293. *Studies in Dielectric Polarisation. Parts VIII, IX, X, and XI.*

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Part VIII. The Dipole Moments of Alkyl Nitrates and Nitrites.

In Part VII of this series (this vol., p. 312) the dipole moments of some nitro-compounds were recorded. The present part describes the moments of a series of alkyl nitrates and nitrites.

Experimental.

The electrical apparatus was the same as that described previously (J., 1932, 2812). The densities were determined in a 12-c.c. pyknometer with ground-glass caps, and the refractivities in a Pulfrich refractometer.

Preparation of Materials.—Benzene used for dielectric work was of A.R. quality. It was shaken over concentrated sulphuric acid and then washed with water. After being shaken with dilute caustic soda and again washed, it was dried with calcium chloride and then with sodium wire for some days, fractionated, head and tail portions being rejected, and was finally frozen out.

The Nitrates.—The distillate from the action of nitric acid on the pure alcohol in the presence of urea nitrate was washed with water and dilute potassium carbonate, re-washed, dried by calcium chloride, and fractionated.

The physical properties of the compounds were :

Nitrate.	B. p.	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	Nitrate.	B. p.	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.
Methyl	65°/760 mm.	1·2075	1·3748	*n*-Propyl	110·4°/770 mm.	1·0548	1·3979
Ethyl	87·2/762 mm.	1·1084	1·3852	*n*-Butyl	135·7/770 mm.	1·0153	1·4063

Results previously recorded are :

Methyl nitrate: b. p. 65°; $D_{20^\circ}^{20^\circ}$ 1·2096 (Perkin, J., 1889, **55**, 682).
Ethyl nitrate: b. p. 87·5—87·7°; $D_{20^\circ}^{20^\circ}$ 1·1099 (Perkin, *loc. cit.*); $n_D^{21\cdot5^\circ}$ 1·3848 (Brühl, *Z. physikal. Chem.*, 1895, **16**, 214).
n-Propyl nitrate: b. p. 110·5° (Wallach and Schulze, *Ber.*, 1881, **14**, 421); $D_{20^\circ}^{20^\circ}$ 1·0580 (Perkin, *loc. cit.*); $n_D^{20^\circ}$ 1·3972 (Brühl, *loc. cit.*).
n-Butyl nitrate: b. p. 136°.

The Nitrites.—The nitrites were obtained by dropping a mixture of dilute sulphuric acid and alcohol into a solution of sodium nitrite. By gentle warming, the nitrite was distilled off, and collected in a vessel surrounded by ice. The compound was washed, dried (sodium sulphate), and fractionated. The measurements were made at 10° for ethyl nitrite and at 20° with propyl nitrite.

Nitrite.	B. p.	$D_{4^\circ}^{t^\circ}$.	$n_D^{t^\circ}$.	Nitrite.	B. p.	$D_{4^\circ}^{t^\circ}$.	$n_D^{t^\circ}$.
Ethyl (10°)	17°/760 mm.	0·9065	1·3418	*n*-Propyl (20°)	48·9—49·4°/760 mm.	0·8861	1·3604

Values in the literature are as follows:

Ethyl nitrite: b. p. 17·5° (Mohr, *Jahresber.*, 1854, **7**, 561); $D_{4^\circ}^{15\cdot5^\circ}$ 0·900 (Brown, *Pharm. J.*, 1856, **15**, 400).
n-Propyl nitrite: $D_{4^\circ}^{20^\circ}$ 0·8864; $n_D^{20^\circ}$ 1·3613 (Löwenhertz, *Z. physikal. Chem.*, 1890, **6**, 588).

Results.—The polarisations and moments were calculated as in previous parts of this series. The atomic polarisation is included in the orientation polarisation. The solvent throughout is benzene, and μ is given in 10^{-18} e.s.u.

Methyl nitrate.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8789	2·275	26·49
0·0143	0·8798	2·437	28·72
0·0195	0·8814	2·492	29·42
0·0407	0·8861	2·737	32·24
0·0488	0·8883	2·822	33·22
0·0639	0·8908	3·007	35·09
0·0680	0·8922	3·033	35·29

$P_{2\infty}$ = 186 c.c.; P_E = 15 c.c.; $P_{2\infty} - P_E$ = 171 c.c.; μ = 2·85.

Ethyl nitrate.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
—	0·8789	2·275	26·49
0·0122	0·8811	2·420	28·53
0·0206	0·8827	2·530	29·96
0·0433	0·8864	2·823	33·52
0·0575	0·8891	3·022	35·66
0·0693	0·8923	3·192	37·33

$P_{2\infty}$ = 198 c.c.; P_E = 19 c.c.; $P_{2\infty} - P_E$ = 179 c.c.; μ = 2·91.

n-*Propyl nitrate.*

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8789	2·275	26·49
0·0145	0·8800	2·455	29·10
0·0258	0·8822	2·597	31·01
0·0371	0·8842	2·747	32·92
0·0444	0·8853	2·848	34·12
0·0577	0·8883	3·016	36·10

$P_{2\infty}$ = 212 c.c.; P_E = 24 c.c.; $P_{2\infty} - P_E$ = 188 c.c.; μ = 2·98.

n-*Butyl nitrate.*

0	0·8786	2·274	26·48
0·0128	0·8793	2·430	28·85
0·0271	0·8818	2·614	31·41
0·0340	0·8834	2·706	32·56
0·0520	0·8864	2·940	35·52
0·0600	0·8872	3·057	36·91

$P_{2\infty}$ = 215 c.c.; P_E = 29 c.c.; $P_{2\infty} - P_E$ = 186 c.c.; μ = 2·96.

