CCCCXXVIII.—*The Association of Aromatic Nitroso-compounds in Solution.*

By Dalziel Llewellyn Hammick.

Our knowledge of the association of aromatic nitroso-compounds in solution has hitherto been derived almost entirely from the work of Bamberger and his co-workers (compare Bamberger and Rising. *Ber.*, 1901, **34**, 3878), who determined the apparent molecular weights of nitrosobenzene and a number of its substituted derivatives by measuring the depression of the freezing point of dilute solutions, benzene being in most cases the solvent. Hammick and Illingworth (J., 1930, 2358) have shown that nitrosobenzene is definitely associated to some extent at the boiling point in carbon disulphide solution, but that its molecular weight, in carefully purified and standardised acetic acid, is in agreement with the simple molecular formula $C_6H_5{\cdot}NO$. Le Fèvre, however, has recently (this vol., p. 810) commented on the fact that Hammick and Illingworth made no reference to a determination of the molecular weight of nitrosobenzene in acetic acid quoted by Bamberger and Renauld (*Ber.*, 1897, **30**, 2278) and Bamberger and Rising (*loc. cit.*). It is therefore necessary to refer in detail to these results. In the first of the two papers is to be found a footnote stating that tne calculated value for the molecular weight of nitrosobenzene is 107 and that the values 102, 112, and 117 had been found in acetic acid solution, no data being given. From these results, Bamberger and Renauld conclude that nitrosobenzene is unimolecular in acetic acid solution. The second paper quotes the same results in the form, $M_{\text{obs.}} = 102, 122, 117$ (one of the values 112 or 122 being thus a misprint), with a note to the effect that the record of the weights of solvent used in the experiments was not available. Results of this kind appeared to be of little value in deciding the important question as to the molecular complexity of nitrosobenzene in acetic acid and were not quoted, even though Bamberger and Renauld's interpretation of them agreed with Hammick and Illingworth's conclusions.

Bamberger and Rising (*loc. cit.*) drew attention to the fact that the presence of two methyl groups in the positions ortho to the nitroso-group greatly increased the stability of the polymerised form in benzene solution. It was in order to investigate this effect more completely that the experiments described below were undertaken. It became apparent at the outset that some at least of Bamberger's experiments would have to be repeated, owing to the fact that nowhere in his papers dealing with molecular weights of aromatic nitroso-compounds does he quote the value taken for the cryoscopic constant or indicate that he ever standardised his benzene. In all of our redeterminations of Bamberger's results we find values for the molecular weights greater than his. The discrepancies thus introduced into the association factors calculated from his results and ours are of minor importance except in the case of nitrosobenzene itself, where Bamberger's results imply no association and ours, based on experiments in carefully standardised benzene, indicate a small association. Owing to Bamberger's omission of standardisation and to the fact that his data in many cases yield molecular weights less than the theoretical, we regard ours as the more correct. The degree of association calculated from our data (2·4%, see below) is not much outside the experimental error involved. Nevertheless, our evidence is at least no less in favour of slight association than Bamberger's is against and Le Fevre's observation (*loc. cit.*) that nitrosobenzene gives *p*-bromonitrosobenzene on bromination in benzene solution thus does not necessarily conflict with the observation of Hammick and Illingworth that para-substitution occurs only when bimolecular nitrosobenzene is present in solution.

Before degrees of association can be calculated from cryoscopic measurements, evidence must be obtained as to the number of molecules concerned in the polymerisation. Ingold and Piggott (J., 1924, **125**, 168) showed, in the case of nitrosomesitylene, that the association is bimolecular, as had been assumed hitherto without direct proof. It does not appear to have been noticed, however, that Bamberger and Seligman's cryoscopic measurements of the rate of depolymerisation of nitrosobutane can readily be made to show that here also the polymeride is bimolecular (*Ber.*, 1903, **36**, 690).

