The hydrochloride, prepared by solution of the base in 0.1 *N* hydrochloric acid and subsequent evaporation in a desiccator, melted at 200° dec.

Anal. Calcd. for $C_{15}H_{20}N_6O_3 \cdot HCl$: C, 48.84; H, 5.74; N, 22.79; Cl, 9.61. Found: C, 48.81; H, 5.72; N, 22.71; Cl, 9.60.

The monobenzamide was prepared by adding 0.15 ml. of benzoyl chloride to 400 mg. of base suspended in pyridine (4.0 ml.). After standing for two hours, the reaction mixture was worked up by addition of 20 ml. of ether, which resulted in the deposition of a gummy solid. After being washed with ether and triturated with chloroform, the solid was crystallized from ethanol. The amide (230 mg.) was secured as colorless needles, m.p. 271°.

Anal. Calcd. for $C_{22}H_{24}N_6O_4$: C, 60.59; H, 5.53; N, 19.28. Found: C, 60.51; H, 5.50; N, 19.22.

The diacetyl derivative of the C_{15}-base was obtained by acetylation with isopropenylacetate in glacial acetic acid, the reaction mixture being refluxed for one hour. The product, isolated by ether precipitation, was recrystallized twice from ethanolic ether, after which it melted at 157–158°.

Anal. Calcd. for $C_{15}H_{18}N_6O_3(CH_3CO)_2$: C, 54.70; H, 5.80. Found: C, 54.78; H, 5.81.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE METCALF LABORATORIES, BROWN UNIVERSITY]

Reactions of Ethylenimines. VIII. Dissociation Constants

BY CHARLES E. O'ROURKE, LEALLYN B. CLAPP AND JOHN O. EDWARDS

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Ethylenimine, 2,2-dimethylethylenimine and 2-ethylethylenimine were found to be weak bases with pK_B values of 5.99, 5.36 and 5.69, respectively.

In spite of the fact that ethylenimines(aziridines) have been known since 1888[1] no apparent attempt has been made to determine their basic strengths in aqueous solution. The problem was avoided in these laboratories for a long time because it appeared that hydrolysis would make such a measurement difficult by the usual techniques. But a hint was available in the literature[2] that the reaction with water was slow and our own recent kinetic work on the hydrolysis of ethylenimines[3] in acid made the measurement of base strength appear feasible.

The dissociation constants of ethylenimine, 2,2-dimethylethylenimine, 2-ethylethylenimine and three related amino alcohols have been determined by use of the glass electrode *p*H meter. While the dissociation constants measured thus and presented in Table I are not true thermodynamic values, the *relative* basicities may be determined quite precisely. In this actual case, the values of K_B may be close to the thermodynamic values since the values of K_a for the conjugate acids of the imines and amino alcohols were found to be independent of ionic strength in the range from 0.01 to 0.1. The constants obtained for the three amino alcohols compare favorably with the thermodynamic values given by Glasstone and Schram.[4]

TABLE I

DISSOCIATION CONSTANTS OF ETHYLENIMINES AND AMINO-ALCOHOLS AT 25°

Compound	pK_B (obsd.)	K_B	pK_B (lit.)[a]
Ethylenimine	5.99	1.0×10^{-6}	
2-Ethylethylenimine	5.69	2.0×10^{-6}	
2,2-Dimethylethylenimine	5.36	4.3×10^{-6}	
Ethanolamine	4.56	2.8×10^{-5}	4.55
2-Amino-1-butanol	4.45	3.3×10^{-5}	4.48
2-Methyl-2-amino-1-propanol	4.29	5.3×10^{-5}	4.28

[a] Ref. 4.

The experimental value for the dissociation constant of ethylenimine is in accord with the prediction of Brown and Gerstein[5] that it would be weaker than dimethylamine ($K_B = 7.4 \times 10^{-4}$). The value for ethylenimine may also be considered to meet the qualification of "low basicity" mentioned by Searles, Tamres and Lippincott.[6] Furthermore, the value of K_B for ethylenimine itself (1.0×10^{-6}) is in agreement with the results of Barb[7] (7 to 9×10^{-7}), reported since this work was completed.

