87. *Studies in Dielectric Polarisation. Parts VI and VII.*

By ERIC C. E. HUNTER and JAMES R. PARTINGTON.

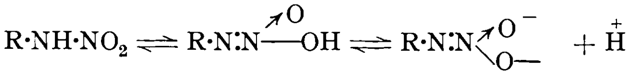
PART VI. BENZENE SOLUTIONS OF ETHYL AND BENZYL HYPONITRITES AND *s*-METHYL SULPHITE; DIOXAN SOLUTIONS OF NITROAMINE; PARACHORS OF METHYL, ETHYL, AND *n*-BUTYL HYPONITRITES.

Two groups of isomeric substances of the formula RHN_2O_2 exist. The members of the first group, the nitroamines (Franchimont; Thiele and Lachmann, *Annalen*, 1895, **288**, 269) are neutral, decomposed by alkali at high temperatures with separation of the two nitrogen atoms, and are nitro-derivatives of ammonia, $NRH\cdot NO_2$, corresponding with the parent substance nitroamine (I). The members of the other group, the *iso*nitroamines,

(I.) $NH_2\cdot NO_2$ (II.) $NH(NO)\cdot OH$

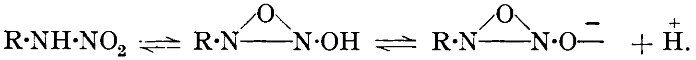
are true acids in aqueous solution or in ether, and are usually unstable. Their chemical reactions do not lead to any very definite structure for them, but they are usually regarded as nitroso-derivatives of hydroxylamine, $NO\cdot NR\cdot OH$, corresponding with the parent nitrosohydroxylamine (II) (Bamberger, *Ber.*, 1894, **27**, 1553; Angeli, *ibid.*, 1896, **29**, 1884; Hantzsch and Sauer, *Annalen*, 1898, **299**, 67; Traube, *ibid.*, 1898, **300**, 81; Hantzsch and Dolfuss, *Ber.*, 1902, **35**, 258; Angeli and Angelico, *Gazzetta*, 1903, **33**, 239). From *iso*-

nitroamines are derived stable nitroamine salts, such as the sparingly soluble mercury salt; the acid strength depends on the electrochemical properties of R, and they give two kinds of esters, $NR_1R_2\cdot NO_2$ and $NR_1{:}NO\cdot OR_2$ (Hantzsch, *Ber.*, 1902, **35**, 265; Baur, *Z. physikal. Chem.*, 1897, **23**, 409). Hantzsch (*loc. cit.*) represents the tautomeric change of *iso*nitroamines as follows :



$$R\cdot NH\cdot NO_2 \rightleftharpoons R\cdot N{:}N\overset{\nearrow O}{—}OH \rightleftharpoons R\cdot N{:}N\begin{smallmatrix}\nearrow O^- \\ \searrow O—\end{smallmatrix} + \overset{+}{H}$$

or

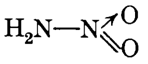


$$R\cdot NH\cdot NO_2 \rightleftharpoons R\cdot N\overset{/O\backslash}{——}N\cdot OH \rightleftharpoons R\cdot N\overset{/O\backslash}{——}N\cdot \overset{-}{O}— + \overset{+}{H}.$$

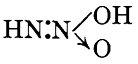
Free nitroamine (Thiele and Lachmann, *Ber.*, 1894, **27**, 1909; *Annalen*, 1895, **288**, 267; Thiele, *Ber.*, 1896, **29**, 78R; *Annalen*, 1897, **296**, 100; Hantzsch and Kaufmann, *ibid.*, 1896, **292**, 317; Baur, *ibid.*, 1897, **296**, 95) was given formula (II) by Thiele, whilst Hantzsch, who at first regarded it as the *cis*-isomeride of hyponitrous acid, $HO\cdot N{:}N\cdot OH$ (*Annalen*, 1896, **292**, 340; 1897, **296**, 84, 111), now considers (*Ber.*, 1930, **63**, 1270) that it has formula (II). Cahili and Szegö (*Ber.*, 1928, **61**, 2081), from an examination of the absorption spectra of diazotates, also reject the hypothesis of stereoisomerism.

Nitroamine does not behave as a true amide of nitric acid, since it does not give nitrate ion and ammonia on alkaline hydrolysis but at once decomposes into water and nitrous oxide (Thiele and Lachmann, *loc. cit.*; Brönsted and King, *J. Amer. Chem. Soc.*, 1927, **49**, 193), thus behaving in presence of alkali in the same way as hyponitrous acid in presence of acid. Free nitroamine was prepared in the crystalline form according to the method of Thiele and Lachmann (*Annalen*, 1895, **288**, 297), and crystalline hyponitrous acid according to the method of Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 317), by Dr. Shah in this laboratory, but the latter substance proved too unstable to allow of any experiments being made with it. Experiments on the polarity of nitroamine were, however, successful.