We have calculated association factors (x% in the tables given below) as the number of double molecules in a total of 100 solute molecules. It may easily be shown that x is given by $100M_0/(M - M_0)$, where M is the apparent molecular weight derived from the cryoscopic data and M_0 is that of the simple molecule. Association factors have been calculated from the mean apparent molecular weights over the experimental concentration ranges, which cover about 0—3 mols. per 100 mols. of solvent. Association must, of course, increase with concentration; but where x is small the increase of apparent molecular weight with concentration lies inside the experimental error. With the more highly associated solutes, such as *s*-tribromonitrosobenzene, the effect of concentration on apparent molecular weight is perceptible, and by taking the mean molecular weight in our calculations of association factors, we are in effect deriving factors for concentrations of 1—1·5 mols.%.

EXPERIMENTAL.

[With WALTER S. ILLINGWORTH, WILLIAM A. M. EDWARDS, and (MISS) ELEANOR EWBANK.]

The apparent molecular weights recorded below were determined in benzene solution. The benzene was purified in the usual manner by repeated freezing out and by shaking with sulphuric acid. It was distilled in a stream of dry air from sodium into a reservoir, from which it was blown, when required, directly into the Beckmann tube. The actual determinations of freezing points were carried out in a slow stream of dry air, readings being taken after 1° of supercooling. The nitroso-compounds investigated were prepared by standard methods and were carefully purified before use.

The molecular weight of nitrosobenzene itself was determined with great care in an extremely pure sample of benzene supplied by Mr. L. E. Sutton of this laboratory. Three separate experiments were carried out with different samples of nitrosobenzene prepared from "molecular weight" nitrobenzene, the benzene being standardised with naphthalene, which has been shown by Jones and Bury (J., 1925, **127**, 1947) to be a normal solute in benzene.

Cryoscopic constants, K, given below are freezing-point depressions for 1 g.-mol. in 100 g. of solvent. M, M_0, and x have already been defined; M_B is the mean of the molecular weights found by Bamberger and Rising (*loc. cit.*); and W_s and W_b are the weights (in g.) of solute and benzene respectively. Nitroso-compounds for which molecular weight data are here presented for the first time are marked with an asterisk.

TABLE I.

Molecular weight of nitrosobenzene in benzene.

Determination of constant.				Nitrosobenzene as solute.			
W_b.	$C_{10}H_8$, g.	Δt.	K.	W_b.	$C_6H_5\cdot NO$, g.	Δt.	M.
22·98	0·1617	0·296°	53·85°	25·20	0·3800	0·743°	109·2
22·98	0·3075	0·565	54·05	22·12	0·1623	0·360	109·6
22·26	0·1969	0·359	53·58	23·47	0·4513	0·941	109·9
			Mean 53·8	Mean M = 109·6; M_B = 104; M_0 = 107; x = 2·4%.			

Discussion of Results.

The association factors we have derived from cryoscopic measurements must not, of course, be interpreted in a rigid numerical sense. For instance, it is impossible to claim that because we have found association factors in dilute benzene solution for *m*- and *p*-bromonitrosobenzene of 2·2% and 1·2%, that the former is more associated than the latter, or even that they are associated at all. What does appear, however, is that if we examine the results for nitrosobenzene

TABLE II.

Molecular weights of substituted nitrosobenzenes.

o-Nitrosotoluene; W_b = 17·33; K = 52·0°.

W_s.	Δt.	M.
0·1289	0·297°	130·3
0·2582	0·590	131·3
0·3390	0·767	132·6

Mean M, 131·4; M_B = 122; M_0 = 121; x = 9·2%.

p-Nitrosotoluene; W_b = 18·38; K = 52·0°.

W_s.	Δt.	M.
0·0832	0·211°	125·1
0·1554	0·390	126·5
0·3238	0·812	126·6

Mean M, 126·1; M_B = 117·8; M_0 = 121; x = 4·2%.

4-Nitroso-*m*-xylene; W_b = 18·22; K = 52·0°.

W_s.	Δt.	M.
0·0708	0·142°	142·2
0·1724	0·350	140·5
0·4144	0·828	142·8

Mean M, 141·8; M_B = 130·8; M_0 = 134; x = 5·8%.

o-Bromonitrosobenzene; W_b = 18·36; K = 52·0°.

