

### 93. *The Orienting Power of the Nitroso-group.*

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It has been shown by Ingold (J., 1925, **127**, 513) that the nitration and the bromination of nitrosobenzene in carbon disulphide give para-substituted products. Hammick and Illingworth (J., 1930, 2358) have found that nitrosobenzene is partially associated in carbon disulphide but that it is unimolecular in acetic acid, and that bromination to give bromonitrosobenzene does not take place in the latter solvent. Le Fèvre has shown that in benzene solution the action of bromine gives *p*-bromonitrosobenzene (J., 1931, 810) and it has been found (Hammick, J., 1931, 3105) that nitrosobenzene is apparently associated to a small extent in that solvent. In the light of these facts, it has been suggested (Hammick and Illingworth, *loc. cit.*) that the  $\text{-N=O}$  group in the simple nitrosobenzene is meta-directing, para-substitution taking place only when the bimolecular form is present in solution. In support of this view attention has been drawn to the reactivity of the bromine atoms in *o*- and *p*-bromonitrosobenzene.

It has been shown by one of us (L. E. S.) that when the dipole moments of monosubstituted benzene derivatives are compared with those of the corresponding tertiary alkyl derivatives (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668) differences are found that appear to correspond to the electron shift in or out of the benzene nucleus postulated by Lapworth and by Robinson and called by them the electromeric effect (Lapworth, J., 1922, **121**, 416; Kermack and Robinson, *ibid.*, p. 427; Allan, Oxford, Robinson, and Smith, J., 1926, 401). Comparison was made for thirteen substituent atoms and groups, and in every case agreement was found with the requirements of the Lapworth-Robinson orientation theory. Thus in all cases where the substituent is ortho-para-orienting, where that theory would require an inward electronic drift ( $+T$ ) the existence of such an effect has been demonstrated. Similarly, a connexion between meta-orientation and a negative, outward electromeric effect has been equally clearly made out. It is thus reasonable to expect that, if the nitroso-group is really meta-directing, an outward or negative electronic shift ( $-T$ ) should be demonstrable. We have therefore measured the electric dipole moments of nitrosobenzene, *p*-chloronitrosobenzene, and 2-nitroso-2 : 5-dimethylhexane.

#### EXPERIMENTAL.

*Preparation and Purification of Materials.*—Nitrosobenzene. This was made from nitrobenzene prepared from specially purified

benzene; it was steam-distilled, crystallised three times from alcohol, and dried in a vacuum. Decomposition of nitrosobenzene at its melting point appears to be more rapid than is usually supposed, so the melting point is not a satisfactory criterion of purity. With rapid heating, it melts at 68—69°. Numerous attempts at further purification yielded products with this melting point. Recrystallisation, as far as possible out of contact with the air, did not affect the melting point, although Jaeger (*K. Akad. Wetensch. Amsterdam*, 1912, **14**, 731) claims that it is raised by this treatment.

*p*-Chloronitrosobenzene. Recrystallised *p*-chloronitrobenzene was reduced with zinc dust in boiling aqueous alcohol, in presence of ammonium chloride. The hydroxylamine solution was oxidised with the theoretical quantity of ferric chloride at 0°, and the solid separating was steam-distilled in portions of 2 g.; yield, 27% of the theoretical (see Ham, *Dissert.*, Zurich, 1904, 29). It was recrystallised three times from alcohol and used for measurement; the m. p. with fairly rapid heating was 88—89° (Ham, 89·5°).

2-Nitroso-2 : 5-dimethylhexane. *iso*Butyl alcohol was fractionated and converted into the iodide; this was made into diisobutyl by the Würtz reaction, and the hydrocarbon nitrated by Konovalov's method (*Ber.*, 1895, **28**, 1853). The nitration was carried out as follows: 4 g. of diisobutyl were heated in a sealed tube for 2 hours at 110—115° with 40 c.c. of nitric acid (*d* 1·15). The non-aqueous layer was separated, washed well with alkali to remove primary and secondary nitro-compounds, then with water, dried, and distilled up to 150°; the distillate was renitrated in the same way, together with fresh hydrocarbon. The united products boiling above 150° from 18 tubes were distilled in a vacuum, the middlefraction being retained. The nitro-compound was reduced with aluminium amalgam, and the hydroxylamine solution oxidised with dichromate to the nitroso-compound (Piloty and Ruff, *Ber.*, 1898, **31**, 457). To ensure that as little reduction to amine as possible should take place, portions of the solution were titrated with dichromate during the course of the reaction; the reaction was stopped when the titre indicated approach to complete reduction to hydroxylamine. The nitroso-compound was steam-distilled and recrystallised from dilute alcohol; m. p. 53—54° (Piloty and Ruff, 54°).

