

315. *Dielectric Polarisation Measurements on some Nitroso-compounds.*

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THE total influence of a substituent radical upon the aromatic nucleus containing it has been analysed into three component types, the inductive, the tautomeric, and the direct effect. The first involves a permanent distortion of the covalency linkages, and, with the third, obviously could be studied directly by dipole-moment determination, if the molecule were only to possess an electrically rigid structure. The second consists of an additional covalency distortion which may arise within a molecule immediately prior to reaction, and will, in a given case, be specific for and caused by the particular approaching reagent molecule under consideration, and will be modified (in a series of cases involving the same reagent) by temperature, reaction medium, etc.

The greater number of known *op*-substitutions occur by this "tautomeric" mechanism, and, in order for this to function, the molecule clearly must be capable of becoming polarised, *i.e.*, of suffering temporary electron displacements. Whether the actuating cause is the electric field of another molecule or the electromagnetic waves of light is immaterial; temporary polarisations will be propagated throughout the molecule, proportional to, *inter alia*, the intrinsic ability of the molecule to become polarised, *i.e.*, to the magnitude of possible "T" covalency changes.

The Dipole Moment of the Nitroso-group.—An aromatic molecule containing a radical capable of materially assisting conjugative polarisations of both $+T$ and $-T$ types, according to the nature of the reagent applied, obviously possesses readily available covalency electrons and might thus be capable of very considerable polarisation (in the absence of reacting molecules or other strong applied electrical forces) at the instance of the weakly intrinsic polar nature of the substituent.

It has been suggested (J., 1931, 810) that an example of such a radical is the nitroso-group. In this case, then, the apparent possession by nitrosobenzene of a large dipole moment, considerably larger than that for 2-nitroso-2:5-dimethylhexane and even equalling that for nitrobenzene (Hammick, New, and Sutton, this vol., p. 742), although apparently indicating an electron drift out of the nucleus ($-I$ effect), could well be quite without prejudice to the ability of the nitroso-group to facilitate *op*-substitution under the action of the usual kationoid reagents. The differences of moments between aliphatic and aromatic isomerides follow only very roughly the same order as directing power (cf. table in *Ann. Reports*, 1931, 393, from which Cl would appear to be a stronger *op*-orienting group than NH_2 or CH_3) and could scarcely be used by themselves to diagnose the orienting nature of a substituent. The critical fact in making applications of this type would seem to be, not so much sign and sense of the differences between moments of aliphatic and aromatic isomerides, but rather whether the conjugative electron displacements caused by the substituent radical can or cannot be maintained against the attack of a strongly kationoid reagent at the *o*- or *p*-positions. If it cannot, then clearly the *o*- or *p*-substitution will occur. *A priori* it would seem that the greater the *op*-directive influence of a group the more will its apparent group moment depend on the specific nature of the remainder of the molecule. The measurements of the dipole moments of *p*-nitroso-dimethyl-, -diethyl-, and -monomethyl-anilines described in this paper, considered alongside existing data (Table I), show clearly that the nitroso-group has a large capacity for producing polarisation of the molecule as a whole, restricted, apparently, only by the specific inherent limitations of the ability of aryl radicals in each case to act further as electron sources and sinks. Thus, in these molecules, the presence of readily mobile electrons both in the nucleus and in the substituent groups causes the normal additivity rules for dipole moments to break down completely. In col. 4 of Table I are given the maximum values of the dipole moment to be expected according to the additivity principle, calculated from the data for nitrosobenzene (Hammick, New, and Sutton, *loc. cit.*), and for dimethyl- and

monomethyl-aniline (Fogelberg and Williams, *Physikal. Z.*, 1931, 32, 27).

TABLE I.

	$10^{18} \mu$ in C_6H_6 .	$10^{18} \mu$ in CCl_4 .	$10^{18} \mu$, calc. (max.).
$CMe_2H \cdot [CH_2]_2 \cdot CMe_2 \cdot NO$	2.51	—	—
$C_6H_5 \cdot NO$	3.14	—	—
<i>p</i> - $NMe_2 \cdot C_6H_4 \cdot NO$	6.89	6.33	4.72
<i>p</i> - $NEt_2 \cdot C_6H_4 \cdot NO$	7.18	6.42	—
<i>p</i> - $NHMe \cdot C_6H_4 \cdot NO$	7.38	—	4.78

The values shown in col. 2 were obtained in benzene solution, and those referring to *p*-nitroso-diethyl- and -monomethyl-aniline appear to be the largest dipole moments yet reported for any organic compound. Since, however, *p*-nitrosodimethylaniline is known to give a solid molecular compound with benzene (Wurster and Roser, *Ber.*, 1879, 12, 1824), which might persist in solution, it was considered desirable to check the determinations by using as solvent carbon tetrachloride, with which combination is unlikely. The values found for the electric moment were of the same order as, but slightly lower than, those obtained in benzene solution (Table I, col. 3), possibly owing to some solvation effect with this solvent. The results are also interesting as indicating clearly that the molecular compound with benzene is broken up in solution (cf. racemic compounds).