0·1293	0·183	200·1
0·2895	0·420	195·2
0·4778	0·692	195·5

Mean M, 196·8; M_B = 177; M_0 = 186; x = 5·8%.

m-Bromonitrosobenzene; W_b = 17·64; K = 52·0°.

0·0807	0·128	185·8
0·2115	0·323	193·1
0·2828	0·435	191·6

Mean M, 190·1; M_0 = 186; x = 2·2%.

p-Bromonitrosobenzene W_b = 27·00; K = 51·5°.

0·0457	0·046	189·5
0·2362	0·241	186·9

Mean M, 188·2; M_B = 188·8; M_0 = 186; x = 1·2%.

o-Nitronitrosobenzene;* W_b = 28·40; K = 52·3°.

0·0501	0·042	219·6
0·0957	0·080	220·2
0·1631	0·136	220·8

Mean M, 220·2; M_0 = 152; x = 38·2%.

p-Nitronitrosobenzene;* W_b = 26·72; K = 52·3°.

0·0254	0·032	155·3
0·0777	0·098	155·2
0·1035	0·131	154·7

Mean M, 155·1; M_0 = 152; x = 2·0%.

o-Nitrosoanisole;* W_b = 17·95; K = 52·2°.

0·0450	0·089	147·0
0·1357	0·275	143·5
0·1870	0·380	143·1

Mean M, 144·5; M_0 = 137; x = 5·5%.

Nitrosomesitylene; W_b = 20·00; K = 52·6°.

0·3232	0·337	252·2
0·5467	0·548	262·4
0·6892	0·678	267·3
0·9359	0·896	274·7

Mean M, 264·2; M_B = 233·5; M_0 = 149; x = 77·3%.

s-Tribromonitrosobenzene;* W_b = 17·61; K = 52·6°.

0·2387	0·130	396·0
0·5964	0·413	431·4
1·1069	0·694	476·3
1·5921	0·957	496·8

Mean M, 450·3; M_0 = 354; x = 30·9%.

m-Nitronitrosobenzene;* W_b = 27·89; K = 52·3°.

0·1195	0·144	155·6
0·2114	0·256	154·8
0·3174	0·387	153·8
0·4143	0·503	154·4

Mean M, 154·7; M_0 = 152; x = 1·8%.

a-Nitrosonaphthalene;* W_b = 26·85; K = 51·7°.

W_s.	Δt.	M.	
0·2172	0·259°	160·8	Mean M, 164·2; M_0 = 157; x = 4·6%.
0·4136	0·486	164·2	
0·5808	0·667	167·7	

itself and its *m*- and *p*-derivatives, we find indications of small associations of about the same order. Passing to nitroso-derivatives in which there is more than one ortho-substituent, we find that they are definitely more associated than nitrosobenzene itself and its *m*- and *p*-derivatives, the effect of the nitro-group being particularly marked *; and in the di-ortho-substituted derivatives we find, in all

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* The magnitude of the influence of the nitro-group in the ortho-position led us to hope that the association of the *s*-trinitronitrosobenzene described by Nietzki and Dietschy (*Ber.*, 1901, **34**, 57) would be extremely high. Unfortunately all attempts to prepare the compound by following their directions failed.

the cases examined, enormously enhanced stability of the bimolecular form. These facts are summarised in Table III.

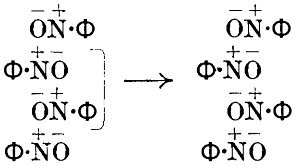
TABLE III.

Substituents.

meta		Br		NO_2		
para	CH_3		Br		NO_2	
x, %	4·2	2·2	1·2	1·8	2·0	Mean $x = 2{\cdot}3\%$.
ortho	CH_3	CH_3	Br	NO_2	OCH_3	α-Nitrosonaphthalene.
para		CH_3				
x, %	9·2	5·8	6·2	38·3	5·5	4·6 Mean $x = 11{\cdot}6\%$.
di-ortho	CH_3	CH_3	Br			
para		CH_3	Br			
x, %	75·8*	80·0	30·9			Mean $x = 61{\cdot}9\%$.

