8. *The Electric Dipole Moments of Nitromesitylene and of the Bimolecular Forms of Nitrosomesitylene and 2-Nitroso-2 : 5-dimethylhexane.*

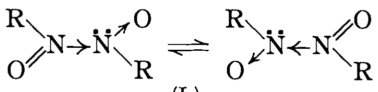
By DALZIEL LL. HAMMICK, RANDAL G. A. NEW, and R. BRANSTON WILLIAMS.

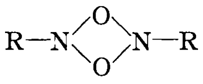
THE structure of the $-N_2O_2-$ complex in the bimolecular forms of nitroso-compounds has been discussed in recent communications (Hammick, J., 1931, 3105; Hammick, New, and Sutton, J., 1932, 742), the conclusion being reached that the properties of the polymerides are best represented by the structural formula (I).

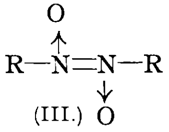
It was pointed out that additional support would be given to this structure if it could be shown that the bimolecular form has the finite dipole moment that the structure requires. Unfortunately, it is not possible to find a suitable bisnitroso-compound that can be dissolved without dissociation. We have, however, been able to arrive at a knowledge of the dipole moment of the $-N_2O_2-$ complex in the bimolecular forms in two ways. In the first we have obtained the necessary data from measurements on solutions of nitrosomesitylene in benzene, in which the proportions of single and double molecules at various temperatures are known (Ingold and Piggott, J., 1924, **125**, 165). In order to allow for the presence of the single molecules, the moment of unimolecular nitrosomesitylene must be known. It cannot be assumed to be the same as that of nitrosobenzene owing to the effects that ortho-substituents are known to exert on the dipole moment of a group attached to the benzene nucleus (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 564). We have therefore determined the moment of nitromesitylene in benzene solution ($\mu = 3{\cdot}67 \pm 0{\cdot}01$ *) and compared it with that of nitrobenzene ($\mu = 3{\cdot}94$). Assuming that the ortho-methyl groups affect the nitroso-group to the same extent as they do the nitro-group, we have calculated polarisations for unimolecular nitrosomesitylene. Making use of these values, we find the following values for the dipole moment of bimolecular nitrosomesitylene : $1{\cdot}37 \pm 0{\cdot}13$ at 8° and $1{\cdot}63 \pm 0{\cdot}10$ at 25°.

A second value for the moment of the dimeric form was obtained from experiments on solutions of 2-nitroso-2 : 5-dimethylhexane in carbon tetrachloride. This compound dissolves in the cold to give a colourless solution of the bimolecular form which slowly depolymerises. By making determinations of dielectric constant at successive intervals of time and extrapolating to zero time, we have found the value $\mu = 0{\cdot}99 \pm 0{\cdot}10$.

The mean value for the dipole moment is lower than might have been expected from the wide separation of charge that is implied in the structure (I). It is probable, however, that resonance of the type suggested by Pauling would occur in such a molecule, valency rearrangement unaccompanied by any atomic migration taking place in less time than that required to orient the molecule in the electric field :


(I.)


(II.)


(III.)

The molecule would then have a small moment analogous to that possessed by ethylene dichloride ($\mu = 1{\cdot}1$—$1{\cdot}4$) and by *p*-phenylenediamine ($\mu = 1{\cdot}5$), due to rotation about

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* This and all subsequent dipole moments are in Debye units, e.s.u. × 10^{-18}.

the central N–N link out of the *trans*-position which the molecule would tend to assume owing to the repulsion of similar dipoles.

Of the three structures for the bisnitroso-group hitherto discussed (Hammick, New, and Sutton, *loc. cit.*), *viz.*, (I), (II), and (III), (II) was considered to be inadmissible on the chemical evidence, and (III) suggests too stable a molecule. It is reasonable to suppose, moreover, that in a dissociating system the stabler *trans*-form would predominate in solution, as is found to be the case for the azo-compounds (Bergmann, Engel, and Sandor, *Ber.*, 1930, **63**, 2572). The fact that the structure has a finite dipole moment therefore rules out (III). Structure (I) therefore remains as the best representation of the chemical properties of bisnitroso-molecules (instability, *o,p*-orienting effect, etc.; cf. Hammick, Sutton, and New, *loc. cit.*).

EXPERIMENTAL.

Preparation of Materials.—The solvents benzene and carbon tetrachloride were carefully purified and were distilled from phosphorus pentachloride in a current of dry air just before use.

Nitromesitylene was prepared by the direct nitration of mesitylene; m. p. 43·5°.