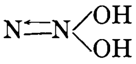
The alternative formulæ (III—IV*b*) are possible for nitroamine :

(III.) 

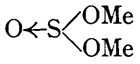
$$H_2N—N\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$$

(IV*a*.) 

$$HN{:}N\begin{smallmatrix}\diagup OH \\ \searrow O\end{smallmatrix}$$

(IV*b*.) 

$$N\equiv N\begin{smallmatrix}\diagup OH \\ \diagdown OH\end{smallmatrix}$$

(V.) 

$$O\leftarrow S\begin{smallmatrix}\diagup OMe \\ \diagdown OMe\end{smallmatrix}$$

In strongly acid solution, in which it is stable, it is reduced to hydrazine (Thiele and Lachmann, *loc. cit.*), which reaction, together with its formation from nitrocarbamic acid, shows that two nitrogen atoms are directly linked in nitroamine and that both oxygen atoms are probably attached to the same nitrogen atom. On the assumption that the oxygen atoms are not labile, the formula may be (IV*a*) or (IV*b*) according as one or both hydrogen atoms take part in tautomeric change.

For hyponitrous acid there is little evidence to show whether the oxygen atoms are attached to the same or different nitrogen atoms. There are six lines of chemical evidence available (Partington and Shah, J., 1932, 2589) : (i) the formation from hydroxylamine and nitrous acid; (ii) the decomposition of acid and salts to give nitrous oxide; (iii) the spontaneous decomposition of the esters to give aldehydes and nitrogen; (iv) the failure to reduce the salts or esters to ammonia, hydroxylamine, or hydrazine; (v) the decomposition of the esters on alkaline hydrolysis to give nitrogen, without formation of hyponitrite ion; (vi) the absence of hyponitrous acid in aqueous solutions of nitrous oxide, since (*a*) the solution has the same conductivity as pure water, and (*b*) alkalis reduce the solubility of the gas, whilst nitric acid slightly increases it (Lunge, *Ber.*, 1881, **14**, 2118; Geffcken, *Z. physikal. Chem.*, 1904, **49**, 257; Knop, *ibid.*, 1904, **48**, 106; Manchot, *Z. anorg. Chem.*, 1924, **141**, 38). The nitrous oxide gas electrode has an abnormal behaviour (Partington; unpublished). The chemical evidence is not closely related to either geometrical isomeride of $HO\cdot N{:}N\cdot OH$ (cf. Jones and Scott, *J. Amer. Chem. Soc.*, 1924, **46**, 2172), since compounds containing the $-N{:}N-$ or the $-N{:}\overset{\nearrow O}{N}—$ group are usually reducible to the corresponding hydrazines.

We have, therefore, measured the polarisations of benzene solutions of ethyl and benzyl hyponitrites, prepared by Dr. Shah (Partington and Shah, J., 1932, 2589), and of *s*-methyl sulphite, and of dioxan solutions of nitroamine, as well as the parachors of some hyponitrous esters. The parachors are in satisfactory agreement with the formula $HO\cdot N\colon N\cdot OH$ if the value 12·5 is taken for the double bond in $-N\colon N-$ (Mumford and Phillips, J., 1929, 2116), but are over 10 units lower than the value calculated with the parachor 23·2 for the double bond in $-N\colon N-$ (Sugden, Reed, and Wilkins, J., 1925, **127**, 1532; Lindemann and Groger, *Ber.*, 1930, **63**, 715). The dipole moments are very small and leave little doubt that hyponitrous acid has the *trans*-formula. It should, however, be remarked that the moments of resorcinol dimethyl ether ($1\cdot58 \times 10^{-18}$) and quinol dimethyl ether ($1\cdot74 \times 10^{-18}$) do not differ appreciably (Weissberger and Sängewald, *Physikal. Z.*, 1929, **30**, 792), indicating the possibility of free rotation around the oxygen bonds, and this might well occur also in the case of the geometrical isomerides of hyponitrous esters. Since azobenzene and *pp'*-dinitroazobenzene have zero moments (Bergmann, Engel, and Sandor, *Ber.*, 1930, **63**, 2572), it seems probable, however, that the *trans*-structure correctly represents hyponitrous acid.