* Bamberger and Rising (*loc. cit.*).

The obvious interpretation of these results is that the presence of a substituent, whatever its polar nature may be, in one or both of the positions ortho to the nitroso-group exerts a steric effect that impedes the dissociation of the bimolecular form more than it hinders the recombination of the simple molecules. It is not easy to see any simple reason for this. It may be noted, however, that the nitroso-group is highly polar, the dipole moment of nitrosobenzene being $3{\cdot}22 \times 10^{-18}$ C.G.S. units (Hassel and Naeshagen, *Z. physikal. Chem.*, 1930, *B*, **6**, 441). Unpublished results obtained in this laboratory by Messrs L. E. Sutton and R. G. A. New have confirmed this figure and shown that the negative end of the dipole is outwards, as in nitrobenzene. Dipole associates must therefore be formed in solutions of nitroso-compounds and are likely to constitute the first step towards the formation of the true bimolecular complex. This step will occur under the influence of electric forces and will be a bimolecular process. The decomposition of the bimolecular dipole complex may occur in several ways, which may be operating concurrently, *e.g.*, as a unimolecular process, or as the result of impact with other molecules, or as the consequence of a purely electrical process in which two polar simple molecules align themselves with respect to the dipole complex in such a way that this complex is "loosened" into two single molecules, thus :

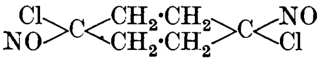


$$\begin{array}{ccc}
\overset{-\,+}{\mathrm{ON}}\cdot\Phi & & \overset{-\,+}{\mathrm{ON}}\cdot\Phi \\
\left.\begin{array}{r}\Phi\cdot\overset{+\,-}{\mathrm{NO}} \\ \overset{-\,+}{\mathrm{ON}}\cdot\Phi\end{array}\right] & \longrightarrow & \begin{array}{l}\Phi\cdot\overset{+\,-}{\mathrm{NO}} \\ \overset{-\,+}{\mathrm{ON}}\cdot\Phi\end{array} \\
\Phi\cdot\overset{+\,-}{\mathrm{NO}} & & \Phi\cdot\overset{+\,-}{\mathrm{NO}}
\end{array}$$

Clearly a termolecular process such as this would be impeded by ortho-substituents more than the bimolecular process that forms the complex, and would result in a stabilisation of the bimolecular form.

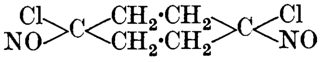
It is unlikely that the bimolecular forms of nitroso-compounds are nothing more than dipole aggregates (compare, however, Bamberger, *Ber.*, 1911, **44**, 3066, who regards them as "molecular compounds"). The properties of the unstable bimolecular forms of the aromatic nitroso-compounds cannot be distinguished from those of the unimolecular form that is always present with them. The properties of the extremely stable bisnitrosobenzyl $(C_6H_5{\cdot}CH_2{\cdot}NO)_2$ (Behrend and König, *Annalen*, 1891, **263**, 212), which is a true nitroso-compound, indicate, however, that there is an N–N link in the bimolecular form : for instance, the action of hydrogen chloride in chloroform in the cold gives a mixture of benzoyl and benzoyl-benzal hydrazines (compare, however, Bamberger, *loc. cit.*). Rather more satisfactory evidence for an N–N link in bisnitroso-compounds is found in the properties of these derivatives of the terpenes; *e.g.*, Baeyer (*Ber.*, 1895, **28**, 642) showed that bisnitrosocarone, $C_{10}H_{15}O{\cdot}N_2O_2{\cdot}C_{10}H_{15}O$, yields with acids a nitrosohydroxylamine $C_{10}H_{15}O{\cdot}N(OH){\cdot}NO$.