A phenomenon similar to the cases described above is observed with *p*-nitroaniline, but to a less marked extent. Thus, μ for aniline = 1.56, μ for nitrobenzene = 4.0 (mean of several authors' results); hence, the maximum value to be expected on an additivity basis = 5.56; actually, values of 6.4 (Tiganik, *Z. physikal. Chem.*, 1931, B, 14, 135) and 7.1 (Højendahl, *Physikal. Z.*, 1929, 30, 391) have been reported. At first sight, therefore, $\cdot NO_2$ and $\cdot NO$ might appear to be similar groups. That this is not the case, follows from the results of nitration of nitrobenzene (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, 19, 79), in which about 7% of *op*-nitration was observed notwithstanding the possession by the nitro-group of an integral positive ionic charge adjacent to the nucleus which should have undergone *m*-substitution. In view of the strongly *m*-directing character of a positive pole, the implication is that the nitroso-group, lacking such a charge, is predominantly *op*-directing.

EXPERIMENTAL.

Preparation of Materials.—(a) *Solvents.* The C_6H_6 used was British Drug Houses "Extra Pure for Molecular Weight Determination" grade; it was free from thiophen. It was dried over Na, recryst. twice, dried again, fractionally distilled, and then treated with successive quantities of Na wire until the latter retained its metallic lustre.

Pure commercial CCl_4 (Hopkin and Williams) was repeatedly washed successively with conc. H_2SO_4 , H_2O , $2N\text{-NaOH}$, and H_2O again. It was dried over anhyd. K_2CO_3 , fractionated, and then dried over KOH sticks. Tests for the usual impurities (COCl_2 , CS_2 , sulphur chlorides, and aldehydes) all gave negative results.

(b) *Nitroso-compounds.* These were prep. from the redistilled bases. No records seem to exist as to the recrystn. of *p*-nitroso-dimethyl- and -diethyl-aniline, which are always isolated by *evaporation* of ethereal solutions. By two successive crystns. of either compound from much light petroleum (b. p. 80—100°), specimens with m. p.'s 92.5—93.5° (lit. 85°) and 87—88° (lit. 84°) respectively were obtained.

Crystn. of nitrosodimethylaniline from C_6H_6 yielded large tablets, m. p. below 50°, which were pure green by transmitted and steel-blue by reflected light. Since, on standing in the air for 2 hrs., 14 g. of these crystals slowly fell to a green powder (9.1 g.), they were evidently the compound $\text{C}_8\text{H}_{10}\text{N}_2\text{O}\cdot\text{C}_6\text{H}_6$.

p-Nitrosomethylaniline was prep. as described by Fischer and Hepp (*Ber.*, 1886, 19, 2991); after two crystns. from C_6H_6 -light petroleum, it formed large blue crystals, m. p. 114—115°.

The cryoscopy of the above compounds has been examined by Auwers (*Z. physikal. Chem.*, 1900, 32, 53), using C_{10}H_8 as a solvent. Very little association of solute was obs. in dil. solutions. No figures for the mol. wts. of these nitroso-compounds in C_6H_6 or CCl_4 are available, but since the solutions in both solvents are strongly green, there can be little doubt that the solute mols. are in the monomeric condition.

Measurements.—The dielectric constns. of dil. solutions of the nitroso-compounds in C_6H_6 and in CCl_4 were determined by the resonance method described previously (*Proc. Roy. Soc.*, 1932, A, 136, 251). These measurements were made at 25° and in some cases also at 45°. The refractive indices of the same solutions were determined at 15° and for the Hg green (5461 Å.) line with a Pulfrich refractometer. The densities of the solutions were measured at the same temps. From these data the mol. polarisations and mol. refractivities of the solutes were calc. by the well-known modifications of the Clausius-Mosotti and Lorenz-Lorentz equations. The significant data are collected in Table II.

In the case of *p*-nitrosomethylaniline, and with *p*-nitrosodimethylaniline in CCl_4 , the range of concns. over which measurements could be made was limited by the relatively sparing solubility. Consequently, the figure for the mol. refraction in the former case is only approx.

In Table II, the symbols M , P , and R refer respectively to the mol. wts., mol. polarisations, and mol. refractivities of the components, and f to their mol.-fractions in the solutions, the subscripts 1 and 2 applying to solute and solvent respectively; ϵ , ρ , and n refer, respectively, to the dielectric constns., densities, and refractive indices of the solution, and P_0 to the orientation polarisation of the solute.