*Measurement of Electric Dipole Moments.*—These were measured in benzene solution at 25° by the method used before (Sutton, *loc. cit.*).

The results are tabulated below, where  $f_2$  is the molar fraction of the solute,  $d_2^{25}$  the density of the solution,  $e$  its dielectric constant, and  $n$  its refractive index (Hg green line, 5461), all at 25°;  $P_2$  is the total polarisation of the solute, and  $\rho P_2$  its electron polarisation. To

minimise errors in the densities, the experimental values have been plotted against  $f_2$ , and values used in the calculations have been obtained from the mean line; these interpolated values are quoted under " $d_4^{25}$ " in the tables.

$f_2$ .	$d_4^{25}$ .	$e$ .	$n$ .	$P_2$ .	${}_eP_2$ .
Nitrosobenzene.					
0.02864	0.8804	2.6946	—	226	—
0.02035	0.8784	2.5706	—	230	—
0.01436	0.8770	2.4826	—	233	—
0.01407	0.8770	2.4769	—	231	—
0.01011	0.8760	2.4202	—	232	—
0.00694	0.8753	2.3743	—	234	—
0.05425	0.8858	—	1.5055	—	32.3
0.02611	0.8798	—	1.5038	—	32.2
0.02521	0.8796	—	1.5037	—	31.7
0.02196	0.8788	—	1.5034	—	31.9
0.01765	0.8778	—	1.5033	—	32.3
0.01228	0.8766	—	1.5029	—	32.5

$P_2$  at infinite dilution = 237 c.c.;  ${}_eP_2 = 32$  c.c.;  $P_2 - {}_eP_2 = 205$  c.c.  
 $\mu = 3.14 \times 10^{-18}$  e.s.u.

(Hassel and Naeshagen, *Z. physikal. Chem.*, 1930, *B*, 6, 441, find  
 $\mu = 3.22 \times 10^{-18}$  e.s.u.)

<i>p</i> -Chloronitrosobenzene.					
0.02299	0.8849	2.3876	—	104.0	—
0.02181	0.8842	2.3815	—	104.4	—
0.01643	0.8817	2.3554	—	105.0	—
0.01531	0.8811	2.3498	—	104.8	—
0.01138	0.8792	2.3306	—	105.3	—
0.01061	0.8787	2.3258	—	104.2	—
0.00804	0.8776	2.3130	—	103.4	—
0.02857	0.8874	—	1.5053	—	38.2
0.02299	0.8849	—	1.5047	—	37.9
0.02181	0.8842	—	1.5044	—	38.0
0.01928	0.8832	—	1.5044	—	38.1
0.01353	0.8803	—	1.5035	—	37.8

$P_2$  at infinite dilution = 104.9 c.c.;  ${}_eP_2 = 37.6$  c.c.;  $P_2 - {}_eP_2 = 67.3$  c.c.  
 $\mu = 1.80 \times 10^{-18}$  e.s.u.

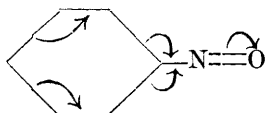
2-Nitroso-2 : 5-dimethylhexane.					
0.006938	0.8730	2.3220	1.5007	151.3	42
0.002875	0.8735	2.2952	1.5014	158.6	41
0.002073	0.8736	2.2902	—	165.9	—
0.001419	0.8737	2.2857	—	169.8	—

$P_2$  at infinite dilution = 173 c.c.;  ${}_eP_2 = 41$  c.c.;  $P_2 - {}_eP_2 = 132$  c.c.  
 $\mu = 2.51 \times 10^{-18}$  e.s.u.

