

358. Studies on Nitroamines. Part VIII. The Dissociation Constants of the Primary Dibasic Nitroamines.

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Thermodynamic dissociation constants have been measured for the series of primary dibasic nitroamines, $\text{NO}_2 \cdot \text{NH} \cdot [\text{CH}_2]_n \cdot \text{NH} \cdot \text{NO}_2$, in which $n = 1, 2, 3$, and 4 . The resulting values of $\text{p}K_1$, $\text{p}K_2$, and $\Delta\text{p}K$ have been compared with those for corresponding members of the series of dicarboxylic acids, $\text{CO}_2\text{H} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$, on the basis of which comparison suggestions are made regarding the structure of the nitroamine anion.

THE ratio of the first to the second dissociation constant (K_1/K_2) of an acid with two equivalent acid groups in the molecule will be equal to 4, provided that these groups are so far apart as to exert no appreciable electrostatic influence upon one another. In other terms, $\Delta\text{p}K (= \text{p}K_2 - \text{p}K_1) = 0.60$, where $\text{p}K = -\log K$. When, as is normally the case, the mutual electrostatic effect is not negligible, $\Delta\text{p}K > 0.60$ and increases as the distance (r) between the charges on the acidic groups diminishes. Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) attempted to put this relation into a quantitative form and deduced the equation, $\Delta\text{p}K - 0.60 = e^2/2.3kTDr$ where e is the electronic charge, k the Boltzmann constant, T the temperature, and D the dielectric constant of the solvent. This equation is only very approximately in agreement with observation, and attempts at a more sophisticated treatment (*e.g.*, by Ingold, *J.*, 1931, 2179; Kirkwood and Westheimer, *J. Chem. Physics*, 1938, **6**, 506; Wynne-Jones and Rushbrooke, *Trans. Faraday Soc.*, 1944, **40**, 99; see also *J.*, 1943, 270) have so far had only limited success. Nevertheless, it seemed possible that by comparing $\Delta\text{p}K$ values for two parallel series of dibasic acids, the structure in one of these series being known, useful inferences might be drawn regarding the separation of the negative charges on the anions of the other series. This empirical procedure would avoid many of the difficulties involved in deducing r directly from $\Delta\text{p}K$.

Thermodynamic dissociation constants of the dinitroamines $\text{NO}_2 \cdot \text{NH} \cdot [\text{CH}_2]_n \cdot \text{NH} \cdot \text{NO}_2$, where $n = 1, 2, 3$, and 4 , have therefore been measured, and the $\Delta\text{p}K$ values have been compared with those for the corresponding dicarboxylic acids.

EXPERIMENTAL.

Thermodynamic dissociation constants were found by potentiometrically titrating the dinitroamines, in *ca.* 0.003M-aqueous solution, with 0.06N-NaOH at 20.0°, using the glass electrode. The methods of standardising the pH scale and of calculating K_1 and K_2 have been described previously (*J.*, 1940, 855). Results (expressed as $\text{p}K$) are shown in Table I; each value is the mean of at least five independent determinations. In general, they are considered to be accurate to within ± 0.05 for $\text{p}K$ and rather better for $\Delta\text{p}K$. Because of slow decomposition (see Part VII), the results for methylenedinitroamine may be a little less accurate than for the others.

Data for the dicarboxylic acids are also included; they are taken from the above-mentioned paper or from that of Gane and Ingold (*J.*, 1931, 2158).

TABLE I.

Thermodynamic dissociation constants at 20.0°.

Dinitroamine.	$\text{p}K_1$.	$\text{p}K_2$.	$\Delta\text{p}K$.	Acid.	$\text{p}K_1$.	$\text{p}K_2$.	$\Delta\text{p}K$.
Methylene	5.0	6.6	1.6	Malonic	2.83	5.69	2.86
Ethylene	5.35	6.66	1.31	Succinic	4.22	5.67	1.45
Trimethylene	5.59	6.85	1.26	Glutaric	4.39	5.50	1.11
Tetramethylene	5.87	6.98	1.11	Adipic	4.43	5.42	0.99

DISCUSSION.

The results in Table I show clearly that $\Delta\text{p}K$ diminishes much less rapidly as the homologous series of dinitroamines is ascended than it does in the dicarboxylic acid series. Qualitatively, therefore, the effective distance between the charges on the double anion increases more slowly in the former series.

