138. *The Influence of Conjugation on the Ionization of Aromatic Amines.*

By N. S. Hush.

The energy changes attending ionization of aromatic mono- and di-amines are discussed. Where the main variable factor controlling ionization may be taken to be the change in π-electron energy on addition of a proton, the variations of dissociation constant can be understood in terms of LCAO molecular orbital and first-order perturbation theory. In particular, it becomes clear why differences in energy of ionization amongst bases of these types are so much smaller than for proton addition to nuclear nitrogen in isoconjugate heteroaromatic amines. The types of energy change for the different ionizations are examined, and approximate values of some Coulomb integrals are obtained. The energetics of prototropic reactions involving aminium ions are also considered.

The electron densities of 15 dicarbanions are given in an appendix.

In this paper, the ionization constants of aromatic monoamines and diamines are correlated with the differences in π-electron energy between the proton donors and acceptors of the acid–base systems. There are two main assumptions underlying this procedure: the first that the difference in standard free energy of ionization of two bases of similar charge distribution in a given solvent at a fixed temperature is equal to the difference of potential energy accompanying proton addition in the gas phase, *i.e.*, to the difference of proton affinity of the molecules; and the second that, for these compounds, the change of potential energy ΔE_p accompanying proton addition in the gas phase is equal to the difference in unsaturation energy $\Delta\varepsilon$ between donor and acceptor plus a constant term, *i.e.*, that the proton affinity E_h of such a molecule in the gas phase is given by $E_h = E_h^\circ + \Delta\varepsilon$, where E_h° is a constant.

Although neither assumption can be strictly correct, it is probable that neither is so much in error that the general correlations of features of electronic structure with basic strength, which are at best semi-quantitative, will be invalidated. This is supported by the reasonable correlation with experimental data of the analogous treatment of proton addition to heterocyclic amines by Longuet-Higgins (*J. Chem. Physics*, 1950, **18**, 275, hereafter referred to as Ref. 1). Wheland's discussion of hydrocarbon ionization (*ibid.*, 1934, **2**, 474) is also of interest in this connection. On this basis, we may write as a fair approximation :

$$\varepsilon_{\text{donor}} - \varepsilon_{\text{acceptor}} = \text{const.} - 2\cdot3RT\text{p}K_a \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

The unsaturation energies of donor and acceptor ions and molecules have been calculated by a combination of LCAO molecular orbital and first-order perturbation theory. Non-orthogonality of adjacent atomic orbitals has been neglected; this will not lead to serious error for these systems (cf. Coulson and Chirgwin, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196).

Electronic Structure.—It is assumed that the proton donors and acceptors are isoconjugate with (*i.e.*, contain the same number of π-electrons in approximately the same geometrical configuration of atomic p-orbitals as) the hydrocarbons obtained by replacing NH_3^+ by H and NH_2 by CH_2^-; *e.g.*, in the simplest case, (I) and (II) are isoconjugate with (III) and (IV), respectively. This representation ignores the possibility of hyperconjugation of NH_3^+, which is reasonable to this approximation. It assumes also that the NH_2 group conjugates with the aromatic residue, and that the magnitude of the N Coulomb and NC resonance integrals are such that this group may be treated in first-order approximation as a perturbed CH_2^-. These assumptions, although usual, merit brief discussion. It is certain that considerable delocalization of NH_2 and NR_2 non-bonding electrons occurs when these groups are attached to aromatic or heteroaromatic residues. The most direct evidence for this (at least in monoamines) is provided by the marked effects of *o*-substituents which are large enough to twist the amino-group out of