As may be seen in Table I, C-alkyl groups on ethylenimines have an effect of considerable size on the basicity of the ring nitrogen atom. The enhancement is an order of magnitude or so larger than would be expected for an inductive effect through a saturated carbon atom. It is of the same magnitude as the effect of 3- or 4-methyl groups in many aromatic systems, although it is less than that caused by a 4-methyl group in either pyridine or aniline.[8] It is well known that three-membered rings of the cyclopropane, ethylene oxide and ethylenimine types behave in a manner similar to an unsaturated system.[9] The large enhancement of nitrogen basicity by C-alkyl substitution which is described here seems to be an example of this "unsaturated character" of three-membered rings.

Experimental

The ethylenimines were prepared by the method of Wenker[10] and distilled from sodium just prior to use. The index

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(1) S. Gabriel, *Ber.*, **21**, 1049 (1888).

(2) H. Freundlich and W. Neumann, *Z. physik. Chem.*, **87A**, 69 (1914), and later papers of Freundlich.

(3) V. B. Schatz and L. B. Clapp, THIS JOURNAL, **77**, 5113 (1955).

(4) S. Glasstone and A. F. Schram, *ibid.*, **69**, 1213 (1947).

(5) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

(6) S. Searles, M. Tamres and E. R. Lippincott, *ibid.*, **75**, 2775 (1953).

(7) W. G. Barb, *J. Chem. Soc.*, 2564 (1955).

(8) A compilation of pK_a values for aromatic systems may be found in D. H. McDaniel and H. C. Brown, THIS JOURNAL, **77**, 3756 (1955).

(9) Lists of pertinent references may be found in (a) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); (b) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson and J. H. Anglin, THIS JOURNAL, **73**, 1044, 5929 (1951); (c) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030, 5034 (1951); (d) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(10) (a) H. Wenker, *ibid.*, **57**, 2328 (1935); (b) T. L. Cairns, *ibid.*, **63**, 871 (1941); (c) G. D. Jones, *J. Org. Chem.*, **9**, 484 (1944).

of refraction of each imine[10] and freshly distilled amino alcohol[11] was an accepted value.

Approximately a 0.1 *M* solution of reagent grade perchloric acid was prepared and its molarity determined to three figures. The acid solution and the imine were cooled to about 20°. The imine was then added quickly from a weight buret to the acid in a vessel in a constant temperature bath at 25.0 ± 0.1°. In later runs it was found to be more convenient to add the imine from a calibrated syringe (precision = ±0.004 g. for a two-gram aliquot).

The temperature of the mixture rose to 25° as a result of the heat of neutralization and remained constant after about 30 seconds. The *p*H was measured with a Beckman model G *p*H meter after equilibrium was reached (about two minutes).

In a solution containing the weak organic base (symbol, B) and its conjugate acid (symbol, HB^+), it can be shown that

$$[OH^-] = K_B \frac{[B]}{[HB^+]}$$

When [B] and $[HB^+]$ are present in equivalent amounts, $[OH^-]$ equals K_B and it follows (assuming pK_a is independent of ionic strength) that $pK_B = 14.00 - pH$. The values given in Table I are the averages of ten runs (after a series of preliminary runs) for each imine. The average deviation from the mean *p*H value was 0.010.

At an ionic strength of 0.1, there was a drift in the *p*H of the solution (under a nitrogen atmosphere) in the case of 2,2-dimethylethylenimine from 8.63 to 8.50 over a 5-hour period. When the solution was diluted threefold, no drifting occurred in one hour. The *p*H value was identical with the highest value obtained at the higher concentration. The drift to a lower *p*H is not due to hydrolysis to an aminoalcohol since the *p*H should increase in that case.

The observed stability of the imines in this system suggested the possibility of obtaining complete neutralization curves. Accordingly an aqueous solution was titrated with dilute perchloric acid and the *p*H measured after addition of each acid increment. All the imines gave sharp endpoints and the *p*H values at the points of half-neutralization were identical with those obtained by direct addition of imine to acid.