The moment found for nitroamine is $3\cdot75 \times 10^{-18}$. In considering formula (III) a comparison with the moment of *p*-nitroaniline (6·4 units; Tiganik, *Z. physikal. Chem.*, 1931, **14**, *B*, 135), which is much higher, does not seem relevant, since some interaction seems likely to occur in this compound, probably on account of the presence of the benzene ring, since the moment of nitrobenzene is about 0·8 unit higher than that of nitromethane. The sum of the moments of nitromethane (about 3·0, see Part VII) and methylamine (1·23 units; Smyth, "Dielectric Constant and Molecular Structure," 1931, 201) is 4·23, which is higher than the observed moment. It is not impossible that a lowering of moment on account of interaction occurs, so that the formula (III) may be considered to be compatible with the observed moment. There is, however, also a possibility that formula (IV*b*) may represent nitroamine in a non-polar solvent. Structures (IV*a*) and (IV*b*) differ only in that the semipolar double bond between nitrogen and oxygen in the first is replaced by a similar bond between nitrogen and nitrogen in the second, so that the moments of the two structures would probably not differ appreciably. Formula (IV*b*) shows a pictorial resemblance to that of *s*-methyl sulphite (V), the moment of which, 2·90 units, was accordingly measured. The effect of alkyl groups in reducing moments by induction (see Parts I and II) would lead us to suppose that the moment of the hypothetical *s*-sulphurous acid corresponding with the ester should be about 3·5 units, which is comparable with the value found for nitroamine. In any case the moment of nitroamine seems to rule out a geometrical isomeride of the molecule $HO\cdot N\colon N\cdot OH$. A choice between (IV*a*) and (IV*b*) involves the structure of nitrous oxide, which is readily formed by the decomposition of hyponitrous acid and nitroamine. The evidence on the whole (cf. Lewis, "Valence and the Structure of Molecules," 1923; *J. Chem. Physics*, 1933, **1**, 26; Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543; 1920, **42**, 274; Pauling, *ibid.*, 1931, **53**, 1386; Mahanti, *Physikal. Z.*, 1931, **32**, 108; Plyler and Barker, *Physical Rev.*, 1931, **38**, 1827; Bailey and Cassie, *ibid.*, 1932, **39**, 534; Bailey, *Nature*, 1932, **130**, 239; Müller, *Z. Elektrochem.*, 1925, **31**, 46, 143; Sidgwick, "Electronic Theory of Valency," 1927, 279; Langseth and Nielsen, *Nature*, 1932, **130**, 92; Clusius, *ibid.*, p. 775) seems to support a linear molecule with direct linkage of two nitrogen atoms rather than a molecule with the oxygen atom between the two nitrogen atoms, although there is not complete agreement as to the nature of the bonds. Mahanti's formula, $\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\colon\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}$, is objectionable from several points of view and cannot be entertained. The old formula of Langmuir, $N\overset{\leftarrow}{-}N{=}O$, seems to account satisfactorily for most of the properties and reactions, and the low polarity of the gas would then require that the moment of the $N\overset{\leftarrow}{-}N$ linkage should compensate the moment of the $N{=}O$ linkage, to which assumption there seems to be no serious objection, although arguments from polarity are admittedly somewhat delicate (see Hammick, New, Sidgwick, and Sutton, J., 1930, 1876). On account of the very unstable character of the hyponitrous esters and nitroamine, the values found for the moments are only approximate, but since it is hardly likely that values of much greater accuracy can be found, there is no object in delaying publication of the present results.

EXPERIMENTAL.

The determinations of surface tension and density for the parachors were made at room temp.

	t.	$D_{4^\circ}^{t^\circ}$.	γ.	$P = M\gamma^{\frac{1}{4}}/D$.	P, calc.	Diff., %.
Ethyl hyponitrite	16°	0·953	21·44	266·5	267·5	0·4
Propyl hyponitrite	20	0·950	24·94	343·5	347·5	1·2
Butyl hyponitrite	18	0·936	26·50	421·7	421·5	1·5

The determinations of polarisations were made with the apparatus previously described and the symbols are those previously used.

Benzene Solutions.

Ethyl hyponitrite, $D_{4^\circ}^{20^\circ}$ 1·0326 (see J., 1932, 2594); $n_D^{20^\circ}$ 1·4047. s-*Methyl sulphite*, $D_{4^\circ}^{20^\circ}$ 1·0673; $n_D^{20^\circ}$ 1·4097.

f_1.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	f_1.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	1	0·8792	2·280	26·55	0	1	0·8785	2·281	26·58
0·0248	0·9752	0·8838	2·356	27·84	0·00828	0·99172	0·8810	2·384	28·06
0·0369	0·9631	0·8860	2·401	28·57	0·01874	0·98126	0·8854	2·511	29·86
	Benzyl hyponitrite.				0·03024	0·96976	0·8892	2·673	31·81
0·0082	0·9918	0·8840	2·286	26·94	0·03663	0·96337	0·8914	2·773	33·01

Dioxan Solutions of Nitroamine.