Nitrosomesitylene was prepared by the oxidation of mesidine with Caro's acid. The use of a large excess of the oxidising agent gave a better yield of a cleaner product than when the ordinary procedure was followed. 290 G. of ammonium persulphate were added to 235 c.c. of concentrated sulphuric acid, cooled to 0°, and the mixture stirred mechanically for an hour at that temperature. It was then poured on to a mixture of 2 kg. of ice and 2 litres of water, neutralised with solid sodium carbonate, and filtered. The filtrate was divided into three parts, to each of which 5 g. of mesidine were added in small portions. After each addition the mixture was well shaken, sodium hydroxide solution added to keep the solution definitely alkaline, and the solid nitrosomesitylene filtered off. The combined solid products were washed with water and finally a little ice-cold alcohol. Two recrystallisations from alcohol at 60° (higher temperatures caused decomposition) gave a product of m. p. 122·5°.

2-Nitroso-2 : 5-dimethylhexane was prepared as described by Hammick, New, and Sutton (*loc. cit.*).

Determination of Electric Dipole Moments.—The method and apparatus described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668) were used.

Nitromesitylene. The results of the measurements, at 25° in benzene solution, are in Table I, where the symbols have their usual significance; the refractive index relates to the mercury green line 5461. To minimise errors in the densities, the experimental values were plotted against *f*, and the values used in the calculations obtained from the mean line.

TABLE I.

f_2.	$d_{4°}^{25°}$.	ϵ.	n^2.	P_2.	${}_eP_2$.
0·00595	0·8959	2·38664	2·25766	320·94	46·94
0·01058	0·8775	2·47472	2·25805	315·51	46·80
0·01735	0·8797	2·60292	2·25882	308·47	46·96
0·01977	0·8806	2·65057	2·25902	307·23	46·86

By extrapolation, $P_2 = 326{\cdot}5$ c.c. and ${}_eP_2 = 46{\cdot}9$ c.c. at infinite dilution, whence $\mu = 3{\cdot}67 \pm 0{\cdot}01$.

Numerous determinations of the dipole moment and electron polarisation of nitrobenzene in benzene are to be found in the literature. Using the same apparatus as ourselves, Mr. H. O. Jenkins of this laboratory has obtained the values $\mu = 3{\cdot}94$ and ${}_\infty P_e = 32{\cdot}6$ c.c. (unpublished results). Taking these values and assuming that, for a given temperature,

$${}_\infty P \text{ (unimolecular nitrosobenzene)} - {}_\infty P \text{ (unimolecular nitrosomesitylene)} = {}_\infty P \text{ (nitrobenzene)} - {}_\infty P \text{ (nitromesitylene)}$$

for both total and electron polarisations at infinite dilution, we have calculated the following polarisations at infinite dilution for unimolecular nitrosomesitylene :

Temp.	${}_\infty P$, c.c.	${}_\infty P_e$, c.c.
8·0°	223·6	46·1
25·0	213·5	46·1

The values taken for nitrosobenzene throughout were $\mu = 3{\cdot}18$ (Hammick, New, and Sutton, *loc. cit.*).

Nitrosomesitylene, in benzene at 8° *and at* 25°. The molar fractions of double and single molecules are given under f_2 and f_3 in Table II and were obtained from the data provided by Ingold and Piggott (*loc. cit.*); dissociation constants for the bimolecular form were found to be 0·00150 at 8° and 0·00596 at 25°, compositions being expressed as molar fractions. Col. 5 gives $P_2f_2 + P_3f_3$, the fraction of the total polarisations due to the single and double molecules taken together. As we wish to find P_2, the polarisation for the bimolecular form, we have to know P_3, that of the single molecule. This has been calculated from the foregoing data at infinite dilution, the polarisation being assumed to vary with concentration in the same way as that of nitrosobenzene.

TABLE II.

f_2.	f_3.	$d_{4°}^{t°}$.	ϵ.	$P_2f_2 + P_3f_3$.	P_3.	P_2.
			1st *Series, at* 8°.			
0·00795	0·00345	0·8985	2·37174	1·70286	222·3	117·7
0·00507	0·00276	0·8961	2·35613	1·22353	222·6	120·3
0·00326	0·00221	0·8946	2·34568	0·91122	222·8	128·3
0·00212	0·00178	0·8937	2·33685	0·67498	222·9	131·4
			2nd *Series, at* 8°.			
0·00803	0·00347	0·8981	2·37322	1·74483	222·3	121·2
0·00691	0·00322	0·8972	2·36785	1·57040	222·4	123·7
0·00279	0·00205	0·8940	2·34264	0·83082	222·9	134·3
0·00179	0·00164	0·8932	2·33548	0·63008	223·0	147·2
			3rd *Series, at* 25°.			
0·00782	0·00663	0·8810	2·3803	2·444	211·2	133·4
0·00519	0·00541	0·8790	2·3596	1·879	211·5	141·5
0·00330	0·00431	0·8775	2·3406	1·398	211·9	147·0
0·00259	0·00381	0·8769	2·3328	1·192	212·2	148·3

The first two sets of values for P_2 give, when plotted against f_2, the polarisations 137·4 c.c. and 141·2 c.c. respectively at infinite dilution. The mean value, 139·3 c.c., has been used to calculate the dipole moment of bimolecular nitrosomesitylene at 8°.