With a view to determine whether there is a large at. polarisation associated with these mols., a measurement was made of the dielectric const. and density of *p*-nitrosodimethylaniline in the solid state. The values found were 3.90 and 1.17 respectively, whence $P_R + P_A = 63.0$ c.c. The figure quoted for the dielectric const. may be slightly too low, owing to the fact that the nitrosodimethylaniline, on solidifying in the test condenser, may have contracted somewhat and thus not completely filled the space between the plates. There-

TABLE II.

p-Nitrosodimethylaniline in benzene.

$f_1 \times 10^6$	0	1166	2333	3735	5278	6231	7925	18,785
$M_1 f_1 + M_2 f_2$	78	78-084	78-168	78-269	78-380	78-449	78-571	79-353
								25°.
ϵ	2-2725	2-353	2-431	2-531	2-628	2-691	2-797	3-483
ρ	0-8738	0-8743	0-8749	0-8755	0-8761	0-8766	0-8776	0-8824
$P_1 f_1 + P_2 f_2$	26-585	27-76	28-85	30-21	31-47	32-26	33-54	40-72
$P_2 f_2$	26-585	26-55	26-52	26-49	26-44	26-42	26-37	26-08
$P_1 f_1$	—	1-21	2-33	3-72	5-03	5-84	7-17	14-64
P_1	—	1033	1000	996	952	937	905	779
								45°.
ϵ	2-233	2-305	2-374	2-459	2-550	2-605	2-703	
ρ	0-8521	0-8527	0-8532	0-8536	0-8547	0-8552	0-8559	
$P_1 f_1 + P_2 f_2$	26-664	27-76	28-78	30-00	31-24	31-99	33-25	
$P_2 f_2$	26-664	26-63	26-60	26-56	26-52	26-50	26-45	
$P_1 f_1$	—	1-13	2-18	3-44	4-72	5-49	6-80	
P_1	—	966	934	921	894	882	858	
								15°.
n	1-5093	—	—	1-5113	1-5122	1-5125	1-5134	
n^2	2-2781	—	—	2-2840	2-2867	2-2877	2-2903	
ρ	0-8842	—	—	0-8860	0-8869	0-8871	0-8882	
$R_1 f_1 + R_2 f_2$	26-355	—	—	26-477	26-528	26-559	26-605	
$R_2 f_2$	26-355	—	—	26-257	26-216	26-191	26-163	
$R_1 f_1$	—	—	—	0-220	0-312	0-368	0-442	
R_1	—	—	—	59-0	59-1	59-1	(60-6)	

P_1 at inf. dilution at 25° = 1044 c.c., at 45° = 988 c.c.; R_1 = 59 c.c.

Whence, at 25°, P_0 = 985 c.c., μ = 6.89×10^{-18} e.s.u.

at 45°, P_0 = 929 c.c., μ = 6.91×10^{-18} e.s.u.

p-Nitrosodimethylaniline in carbon tetrachloride (at 25°).

$f_1 \times 10^6$	0	518	1140
$M_1 f_1 + M_2 f_2$	154	153-998	153-996
ϵ	2-227	2-257	2-286
ρ	1-5844	1-5842	1-5838
$P_1 f_1 + P_2 f_2$	28-214	28-65	29-17
$P_2 f_2$	28-214	28-20	28-18
$P_1 f_1$	—	0-45	0-99
P_1	—	878	869

P_1 at inf. dilution at 25° = 890 c.c.

Taking R_1 as 59 c.c., P_0 = 831 c.c., μ = 6.33×10^{-18} e.s.u.

p-Nitrosodiethylaniline in benzene.

$f_1 \times 10^6$	0	2274	4908	8415
$M_1 f_1 + M_2 f_2$	78	78-227	78-491	78-841
				25°.
ϵ	2-2725	2-440	2-627	2-859
ρ	0-8738	0-8746	0-8754	0-8768
$P_1 f_1 + P_2 f_2$	26-585	29-01	31-53	34-40
$P_2 f_2$	26-585	26-52	26-46	26-36
$P_1 f_1$	—	2-49	5-07	8-04
P_1	—	1095	1033	955
				15°.
n	1-5093	1-5106	1-5120	1-5139
n^2	2-2781	2-2819	2-2861	2-2919
ρ	0-8842	0-8850	0-8858	0-8872
$R_1 f_1 + R_2 f_2$	26-355	26-462	26-589	26-749
$R_2 f_2$	26-355	26-295	26-226	26-133
$R_1 f_1$	—	0-167	0-363	0-616
R_1	—	73-4	73-9	73-2

P_1 at inf. dilution at 25° = 1144 c.c.; R_1 = 73.5 c.c.