the aromatic plane on the frequency and intensity of electronic transitions (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838; Klevens and Platt, *ibid.*, 1949, **71**, 1714) and on the dipole moments (Ingham and Hampson, *J.*, 1939, 981) of the molecules. Also, it has long been recognized that the basicity of an aromatic amine can be increased by a predominantly steric effect by introduction of bulky *o*-substituents (Davies and Addis, *J.*, 1937, 1622), and the highest pK known for an aromatic monoamine is for a sterically-hindered molecule of this type, *viz.*, NN-diethyl-*o*-toluidine, pK 7·2 (cf. Albert, *Chem. and Ind.*, 1947, 51). Since dipole measurements on *p*-diamines (Bretscher, *Helv. Phys. Acta*, 1928, **1**, 355; Williams and Weissberger, *J. Amer. Chem. Soc.*, 1928, **50**, 2332; Weissberger and Sängewald, *Z. physikal. Chem.*, 1929, B, **5**, 237; Linke, *ibid.*, 1940, **46**, 261) show that the NH_2 groups are far from flat in molecules of this sort, a considerable approximation is involved
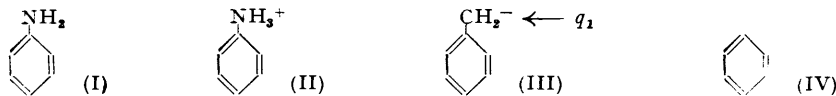
in treating the N wave-function as pure $2p\pi$.* However, this wave-function has sufficient π-character to conjugate strongly with an aromatic ring, so that it is reasonable to suppose that (to first-order approximation) deviations from trigonal hybridization can be regarded as part of the perturbation H' applied to the one-electron Hamiltonian of the hydrocarbon analogue by nitrogen substitution. This assumption is justified *a posteriori* by the success of treatments of related phenomena in which it is implicit (see Longuet-Higgins, Ref. 1; Longuet-Higgins, Rector, and Platt, *J. Chem. Phys.*, 1950, **18**, 1174; Hush, *ibid.*, 1952, **20**, 1660).

Calculation of Unsaturation Energies.—Where $e_H{}^j$ is the energy of a π-electron in the MO ψ^j of the isoconjugate hydrocarbon ($\psi^j = \Sigma c_r{}^j\phi_r$), the energy e^j in the nitrogen-substituted molecule is, to first-order approximation,

$$e^j = e_H{}^j + \Sigma\Sigma c_r{}^j c_s{}^j \int \phi_r H' \phi_s{}^* d\tau$$

Assuming that integrals other than Coulomb terms of the type $\int \phi_r H' \phi_r{}^* d\tau = \delta\alpha_r$ are small enough to be ignored,† and summing over all π-electrons, we obtain (cf. Ref. 1)

$$\varepsilon - \varepsilon_{(H)} = \Sigma q_r \delta\alpha_r \qquad \qquad \cdots \qquad (2)$$

where ε is the unsaturation energy of the amine molecule or ion, $\varepsilon_{(H)}$ is that of the iso-conjugate hydrocarbon, and q_r is the π-electron density at atom r in the hydrocarbon. Unless otherwise specified, energy terms are expressed in units of β_{CC}, the CC resonance integral.

The two important $\delta\alpha_r$ terms to be taken into account are y, the difference in Coulomb integral between NH_2 and CH_2, and z, the change in Coulomb integral of carbon in the aromatic $\geqslant CH$ grouping when H is replaced by $NH_3{}^+$. (The small change in Coulomb integral of the ring carbon atom on substitution of NH_2 can be ignored in this approximation.) Thus, the unsaturation energy change $\Delta\varepsilon$ accompanying addition of a proton to an amine can be expressed as :

$$\Delta\varepsilon = \varepsilon_{donor} - \varepsilon_{acceptor} = \varepsilon_{(H)\ donor} - \varepsilon_{(H)\ acceptor} - f(y) - g(z).$$

The term $\varepsilon_{(H)\ donor} - \varepsilon_{(H)\ acceptor}$ will be written for brevity as $-\varepsilon_{conj.}$; and substituting in eqn. (1) we have, for any amine,

$$2\cdot 3\ RT p K = \varepsilon_{conj.} + f(y) + g(z) + A \qquad \cdots \qquad (3)$$

where A is a constant. In the case of diamines, a small statistical correction must be made to the constant A, since, where there is no interaction between the amino-groups in a symmetrical diamine, the statistical ratio K_2/K_1 is 4, whence $pK_1 - pK_2 = 0\cdot6$ unit

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* For discussion, see Sklar, *J. Chem. Phys.*, 1939, **7**, 984; Goeppert-Mayer and McCallum, *Rev. Mod. Phys.*, 1942, **14**, 248; Coulson, "Valence," Oxford, 1952, p. 246. The uncertainty introduced into the MO treatment by this effect has been mentioned by de Heer (Thesis, Amsterdam, 1950, p. 70) and by Coulson and de Heer (*J.*, 1952, 483).

† The validity of this assumption is discussed below.

(cf. Greenspan, *Chem. Reviews*, 1933, **12**, 339). [This appears to hold for crystal-violet, for which $K_2/K_1 = 4\cdot08 \pm 5\%$ (Adams and Rosenstein, *J. Amer. Chem. Soc.*, 1914, **36**, 1452).]