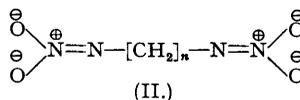
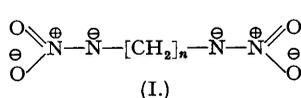
This conclusion can be extended semi-quantitatively by the following procedure. It seems probable that "straight-chain" molecules of the type considered here are most stable when in the fully extended form with the carbon chain in a flat zig-zag (Gane and Ingold, *J.*, 1931, 2158; Pauling, "The Nature of the Chemical Bond," 1942, p. 91; see also *J.*, 1941, 492). If so, the distance (r) between the negative charges on the double anions of the carboxylic acids can be easily calculated (Gane and Ingold, *loc. cit.*). If the values of $\Delta\text{p}K$ and r (columns 2 and 3 of Table II) are plotted graphically, the relation between them is thereby established on a purely

empirical basis. [Consideration of the Bjerrum equation suggests that it might be more convenient to plot $(\Delta pK - 0.60)$ against $1/r$; and in fact both methods of plotting have been used.] Now it appears reasonable to assume that the same, or a very similar, relation should apply in the series of dinitroamines; and with the use of this assumption empirical values of r_e , the effective separation of the charges, have been deduced and are shown in column 7 of Table II. Distances are given in Å.

TABLE II.

Acid.	ΔpK .	r .	Dinitroamine.	ΔpK .	r_I .	r_e .	r_{II} .
Malonic	2.86	4.26	Methylene	1.6	2.4	5.6	6.2
Succinic	1.45	5.87	Ethylene	1.31	3.8	6.1	7.7
Glutaric	1.11	6.84	Trimethylene	1.26	5.0	6.3	8.4
Adipic	0.99	8.36	Tetramethylene	1.11	6.3	6.8	10.2

A possible interpretation of these values is provided by considering the formulation of the dinitroamine ion, viz.:



Presumably resonance occurs between such forms as (I) and (II). If methylenedinitroamine existed mainly in form (I), the negative charges on the two inner nitrogen atoms would be separated by only about 2.5 Å, giving rise to a powerful mutual repulsion. Consequently, this anion should exist mainly in form (II), where r is effectively much greater. As the homologous series is ascended, this repulsion would become less pronounced, with the result that the resonance would involve an increasing contribution from form (I).

This conclusion may be amplified by calculating values of r_I (minimum) and r_{II} (maximum), corresponding to formulæ (I) and (II), as shown in Table II (accepted values of interatomic distances and valency angles have been used). It is not at once obvious just where, on each $-\text{N}_2\text{O}_2$ group, is located the effective negative charge which influences the loss or recapture of a proton by the other group; but, in a very approximate treatment, it seems justifiable to take this charge as being on the inner nitrogen atom in (I) and at the centre of the O-N-O triangle in (II). Comparison with the values of r_e supports the conclusion that the methylenedinitroamine and tetramethylenedinitroamine anions exist mainly as (II) and (I), respectively.

In general it is concluded that the normal condition of the nitroamine group is $-\text{NH}\cdot\text{NO}_2$, giving the anion $-\overset{\ominus}{\text{N}}\cdot\text{NO}_2$, but that, when two such groups are close enough together for the repulsion between their negative charges to become important, the anion exists mainly as $-\overset{\ominus}{\text{N}}\cdot\overset{\oplus}{\text{N}}\text{O}_2$, formally derived from the group $-\overset{\oplus}{\text{N}}\cdot\text{NO}\cdot\text{OH}$.

In the series of dicarboxylic acids, pK_1 increases with n , but pK_2 diminishes, whilst with the dinitroamines both pK_1 and pK_2 increase, although the latter increases more slowly. This is consistent with the above conclusion if it is assumed that $-\overset{\oplus}{\text{N}}\cdot\overset{\oplus}{\text{N}}\text{O}_2$ accepts a proton less readily than does $-\overset{\oplus}{\text{N}}-\overset{\oplus}{\text{N}}\text{O}_2$, an assumption that seems justifiable on general grounds.

On the basis of an X-ray study of the crystals, Llewellyn and Whitmore (*J.*, 1948, 1316) have discussed the structure of the ethylenedinitroamine *molecule*; and they tentatively conclude that it is a resonance hybrid involving important contribution from structures with double positive formal charges on the nitrogen atoms. It appears unlikely that the corresponding structures can make any significant contributions in the *anion*.

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