Whence P_0 = 1070 c.c., μ = 7.18×10^{-18} e.s.u.

TABLE II (contd.).

p-Nitrosodiethylaniline in carbon tetrachloride.

$f_1 \times 10^6$	0	1586	2598	5468	6511	10,963
$M_1 f_1 + M_2 f_2$	154	154.038	154.062	154.131	154.156	154.263
25°.						
ϵ	2.227	2.325	2.385	2.555	2.621	2.876
ρ	1.5844	1.5830	1.5821	1.5798	1.5789	1.5751
$P_1 f_1 + P_2 f_2$	28.214	29.81	30.74	33.30	34.24	37.67
$P_2 f_2$	28.214	28.17	28.14	28.06	28.03	27.90
$P_1 f_1$	—	1.64	2.60	5.24	6.21	9.77
P_1	—	1034	1002	959	954	891
45°.						
ϵ	2.195	2.284	2.340	2.490	2.548	2.786
ρ	1.5459	1.5447	1.5439	1.5419	1.5409	1.5376
$P_1 f_1 + P_2 f_2$	28.38	29.89	30.81	33.17	34.05	37.43
$P_2 f_2$	28.38	28.33	28.30	28.22	28.19	28.07
$P_1 f_1$	—	1.56	2.51	4.95	5.86	9.36
P_1	—	980	965	905	900	854
15°.						
n	1.4665	1.4674	1.4680	1.4697	1.4703	1.4730
n^2	2.1506	2.1533	2.1550	2.1600	2.1618	2.1697
ρ	1.6036	1.6022	1.6013	1.5990	1.5979	1.5941
$R_1 f_1 + R_2 f_2$	26.622	26.697	26.744	26.879	26.932	27.147
$R_2 f_2$	26.622	26.580	26.553	26.476	26.449	26.331
$R_1 f_1$	—	0.117	0.191	0.403	0.483	0.816
R_1	—	73.8	73.5	73.7	74.2	74.4

P_1 at inf. dilution at 25° = 1054 c.c., at 45° = 1000 c.c.; $R_1 = 74$ c.c.

Whence, at 25°, $P_0 = 980$ c.c., $\mu = 6.87 \times 10^{-18}$ e.s.u.

at 45°, $P_0 = 926$ c.c., $\mu = 6.90 \times 10^{-18}$ e.s.u.

p-Nitrosomethylaniline in benzene.

$f_1 \times 10^6$	0	1029	1536	2318
$M_1 f_1 + M_2 f_2$	78	78.059	78.089	78.135
25°.				
ϵ	2.2725	2.351	2.389	2.444
ρ	0.8738	0.8740	0.8741	0.8743
$P_1 f_1 + P_2 f_2$	26.585	27.732	28.273	29.039
$P_2 f_2$	26.585	26.558	26.544	26.523
$P_1 f_1$	—	1.174	1.729	2.516
P_1	—	1141	1126	1085
15°.				
n	1.5093	1.5098	1.5100	1.5104
n^2	2.2781	2.2795	2.2802	2.2813
ρ	0.8842	0.8844	0.8845	0.8847
$R_1 f_1 + R_2 f_2$	26.355	26.389	26.406	26.431
$R_2 f_2$	26.355	26.328	26.315	26.294
$R_1 f_1$	—	0.061	0.091	0.137
R_1	—	59.3	59.2	59.1

P_1 at inf. dilution at 25° = 1190 c.c.; $R_1 = 59$ c.c.

Whence $P_0 = 1131$ c.c., $\mu = 7.38 \times 10^{-18}$ e.s.u.

fore, the value of $P_E + P_A$ may be somewhat higher than that given above. Owing to the great dilution of the solutions employed, no attempt was made to measure the dispersivity of the compounds, but from the value of the refractivity for the Hg green line it is evident that there must be an atomic polarisation of more than 4 c.c. However, the measurements made with the substance in the

solid state serve to show that no great error is introduced into the dipole moment calc. by taking the value of $P_E + P_A$ as equal to the mol. refraction for the 5461 Å. line.

There is some evidence that the dipole moments of *p*-nitrosodimethyl- and -diethyl-aniline increase slightly with rise of temp., the values for the former in C_6H_6 and for the latter in CCl_4 changing from 6.89 to 6.91 and from 6.87 to 6.90, respectively, over the temp. range 25—45°.

Summary.

The dielectric constants, refractive indices, and densities of dilute solutions of *p*-nitroso-dimethyl-, -diethyl-, and -monomethyl-aniline in benzene and in carbon tetrachloride have been measured, and the corresponding electric dipole moments calculated. The results, along with previous data, are discussed with reference to the behaviour of the nitroso-group in organic compounds.

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