0	1	1·0341	2·320	26·01	0·01398	0·98602	1·0379	2·620	29·64
0·00665	0·99335	1·0360	2·465	27·92	0·02247	0·97753	1·0400	2·847	32·06

	$P_{2\infty}$.	P_E.	P_O.	$\mu \times 10^{18}$, E.S.U.
Ethyl hyponitrite	80	29	51	1·5 (in C_6H_6)
Benzyl hyponitrite	75	71 *	4	0·4 ,,
s-Methyl sulphite	202	25·5	176·5	2·90 ,,
Nitroamine	305	10 *	295	3·75 (in dioxan)

* Approx. values calc. from sum of at. refractions.

PART VII. BENZENE SOLUTIONS OF NITROMETHANE, NITROETHANE, AND NITRO-*n*-BUTANE.

The dipole moments of nitromethane in solution and in the gaseous state have been determined by Höjendahl (*Thesis*, Copenhagen, 1928) and in solution in benzene by Weissberger and Sängewald (*Ber.*, 1932, **65**, 701); that of nitroethane in the gaseous state was found by Höjendahl (*op. cit.*) and by Whitman (*J. Opt. Soc. America*, 1926, **21**, 31), but no other measurements in solution beyond those quoted seem to be available. The moments of nitromethane, nitroethane, and nitro-*n*-butane have therefore been determined in benzene solution. The substances were specially purified by Dr. D. C. Jones and Mr. H. J. Moss, who kindly placed specimens at our disposal.

EXPERIMENTAL.

Nitromethane, $D_{4^\circ}^{25^\circ}$ 1·1312; $n_D^{25^\circ}$ 1·3797. *Nitroethane*, $D_{4^\circ}^{25^\circ}$ 1·0448; $n_D^{25^\circ}$ 1·3899.

f_1.	f_2.	$n_D^{20^\circ}$.	ϵ.	P_{12}.	f_1.	f_2.	$n_D^{20^\circ}$.	ϵ.	P_{12}.
0	1	0·8792	2·280	26·550	0·00881	0·99119	0·8806	2·409	28·308
0·01127	0·98873	0·8809	2·424	28·449	0·02020	0·97980	0·8823	2·579	30·481
0·01713	0·98287	0·8821	2·495	29·312	0·02228	0·97772	0·8826	2·614	30·907
0·02495	0·97505	0·8833	2·612	30·714	0·03355	0·96645	0·8843	2·790	32·940
0·03024	0·96976	0·8842	2·673	31·393	0·04095	0·95905	0·8855	2·924	34·383
0·03277	0·96723	0·8848	2·710	31·790					
0·04126	0·95874	0·8860	2·834	33·120					

Nitrobutane, $D_{4^\circ}^{25^\circ}$ 0·9662; $n_D^{25^\circ}$ 1·4085.

0·00803	0·99197	0·8800	2·403	28·335	0·03394	0·96606	0·8829	2·800	33·508
0·01761	0·98239	0·8811	2·548	30·315	0·03835	0·96165	0·8835	2·880	43·453
0·02543	0·97457	0·8820	2·668	31·875					

	$P_{2\infty}$.	P_E.	P_O.	$\mu \times 10^{18}$, E.S.U.
Nitromethane	205	12·5	192·5	3·02 (in C_6H_6)
Nitroethane	232	17·0	215	3·19 ,,
Nitro-*n*-butane	253	26·4	228·6	3·29 ,,

The result for nitromethane is in good agreement with that found in solution by Höjendahl (*op. cit.*), *viz.*, 3·05 : Weissberger and Sängewald (*Ber.*, 1932, **65**, 701) find 3·13. The value found for nitroethane vapour by Höjendahl and by Whitman (*loc. cit.*) was 4·03, which is considerably higher than that now obtained in solution. Since, however, the value for nitromethane in the vapour state found by Höjendahl, 3·78, is considerably higher than that in solution, this result is to be expected. The results show that appreciable induction occurs in the hydrocarbon chain, the effect of the nitro-group extending at least as far as the third carbon atom. This is in striking contrast to the results for the corresponding nitrates, recently measured in this laboratory by Mr. E. G. Cowley, which show that little, if any, induction occurs. These results, and those for the corresponding nitrites, will shortly be submitted to the Society.

The results also show that the moment of the nitro-group is distinctly smaller in the aliphatic series than in the aromatic series, the value for nitrobenzene being about 3·9 (Williams, *Fortschr. Chem.*, Band 20, Heft 5, Molekulare Dipolmomente, 1930, 36). Further discussion of this point is postponed until the results for the nitrites and nitrates are fully available.

The authors thank the Chemical Society for a research grant and one of them (E. C. E. H.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

East London College, University of London. [*Received, February 7th,* 1933.]