In applying eqn. (3), it will be assumed that the isoconjugate hydrocarbon is always an alternant molecule, *i.e.*, one containing no odd-membered rings (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, A, **191**, 39); in all cases, the extension to non-alternant systems is obvious.

The values of the Coulomb terms y and z are fixed, but the functions $f(y)$ and $g(z)$ differ according as the proton acceptor is a monoamine, a diamine mono-ion, or a diamine.

(a) *Monoamines.* In this case,

$$f(y) = q_1 y, \quad g(z) = -z$$

where q_1 is the π-electron density at the extracyclic position in the monocarbanion isoconjugate with the acceptor [cf. (III)]. The carbanion contains one non-bonding MO, while the hydrocarbon isoconjugate with the proton acceptor contains no such MO; since the discussion is limited to alternant molecules it follows (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193) that $g(z) = -z$.

(b) *Second ionization of diamines* (K_2). Here a proton is added to a diamine mono-ion, *e.g.*, (V) + H$^+$ ⟶ (VI). Hence for this ionization,

$$f(y) = q_1 y, \quad g(z) = (q_2 - 2)z$$

where q_2 is the π-electron density in the carbanion isoconjugate with the acceptor at the position of substitution of NH$_3^+$. [In the above example, this is the position in (III) marked with an arrow.]
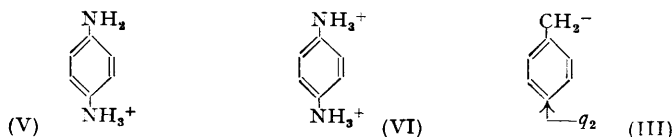
(c) *First ionization of diamines.* The acceptor in this reaction is the donor of the corresponding second ionization, as *e.g.*, (VII) + H$^+$ ⟶ (VIII). Hence

$$f(y) = (q_3 + q_4 - q_1)y, \quad g(z) = -q_2(z)$$

where q_3 and q_4 are the π-electron densities at the extracyclic carbon atoms in the dicarbanion isoconjugate with the diamine [*e.g.*, (IX)]. The dicarbanion may or may not contain non-bonding MO.
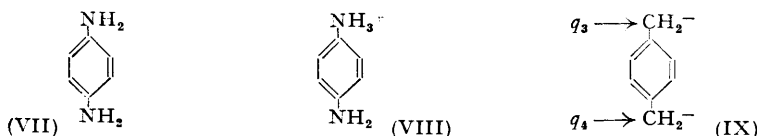
The values of $\varepsilon_{\text{conj.}}$, $f(y)/y$, $g(z)/z$, and pK are tabulated in the Table for all systems for which reliable data are available.

Magnitude of Perturbation Terms.—In order to test the theory, values of the Coulomb terms y and z are required. The magnitude of y should not differ greatly from the corresponding value of $\delta\alpha$, for heterocyclic nitrogen; typical values proposed for this term are 1·0 (Brown, *Quart. Reviews*, 1952, **6**, 1) and 0·6 (Löwdin, *J. Chem. Phys.*, 1951, **19**, 1323). In order to obtain a value appropriate to these systems from the experimental data, it is necessary to express $\varepsilon_{\text{conj.}}$ in absolute units, and the usual value of $\beta_{CC} = ca. -20\cdot0$ kcals. mole^{-1} (cf. Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025) is assumed. For monoamines, a plot of $2\cdot3RT$p$K - \varepsilon_{\text{conj.}}$ against q_1 yields a fairly straight line of negative gradient, which, according to eqn. (3), should be y. The value found in this way is -13 kcal. mole^{-1} or $0\cdot65\beta$. This value has been assumed in all subsequent calculations.

Since an aromatic carbon atom will have less electronic charge when bound to NH$_3^+$ than when bound to H, z should also be negative, and on general grounds (Coulson and Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 57), z would be expected to be of the order of $\sim 0\cdot5\beta$.

A value of z has been found from the plot of $2 \cdot 3RT \mathrm{p}K_1 - \varepsilon_{conj.} - \mathrm{f}(y)$ against q_2 for the first ionization of diamines; this yields $z = ca. -9$ kcal. mole^{-1}, or $0 \cdot 45\beta$. The value is reasonable, and is assumed in subsequent calculations.*

Comparison with Experimental Ionization Data.—The Table contains the appropriate data for a number of amines and diamines. For a direct test of the theory, it has been thought best to list observed and calculated differences of pK for an amine from those for a standard amine; this avoids the introduction of further parameters. The amine chosen arbitrarily as standard is β-naphthylamine.