The densities and refractive indices at 25° used in calculating the total electron polarisation ${}_eP_2 + {}_eP_3$ for the two solutes (single and double molecules) are given in Table III. The value of ${}_eP_3$, the electron polarisation of the unimolecular form, has been taken as 46·1 c.c. (see above) in all cases, the electron polarisation–molar fraction curve for nitrosobenzene, and hence, it is assumed, for nitrosomesitylene also, being a horizontal straight line.

TABLE III.

f_2.	f_3.	$d_{4°}^{25°}$.	n^2.	${}_eP_{f_2} + {}_eP_{f_3}$.	${}_eP_2$.
0·00661	0·00628	0·8805	2·26466	0·89934	92·2
0·00654	0·00624	0·8809	2·29624	0·90065	93·7
0·00561	0·00578	0·8795	2·26406	0·79536	94·2
0·00400	0·00488	0·8785	2·26341	0·60803	95·8
0·00206	0·00350	0·8762	2·25978	0·35965	96·2

${}_eP_2$ plotted against f_2 extrapolates to 98·6 c.c. Using this value for the electron polarisation together with the values for the total polarisations at 8° and 25°, we obtain $\mu_{8°} = 1·37 \pm 0·13$ and $\mu_{25°} = 1·63 \pm 0·09$.

The degrees of accuracy assigned to the above values for the dipole moment depend mainly upon the uncertainty in the extrapolated values at infinite dilution, errors in the other data, including the dissociation constant, being negligible in comparison. It will be seen that the values at the two temperatures agree practically to within the limits of experimental error.

2-*Nitroso*-2 : 5-*dimethylhexane.* Determinations of dielectric constants in carbon tetrachloride solution were carried out at 0° in order to keep the rate of dissociation of the bimolecular form as low as possible. Solutions were made up with solvent at 0° and introduced rapidly into the condenser. Readings on the balancing variable condenser were taken at intervals over about 2 hours. These readings, when plotted against time, lay on a straight line, which, when extrapolated to zero time, gave the values shown in Table IV for the dielectric constants ε and total polarisations P_2 for the molar fraction f_2 of solute. The electron polarisations for the unimolecular form were obtained from refractive indices of carbon tetrachloride solutions at 25°, equilibrium in such solutions being known (Piloty and Ruff, *Ber.*, 1898, **31**, 456) to correspond to almost complete dissociation. Refractivities of solutions of the colourless bimolecular form could not be determined at temperatures sufficiently low for the method of extrapolation to zero time to be applied, and the electron polarisation of the bimolecular form has therefore been taken as twice that of the unimolecular.

TABLE IV.

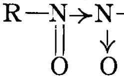
f_2.	$d^{0°}_{4°}$.	ϵ.	P_2, c.c.	f_2.	$d^{25°}_{4°}$.	n^2.	${}_eP_2$, c.c.
0·00178	1·6288	2·27486	106·8	0·00356	1·5802	2·13188	43·5
0·00194	1·6284	2·27583	113·6	0·00560	1·5773	2·13144	44·1
0·00281	1·6263	2·27573	107·2				
0·00334	1·6250	2·27599	106·5				
0·00412	1·6231	2·27823	112·7				

The mean of the above values of P_2, *viz.*, 109·4 c.c., has been taken as the value at infinite dilution. This is justifiable because the total polarisation–molar fraction curve will be almost parallel to the molar fraction axis since the substance has a small moment. The mean value 43·8 c.c. for ${}_eP_2$ was taken as the refractivity of the unimolecular form at infinite dilution, and that of the bimolecular form as 87·6 c.c. Hence we find $\mu = 0·99 \pm 0·10$ for 2-nitroso-2 : 5-dimethylhexane.

The experimental errors and the errors involved in the various assumptions made are not inconsiderable. The fact, however, definitely emerges that the moment of the $^-N_2O_2{}^-$ complex in the bisnitroso-compounds is finite and of the order 1—1·5.

SUMMARY.

The electric dipole moments of bimolecular nitrosomesitylene and 2-nitroso-2 : 5-dimethylhexane have been found to be finite, which is evidence in support of the structure



$\underset{\underset{O}{\|}}{R—N}\rightarrow\underset{\underset{O}{\downarrow}}{N}—R$ for the bimolecular forms.

We wish to acknowledge a grant from Imperial Chemical Industries, Ltd., and to thank Dr. L. E. Sutton for much valuable advice and criticism.

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