The properties of 1 : 4-dichloro-1 : 4-dinitroso*cyclo*hexane (Piloty, *Ber.*, 1902, **35**, 3101) throw further light on the question. Two forms of the compound exist, one blue and the other colourless. Each gives the simple molecular weight in solution. The colourless form becomes blue on being heated in solution, and colourless again on cooling. There is little doubt that the two forms are *cis*- and *trans*-isomerides and that the nitroso-groups, though too far apart to interact within the molecule in the blue *trans*-form (I), do so in the *cis*-form (II), the N_2O_2 complex being disrupted on heating. If, now, we suppose that the structure of the N_2O_2 group is $\overset{O}{\overset{\uparrow}{-N}}=\overset{O}{\overset{\uparrow}{N}}-$, we can represent the *cis*-isomeride (colourless) as having two fused six-membered rings (III), which, as well as being more probable than the 7- or 8-membered rings that are necessary for any other possible structure, is in accordance with the evidence already quoted that points to an N–N link. The oxyazoxy-structure, $O\leftarrow\dot{N}=\dot{N}\rightarrow O$, is found in diphenyleneazone oxide (IV), which is obtained by the reduction of *oo'*-dinitrodiphenyl (Täuber, *Ber.*, 1891, **24**, 308)



$$\begin{matrix}Cl\\NO\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}NO\\Cl\end{matrix}$$

(I.)

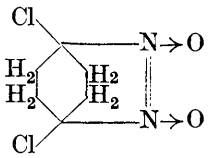


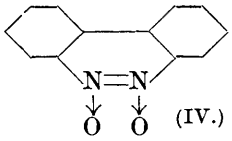
$$\begin{matrix}Cl\\NO\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\NO\end{matrix}$$

(II.)

and appears to be the completely stabilised form of *oo'*-dinitrosodiphenyl.

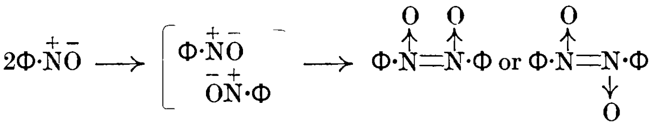
(III.)





(IV.)

It is suggested, therefore, that the first step in the polymerisation of simple nitroso-molecules is the formation of a dipole aggregate, which passes into an oxyazoxy-structure, thus :



$$2\Phi\cdot\overset{+\,-}{NO} \longrightarrow \left[\begin{array}{l}\Phi\cdot\overset{+\,-}{NO}\\ \overset{-\,+}{ON}\cdot\Phi\end{array}\right] \longrightarrow \Phi\cdot\overset{O}{\overset{\uparrow}{N}}{=}\overset{O}{\overset{\uparrow}{N}}\cdot\Phi \text{ or } \Phi\cdot\overset{O}{\overset{\uparrow}{N}}{=}\underset{O}{\underset{\downarrow}{N}}\cdot\Phi$$

It is not improbable that as an intermediate step the process passes through the stage $\Phi{\cdot}N{<}\substack{O\\O}{>}N{\cdot}\Phi$, which is the structure suggested by Ingold and Piggott (J., 1924, **125**, 168) for the bimolecular form and is analogous to what is presumably the intermediate phase in the isomerism of the substituted azoxybenzenes (Angeli, Ahrens Sammlung, 1913, XIX, 458).

Summary.

Molecular weights have been found in benzene solution for nitrosobenzene and a number of its substituted derivatives. It has been shown that nitrosobenzene itself and its *m*- and *p*-derivatives are slightly associated in dilute solution, and that a steric effect by mono- and di-ortho-substituents can be detected.

It is suggested that the first stage in the polymerisation is the formation of a dipole aggregate, which passes into an oxyazoxy-structure.

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THE DYSON PERRINS LABORATORY,
OXFORD.

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Note added, November 30th.—It has been pointed out to the author by Dr. S. G. P. Plant that $\begin{array}{c}R{\cdot}N\rightarrow N{\cdot}R\\ \|\qquad\downarrow\\ O\qquad O^{\cdot}\end{array}$ is a possible formula for the bimolecular forms of nitroso-compounds. It would obviously account for their instability; its further implications will be discussed in a later communication.