The calculated and observed pK values in the last two columns of the Table show a general parallelism which is as close an agreement as can be expected in this approximate treatment. Large deviations are found only for the diamines (16, 21) in which the amino-groups are in the *o*-position to each other or (to a lesser extent) in the *peri*-position (20); special effects of this sort are well-known for aromatic base systems (Albert and Goldacre, *J.*, 1946, 706). Apart from these extreme cases, energy and entropy terms arising from the proximity of the two groups are not large enough to upset the trends of pK

Extracyclic electron densities and conjugation energies of aromatic methyl radicals.

Numbering as in the Table for 2, 3, 4, 5, and 7, with addition of 9-anthrylmethyl (8), 4-stilbenylmethyl (9), and 4-styrylmethyl (10). Sources of energy data are those given in the Table.
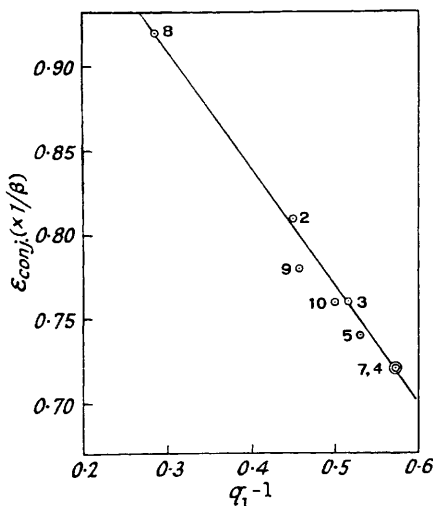
with structure predicted by eqn. (3); in particular, the effect of a charged NH_3^+ group on the distribution of H^+ ions about a diamine mono-ion in solution on the second ionization of the base appears to be small. The magnitudes of similar effects in dicarboxy-compounds have been discussed by Greenspan (*loc. cit.*).

Discussion.—The most striking feature of the ionization of aromatic monoamines is the very small variation in pK in a range of molecules in the hydrocarbon analogues of which there is a reasonably large variation in conjugation energy and charge density of the extracyclic atom. This approximate constancy is in marked contrast to the very large variations of dissociation constant for addition to the ring-nitrogen atom of heteroaromatic amines such as aminoacridines (Albert, " The Acridines," Edward Arnold & Co., 1951, Chap. IX) and aminoquinolines with similar changes in charge density at the position of proton-addition. This suggests a compensation of competing effects for molecules of the former type; and in fact, the main reason for the lack of variation of K for monoamines is that in carbanions of the type $Ar–CH_2^-$, where Ar is an aromatic residue, the conjugation energy of the extracyclic group is a linear function of q_1, such that increase in conjugation energy is always accompanied by decrease in q_1. This linear relation is illustrated in the Figure.

The fundamental relation here is that between the conjugation energy and the modulus

* The difference of intercepts for the plots for monoamines and second diamine ionization yields approximately the same value. That z is small is shown by the small effect of NH_3^+ substitution on the ultra-violet absorption envelope of the hydrocarbon (Jones, *Chem. Reviews*, 1943, **32**, 1; Sklar, *loc. cit.*).

of the extracyclic AO coefficient in the non-bonding MO of the radical, which is similarly linear. This relation can be understood theoretically, and will be discussed elsewhere.

The gradient in the figure indicates that, since y is negative and of the same order as β_{CC}, in monoamines base-weakening increase in conjugation energy of the CH_2^- group is always compensated by base-strengthening decrease in π-electron density at this position in the carbanion; the approximate constancy of pK is thus understandable.