Piloty and Ruff (*Ber.*, 1898, **31**, 456) have shown by freezing-point determination that the solute in a benzene solution of the last compound is bimolecular when the solution is first made up, but that it gradually dissociates, equilibrium corresponding to almost complete dissociation. To make sure that the solute should be present in the unimolecular form, the solutions in the present measurements were made up and left over-night at room temperature, with precautions against evaporation.

*Discussion of Results.*

From the fact that the moment of *p*-chloronitrosobenzene ( $1.80 \times 10^{-18}$  e.s.u.) is nearer the difference than the sum of the moments of nitrosobenzene and chlorobenzene ( $3.14$  and  $1.56 \times 10^{-18}$  e.s.u., respectively) it follows that the moment of the nitroso-group is negative in sense (Sutton, *loc. cit.*, pp. 678, 684; previous references are there given). Moreover, since the moment of nitrosobenzene is numerically greater than that of 2-nitroso-2 : 5-dimethylhexane, it is clear that the nitroso-group causes a negative electromeric effect when introduced into the benzene ring, *i.e.*, that of the two possible systems discussed by Robinson (*Chem. and Ind.*, 1925, **44**, 456) only the crotonoid system is set up to an appreciable extent :—



The actual value of the moment due to the electromeric effect is not equal to the numerical difference of these two moments, since the group is unsymmetrical about the valency joining it to the benzene ring, and any attempt to calculate it involves a knowledge not merely of the magnitudes of the moments but also of their directions, *i.e.*, the angles which they make with the C-N link (Sutton, *loc. cit.*, pp. 690—694). Though this can be calculated for the aryl derivative, from the moments of nitrosobenzene, chlorobenzene, and *p*-chloronitrosobenzene, to be  $157.7^\circ$  (see Fig. 3), it can only be calculated for the aliphatic derivative if the moments of the  $\text{CH}_3$  group and the C-N link, and the angle between the latter and the N=O link are known. The vector sum of the  $\text{CH}_3$  and C-N moments in this case may be taken as approximately equal to that which may be calculated from the moment of methylamine ( $1.23 \times 10^{-18}$  e.s.u.) by allowing for the moment of the  $\text{NH}_2$  group from the moment of ammonia ( $1.5 \times 10^{-18}$  e.s.u., taking the angles in this as equal to the tetrahedral angle,  $109.5^\circ$ ) and solving the vector triangle for the minimum angle between the C-N link and the plane containing the N-H valencies which can give a real value ( $135^\circ$ ; see Fig. 1).

This gives a value of  $1.2 \times 10^{-18}$  e.s.u. for the moment of the  $\text{H}_3\text{C-N}$ -group. The angle required may be taken as that between one of the axes of three-fold symmetry of a regular tetrahedron and a plane containing two of the others, *viz.*,  $125^\circ 16'$ . From these data the value found for the angle between the moment of the tertiary alkyl nitroso-compound and the C-N link is  $148^\circ$  (see Fig. 2). The moment due to the electromeric effect ( $m_e$ ) is then found to be  $-0.8 \times 10^{-18}$  e.s.u. (see Fig. 3). In view of the assumptions

involved in obtaining some of the data for the final calculation, this value can only be regarded as approximate, but it shows that the simple numerical difference of the aromatic and the aliphatic moments of  $-0.64 \times 10^{-18}$  e.s.u. is a minimum probable value. The electromeric effect is therefore roughly the same as that found previously for the nitro- and aldehydo-groups (Sutton, *loc. cit.*) and in view of this and of the negative induced effect ( $-I$ ) set up by the negative moment, the nitroso-group will be meta-directing. This is in agreement with the observations of Hammick and Illingworth and of Le Fèvre referred to in the introduction.

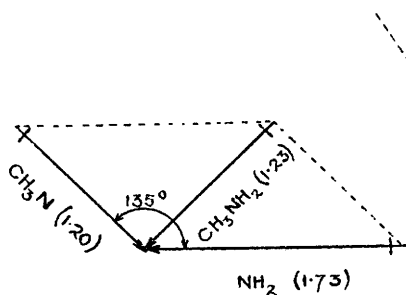


FIG. 1.

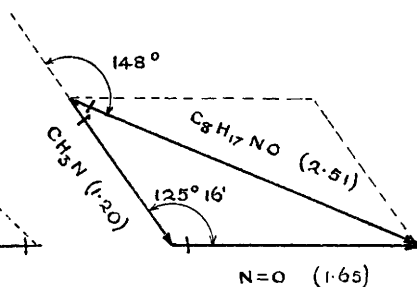


FIG. 2.