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(11) C. D. Hodgman. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, Ed. 36, 1954.

[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ACTON TECHNICAL COLLEGE, AND THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

The Absorption Spectra of Aromatic Azo and Related Compounds. I. Azoxybenzenes

BY PETER H. GORE[1a] AND OWEN H. WHEELER[1b]

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The ultraviolet absorption of a number of azoxybenzenes has been measured. The results are interpreted in terms of the electronic and steric effects of the substituents.

Apart from some early studies[2] of the effects of substituents on the absorption spectra of azoxybenzene, no systematic study has been attempted. It is the purpose of this paper to give such data, in particular for symmetrically disubstituted *trans*-azoxybenzenes.

The ultraviolet absorption of aliphatic azoxy compounds recently has been shown[3] to consist of two bands, a maximum near 220 mμ (ε 7,000) and an inflection near 275 mμ (ε 50); however, an assignment of the two bands was not attempted. It seems probable that the band near 220 mμ, being of high intensity, is due to an electronic transition (E-band) involving the –N=N– system and, as would be expected, alkyl groups shift this band by 4–7 mμ. The weaker band near 270 mμ is probably due to a radical transition (R-band) in the azoxy groups, corresponding to the band near 350 mμ (ε ∼ 10) in azomethane.[4] Coördination of an oxygen atom leads to a hypsochromic shift, as well as an increase in absorption intensity, and this is the typical effect of substitution on R-bands.[5]

A series of disubstituted azoxybenzenes has been prepared and their spectra taken (see Table I). Absorption occurs in three main regions: *ca.* 230, 260 and 320 mμ (designated E_1-, E_2- and K-bands). The R-band of aliphatic azoxy compounds will be submerged in the high intensity band at *ca.* 320 mμ. This is a point of distinction from the otherwise very similar spectra of azobenzenes,[6] in which the R-bands occur in the visible region, since the R-band of aliphatic azo compounds is at a higher wave length,[4] and undergoes a bathochromic shift in the benzene derivatives into the near visible region.

The band (E_1) at *ca.* 230 mμ[7] is not appreciably affected in wave length by substitution, changes only occurring in the absorption intensity. A similar band is also present in the spectra of phenylnitrones[8a] and azobenzenes,[8b] and is attributed to electronic transitions in the benzene rings, arising from the E-band of benzene (*ca.* 205 mμ, ε 6,300)[9] which has been displaced by substitution of the azoxy group to *ca.* 230 mμ, and is not appreciably displaced by further substitution. This E_1-band sometimes appears as two separate peaks, which may be due to unequal polarization of the two benzene rings[10] by the unsymmetrical azoxy group; such double maxima are not found in azo compounds.[8b]

A second band (E_2) is shown by azoxybenzene itself and a few of its derivatives. The actual position of the absorption band (at *ca.* 250 mμ) suggests that the E_2-transition involves one of the benzene rings and the azoxy linkage. In many of the disub-

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(1) (a) Acton Technical College, London; (b) Universidad Nacional Autónoma de México, Mexico.

(2) (a) E. Müller and E. Hory, *Z. physik. Chem.*, **A162**, 281 (1932); (b) L. Szegö, *Ber.*, **61**, 2087 (1928); **62**, 736 (1929).

(3) B. W. Langley, B. Lythgoe and N. V. Riggs, *J. Chem. Soc.*, 2309 (1951); B. W. Langley, B. Lythgoe and L. S. Rayner, *ibid.*, 4191 (1952).

(4) A. Hantzsch and J. Lifschitz, *Ber.*, **45**, 3011 (1912).

(5) A. Buraway, *J. Chem. Soc.*, 1177 (1939).

(6) A. Buraway, *ibid.*, 1865 (1937); A. H. Cook, D. G. Jones and J. B. Polya, *ibid.*, 1315 (1939).

(7) This band was not detected in much of the early work.

(8) (a) Part II, THIS JOURNAL, **78**, in press (1956); (b) Part III, in preparation.

(9) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(10) α denotes substitution in the ring remote from the N→O group, and β in the other ring.