Amine	No.	Carbanion*	$\varepsilon_{conj.}$	$f(y)/y$	$g(z)/z$	pK_i	$pK-pK(\beta-C_{10}H_7\cdot NH_2)$: obs.	calc.
1-Anthrylamine	1	CH_2^- (structure)	0.84^a	1.381	-1	$4.1_{25}{}^c$	-0.2	-0.1
α-Naphthylamine	2	CH_2^- (structure)	0.81	1.450	-1	$4.10_{22}{}^d$	-0.2	-0.3
p-Aminodiphenyl	3	$-CH_2^-$ (structure)	0.76	1.516	-1	$4.38_{18}{}^e$	0.1	-0.2
Aniline	4	CH_2^- (structure)	0.72	1.572	-1	$4.67_{21}{}^d$	0.4	-0.1
β-Naphthylamine	5	CH_2^- (structure)	0.74	1.529	-1	$4.25_{23}{}^d$	0	0
o-Aminodiphenyl	6	CH_2^- (structure)	0.76^a	1.516	-1	$3.85_{18}{}^e$	-0.4	-0.2
m-Aminodiphenyl	7	CH_2^- (structure)	0.72	1.572	-1	$4.28_{17}{}^e$	0	-0.1
p-Phenylenediamine$_2$	8	$-CH_2^-$ (structure)	0.72	1.572	-0.857	$3.11_{25}{}^f$	-1.1	-1.1
Benzidine$_2$	9	$-CH_2^-$ (structure)	0.76	1.516	-0.968	$3.85_{25}{}^g$	-0.4	-0.4
Stilbene-pp'-di-amine$_2$	10	$-CH:CH-\cdots-CH_2^-$ (structure)	0.78	1.457	-0.971	$\sim3.9_{25}{}^c$	-0.4	-0.1
1 : 4-Naphthylene-diamine$_2$	11	CH_2^- (structure)	0.81	1.450	-0.800	$2.78_{25}{}^c$	-1.5	-1.6
p-Phenylenedi-amine$_1$	12	A	0.58	1.758	-1.143	6.34_{25}	2.1	1.7
Stilbene-pp'-di-amine$_1$	13	O	0.74	1.563	-1.029	$\sim5.2_{25}{}^c$	1.0	0.5
1 : 4-Naphthylene-diamine$_1$	14	D	0.59	1.778	-1.200	$5.87_{25}{}^c$	1.6	1.7
m-Phenylenedi-amine$_1$	15	B	0.72^b	1.594	-1	$5.02_{20}{}^h$	0.8	0.3
o-Phenylenedi-amine$_1$	16	C	0.65	1.608	-1.143	$4.60_{20}{}^i$	(0.4 *ortho-*	2.1)
Benzidine$_1$	17	N	0.71	1.598	-1.032	$4.95_{25}{}^g$	0.7	0.6
1 : 5-Naphthylene-diamine$_1$	18	H	0.75	1.586	-1.050	$4.70_{20}{}^{j}{}^*$	0.2 †	0.2
1 : 4-Naphthylene-diamine$_1$	19	D	0.59	1.778	-1.200	$5.54_{21}{}^j$	1.6	1.7
1 : 8-Naphthylene-diamine$_1$	20	G	0.77	1.576	-1	$4.29_{17}{}^j$	(0.4 *peri-*	-0.3)
2 : 3-Naphthylene-diamine$_1$	21	F	0.77	1.419	-1.059	$3.54_{21}{}^j$	(-0.4 *ortho-*	1.6)
2 : 6-Naphthylene-diamine$_1$	22	J	0.68	1.653	-1.059	$4.93_{20}{}^j$	1.0	0.7
2 : 7-Naphthylene-diamine$_1$	23	K	0.76	1.533	-1	$4.55_{18}{}^j$	0.6	0.3

* The carbanions corresponding to 12—23 are given in the appendix.

[Footnotes on p. 689]

It will be noticed that there is much more variation of pK_1 of diamines with variation in structure than is found for monoamines; this is largely due to the fact that for these molecules there is no such regular compensation of differences in $\varepsilon_{conj.}$ by the perturbation term $f(y)$.

The conjugation term contributing to differences in ionization constant between a diamine mono-ion and the corresponding monoamine is simply $g(z)$; from eqn. (3) and the listed values of $g(z)$, it follows that

$$pK(\text{monoamine}) - pK(\text{diamine mono-ion}) = -(q_2 - 1)z/2 \cdot 3RT$$

Since q_2 is always $\geqslant 1$ and z is negative, the monoamine should always have the higher pK. This is so for all systems of this type listed in the Table.