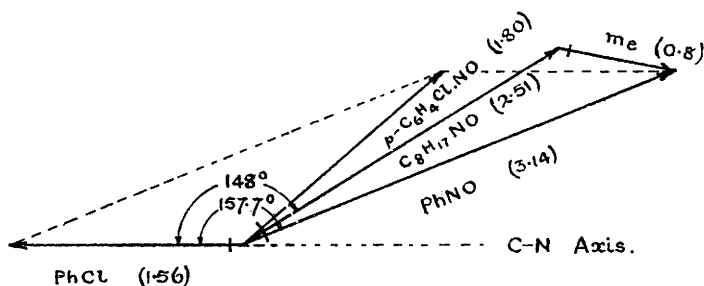
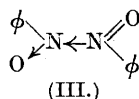
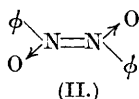
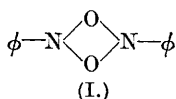


FIG. 3.

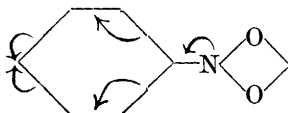
(For a note on the diagrammatic representation of dipoles, see Hammick, New, Sidgwick, and Sutton, J., 1930, 1880.)

It is to be inferred, therefore, that the ortho-para-substitution occurs only in the bimolecular polymeride, and it remains to find a structure for it which can explain this. That the type of polymeride formed by these nitroso-compounds is a definite chemical compound and not solely a dipole complex (see Debye, "Handbuch der Radiologie," Marx, Leipzig, 1925, p. 636; Smyth, "Dielectric Constant and Molecular Structure," New York, 1931, p. 169) is shown by the facts that *tert.*-nitrosobutane (Bamberger and Seligmann, *Ber.*, 1903, **36**, 690) and 2-nitroso-2 : 5-dimethylhexane (Piloty and Ruff, *loc. cit.*), when freshly dissolved in benzene, are nearly bimolecular,

but that the molecular weights *slowly* fall (showing that a critical increment or heat of activation is necessary for the dissociation of the polymeride) almost to those of the unimolecular forms, this being accompanied by a marked colour change. Moreover, Ingold and Piggott (J., 1924, **125**, 168) showed, by colorimetric determinations of the variation of equilibrium with temperature, that nitroso-mesitylene formed a definitely dimeric polymeride. The following structures are possible :—



(I) and (II) have been discussed in connexion with the mechanism of the association process (Hammick, *loc. cit.*), the suggestion being made that all three structures may be in tautomeric equilibrium. (III) has been suggested to the authors by Dr. S. G. P. Plant of this Laboratory. Of these structures, (II) could not exert an ortho-para-activating effect by induction (+ *I*) on the phenyl groups attached to it, and a positive electromeric effect (+ *T*) is unlikely in the light of the known properties of the azoxy-compounds (compare Angeli, *Ahrens Sammlung*, 1913, **19**, 461). In structure (I), on the other hand, ortho-para-activation could obviously occur, the unshared electrons on the nitrogen atoms making it possible for a crotonoid system to be set up (Robinson, *loc. cit.*):—



In structure (III) the nitrogen atom attached to the left hand ring can set up a crotonoid system, which will not be opposed by a negative inductive effect because the influence of the negative  $N \rightarrow O$  moment will be opposed and probably neutralised by the positive  $N \rightarrow N$  moment, so that in this nucleus strong ortho-para-activation should occur. This structure, moreover, has the merit of explaining the instability of the bimolecular form, and may be considered as less inherently improbable than (I), in which the formation of a four-membered ring is postulated.

Of these structures, (III) is the only one which is unsymmetrical and hence could possess a finite dipole moment. It is true that *cis*- and *trans*-forms of (I) and (II) are possible, and that only the *trans*-forms will be symmetrical. We are, however, proceeding on the assumption that the stabler *trans*-forms will predominate in solution, as is found to be the case for the azo-compounds (Bergmann, Engel, and Sandor, *Ber.*, 1930, **63**, 2572), and propose to measure the

apparent dipole moments of highly associated nitroso-compounds such as nitrosomesitylene.

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