solar Energy Fellow, 1956–1957.