Prototropic Equilibria of Diamine Ions.—For all diamines so far discussed, reference to the monocarbanion isoconjugate with the proton donor of the first ionization has been unambiguous since, in these symmetrical molecules, the ion obtained by addition of a proton to either of the two amino-groups is the same. This is, of course, not always so; amines such as 1 : 6-naphthylenediamine (X) or diphenyline (XI) can accept a proton at either of the two amino-groups to form a different aminium ion in each case. The carbanions isoconjugate with the aminium ions obtained on addition to the 1- and 6-amino-groups of (X) are respectively Nos. 5 and 2 (Table). Where $\varepsilon\beta_1$, $\varepsilon\alpha_1$, $q\beta_1$, $q\alpha_1$ are the


unsaturation energies and extracyclic-carbon atom electron densities of Nos. 5 and 2 the difference in first ionization constant of the two centres is

$$pK(1)_1 - pK(6)_1 = (1/2 \cdot 3RT)[\varepsilon\alpha_1 - \varepsilon\beta_1 + y(q\alpha_1 - q\beta_1)] \simeq -0.2$$

Therefore the 6-position is the more basic in (X); the difference of basicity is approximately the difference between that of α- and of β-naphthylamine.

It is noteworthy that since the equilibrium constant for the prototropic reaction
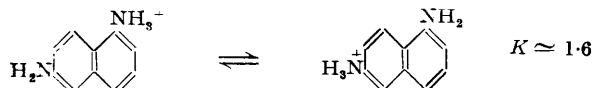
is not far from unity, determination of the dissociation constant by a potentiometric method will yield, not the true value, but a composite constant $K(1)_1 K(6)_1/[K(1)_1 + K(6)_1]$. This source of error will generally be appreciable with amines of this type, as the basicities of the two groups are usually not very different.

Proton Dismutation in Diamine–Diaminium Ion Systems.—A further general feature of diamines so far discussed is that in all cases the free energy of the proton dismutation reaction

$$2AH^+ \rightleftharpoons A + AH_2^{++}; \quad \Delta G_D = 2 \cdot 3RT(pK_1 - pK_2)$$
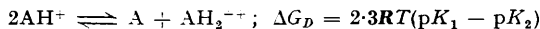
is positive. There is, however, an appreciable variation in this quantity over the range

Values of $\varepsilon_{conj.}$ (in units of β_{CC}) are calculated from data listed by Wheland (*loc. cit.*), Syrkin and Diatkina (*Acta Physicochem. U.R.S.S.*, 1946, **21**, 23. 641), and Pullman, Berthier, and Pullman (*Bull. Soc. chim.*, 1948, **15**, 540) except where otherwise specified. Charge densities in the dicarbanions (A—O) are listed in the Appendix, p. 691. Dissociation constants were measured in water at the indicated temperature, unless otherwise specified.
   [a] Approximate values, from linear plot of $\sqrt{\text{self-polarizability}}$ (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 197) of ring-carbon atom in hydrocarbon residue at point of attachment of extracyclic carbon for aromatic methyl radicals.   [b] Estimated value.   [c] Unpublished work (with J. L. Morgan). Measurements at ionic strength 0·3.   [d] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469. For consistency with other values quoted, the "P_{ab}" data are used.   [e] Kieffer and Rumpf, *Compt. rend.*, 1950, **230**, 1874.   [f] Measurements as in *c*. Kolthoff and Bosch, *Rec. Trav. chim.*, 1929, **48**, 37, give pK_1 6·29$_{18}$, pK_2 2·80$_{18}$.   [g] Measurements as in *c*. Clark, Cohen, and Gibbs, U.S. Public Health Reports, 1926, Supp. 54, give pK_1 4·70$_{30}$, pK_2 3·48$_{30}$.   [h] Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 3.   [i] Kuhn and Zumstein, *Ber.*, 1926, **59**, 488.   [j] Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 79.
   * This and the following pK values were measured in 50% MeOH.
   † This and the following values are referred to the H_2O standard, it being assumed that $\Delta pK_1(H_2O \longrightarrow 50\% \text{ MeOH})$ has the same value as for 1 : 4-naphthylenediamine (-0.33 unit).

studied. This raises the question of the conditions, if any, under which the free energy of proton dismutation would be negative, in which case pK_1 would be less than pK_2. The possibility of this is brought out by the analogy between this reaction and electronic dismutation among species capable of existence in at least three oxidation states. The formal analogy between these equilibria was first discussed by Michaelis and Schubert (*Chem. Reviews*, 1938, **22**, 437); electronic dismutation is known to occur among the ions formed by oxidation of diamines, and the changes of unsaturation energy on ionization and on oxidation are closely related.

From eqn. (3), and including the statistical term ($RT \ln 4$), the free energy of proton dismutation for any diamine at $\sim 20°$ should be

$$\Delta G_D = ca. \ \varepsilon_{\text{conj. (2)}} - \varepsilon_{\text{conj. (1)}} + y(q_4 + q_3 - 2q_1) - 2z(q_2 - 1) + 0.8 \text{ kcal. mole}^{-1} \quad . \quad (4)$$

where $\varepsilon_{\text{conj. (1)}}$ and $\varepsilon_{\text{conj. (2)}}$ are the conjugation energies of the first and the second CH_2^- group to the hydrocarbon to form the isoconjugate dicarbanion. Equation (4) predicts the general trend of ΔG_D values reasonably well; thus, for the diamines 13, 9, 12, and 14 of the Table, the calculated sequence is 0·7, 1·3, 3·8, and 4·5 kcal. mole^{-1}, and the experimental sequence is $\sim$1·8, 1·5, 4·4, and 4·2 kcal. mole^{-1}. Examination of the data in the Table for other systems shows that, although ΔG_D becomes small as the two amino-groups tend to become independent [*i.e.*, as $\varepsilon_{\text{conj. (1)}}$ approaches $\varepsilon_{\text{conj. (2)}}$], yet it does not become negative, so that the possibility that $pK_2 \gg pK_1$ (at ordinary temperatures) is unlikely.

Non-Coulombic Terms.—No account has so far been taken of integrals of the type $\int \phi_r H' \phi_s^* d\tau (r \neq s) = \delta\beta_{rs}$. If some terms of this kind are non-vanishing in the expansion of the original perturbation expression, eqn. (3) must be modified to :

$$\varepsilon = \varepsilon_{(\text{H})} + \Sigma_r q_r \delta a_r + 2\Sigma\Sigma_{r<s} p_{rs} \delta\beta_{rs} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where p_{rs} is the mobile order of the *rs* bond (Coulson and Longuet-Higgins, *loc. cit.*, 1947). The main $\delta\beta$ term that may be important is the difference x between the $\geqslant\text{C-NH}_2$ (in amine) and $\geqslant\text{C-CH}_2^-$ (in carbanion) resonance integrals.

We consider first molecules containing only one NH_2 group. The isoconjugate hydrocarbon is a monocarbanion, and it can easily be shown that the mobile order $p_{\text{ex.}}$ of the ring-extracyclic bond is the same as in the corresponding radical. Now it is known (*idem*, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188) that for the linking of two unsaturated systems R and S at atoms r and s, $\varepsilon_{\text{conj.}} \simeq p_{rs}$, and this should hold for conjugation of $-\dot{\text{C}}\text{H}_2$ or $-\text{CH}_2^-$ to an aromatic residue. [It has recently been shown by Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3341) that in such a case,

$$\varepsilon_{\text{conj.}} \simeq p_{rs} \simeq 2\overset{\text{unocc.}}{\underset{m}{\Sigma}} \frac{(a_r^m)^2 \beta_{rs}}{E_m}$$

where a_r^m = coefficient of ϕ_r in Ξ, the m'th MO of R, of energy E_m.] Strict equality will not be expected; from the limited data available (Jacobs, *J.*, 1952, 292) we may set

$$p_{rs} \simeq 0.87 \ \varepsilon_{\text{conj.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It has been mentioned above that over the range of structure being considered, $\varepsilon_{\text{conj.}}$ varies linearly with $-q_1$; the equation of the line in the figure is

$$\varepsilon_{\text{conj.}} = 1.82 - 0.7q_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Combining (5)—(7), we thus have for the energy of conjugation $\varepsilon'_{\text{conj.}}$ of an NH_2 group to an aromatic residue,

$$\varepsilon'_{\text{conj.}} \simeq \varepsilon_{\text{conj.}} + 3.16\delta\beta + q_1(\delta a - 1.28\delta\beta) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equation (8) indicates that if $\delta\beta$ is appreciable compared to δa, the magnitude of the total perturbation term ($\varepsilon'_{\text{conj.}} - \varepsilon_{\text{conj.}}$) is governed largely by $\delta\beta$; this is in general agreement with the results of Coulson and de Heer (*loc. cit.*; *Trans. Faraday Soc.*, 1951, **47**, 681), derived in a different way.

Even if $\delta\beta$ were large, however (provided that it is not large enough to render the use of perturbation theory invalid), the discussion of the energetics of ionization of monoamines

and diamine mono-ions would require little modification; *e.g.*, for a monoamine, the appropriate modification of eqn. (3) would be

$$2\cdot3RTpK = \varepsilon_{conj.} + q_1(y - 1\cdot2x) - z + (A + 3\cdot16x)$$

The only point of difference in the variable terms, which are the ones taken directly into account, is that, whereas the slope, $2\cdot3RTpK - \varepsilon_{conj.} - g(z)/q_1$, was formerly interpreted as being equal to y, it must now be set equal to $(y - 1\cdot2x)$.

The situation is different for addition of a proton to a diamine, and this permits of an approximate estimate of $\delta\beta$. In this case, a similar treatment, taking into account regularities of extracyclic bond order with structure, yields $(y - 2\cdot7x) \simeq -16$ kcal. mole^{-1}. Now it has previously been found that $(y - 1\cdot2x) \simeq -13$ kcal. mole^{-1}, and the two numerical values can be regarded as identical within the limits of error of the calculation. This yields the result that $\delta\beta$ is close to zero, *i.e.*, that, to this approximation, the $>C-CH_2^-$ and $>C-NH_2$ resonance integrals have nearly the same value. As it is fairly certain that the nitrogen AO's are not pure $2p\pi$ functions, it is perhaps understandable that $\delta\beta$ should be small, and this rough calculation indicates that in these systems perturbation terms in $\delta\beta$ can be ignored without introducing serious error.

Electron Densities in Dicarbanions.—In the Appendix, the electron densities in a number of dicarbanions are shown; these have been used in the table. In calculating the distributions for the molecules A, C, D, F, G, L, M, N, and O, the A.O. coefficients listed by Pullman, Berthier, and Pullman (*loc. cit.*) have been employed. Where the dicarbanions contain two non-bonding MO (as also in G), the required orthonormal sets of A.O. coefficients have been obtained from those of two arbitrary sets satisfying the condition $\varepsilon = 0$ by the method of Coulson and Longuet-Higgins (*Phil. Mag.*, 1949, **40**, 1172). The values shown are those of $q_r - 1$ for atom r of a molecule.

Appendix : net π-electron densities in dicarbanions.
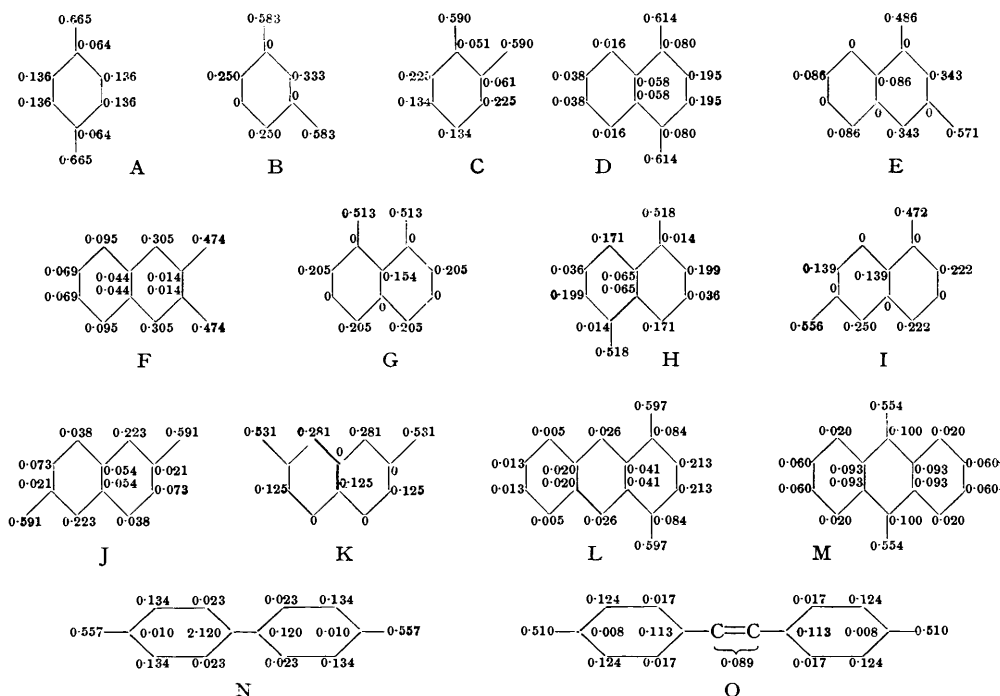
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