Ethyl nitrite.

0	0·8861	2·312	26·73
0·0302	0·8897	2·526	29·53
0·0366	0·8912	2·568	30·01
0·0518	0·8920	2·703	31·62
0·0545	0·8926	2·724	31·85

$P_{2\infty}$ = 124 c.c.; P_E = 18 c.c.; $P_{2\infty} - P_E$ = 106 c.c.; μ = 2·20.

n-*Propyl nitrite.*

0	0·8787	2·282	26·60
0·0152	0·8788	2·393	28·23
0·0256	0·8789	2·467	29·25
0·0392	0·8790	2·565	30·58
0·0523	0·8793	2·666	31·93

$P_{2\infty}$ = 132 c.c.; P_E = 22 c.c.; $P_{2\infty} - P_E$ = 110 c.c.; μ = 2·28.

Discussion of Results.

The moments found are summarised in the following table:

Methyl nitrate	2·85		
Ethyl nitrate	2·91	Ethyl nitrite	2·20
n-Propyl nitrate	2·98	*n*-Propyl nitrite	2·28
n-Butyl nitrate	2·96		

No previous determinations of the moments of these compounds can be found. Weissberger and Sängewald (*Ber.*, 1932, **65**, 701) determined the moment of amyl nitrite as 2·27, which is very near our value for propyl nitrite.

The moments of the aliphatic nitrates show a small increase from methyl to *n*-propyl nitrate, the moment there becoming constant. By assuming an oxygen valency angle of 90°, which is supported by several recent results, and the moment of the CH_3O– group as 0·81, calculated from the value 1·32 for dimethyl ether, the nitrate group moment is found to be 2·73. The decrease in the moment of the ethers as the molecular weight of the alkyl

group increases is accounted for by a repulsion between the groups, so that the R–O– moment, where R is an alkyl group, may be assumed to be constant. Whilst the magnitude of the nitrate group moment approaches the values for the cyano- and the nitro-group, there is a much greater increase in the moment in the series of nitriles and nitro-compounds, as is shown below.

	Cyanide.	Nitro-compound.	Nitrate.		Cyanide.	Nitro-compound.	Nitrate.
Methyl	3·11*	3·04†	2·85	*n*-Propyl	3·46*	—	2·98
Ethyl	3·34*	3·21†	2·91	*n*-Butyl	—	3·32†	2·96

* Werner, *Z. physikal. Chem.*, 1929, *B*, **4**, 371; Eide and Hassel, *Chem. Zentr.*, 1930, 2235, give MeCN 3·51; EtCN 3·66.

† Hunter and Partington, this vol., p. 312.

It is evident that the nitro-group gives rise to induction along the hydrocarbon chain, while, as the moments of the nitrates are nearly constant, the nitrate moment may be assumed to act at an angle approaching a right angle with the chain. The noticeable difference between the nitro-compounds and the nitrates is thus due to the introduction of the oxygen atom. It is interesting to note that erythritol tetranitrate, $C(CH_2{\cdot}O{\cdot}NO_2)_4$, of moment 2·0 (Ebert, Eisenschitz, and Hartel, *Z. physikal. Chem.*, 1928, *B*, **1**, 94), was one of the tetra-substituted methanes found to be polar.

In the series of aliphatic alcohols and mercaptans the moment is constant : the polarity is due solely to the polar group, and induction effects do not intervene. This conclusion agrees with the fact that phenol and thiophenol have the same moment as the corresponding aliphatic compounds. The nitrates and nitrites have a **V**-shaped structure, and it is not surprising that these two groups of compounds behave differently, since the nitrate group is a large one. The reason for a decrease in moment in the case of the ethers and a slight increase in these compounds, may be due to the difference in sign of the alkyl and the nitro-group, which tends to diminish the angle between them by electrostatic interaction.

The measurements on ethyl nitrite were made at 10°, very close to the boiling point, so that the recorded moment may be somewhat low. The agreement between the present value for propyl nitrite and that of Weissberger and Sängewald for amyl nitrite indicates that, as for the nitrates, no further increase in moment occurs after the propyl compound. The group moment for the nitrite radical is calculated as 2·05. The isomeric nitro-compounds possess a distinctly higher moment, as would be expected from their other properties. The wide difference in the boiling points of the nitro-compounds $\left(R{-}N\begin{matrix}O\\ \nearrow\\ \searrow\\ O\end{matrix}\right)$ and the nitrites (R–O–N=O) is usually accounted for by the presence of a semipolar bond in the former compounds, in agreement with the result that nitroethane has a higher moment (3·21) than ethyl nitrite (2·20). It is also evident that the nitro-group structure is retained in the nitrates.

Mr. H. J. Moss has found (unpublished work in this Department) that the nitro-compounds are less soluble in non-polar solvents than the nitrates, which in turn are less soluble than the nitrites. The order of solubilities is the same as that of moments, nitroethane (3·21) being more polar than ethyl nitrate (2·91) and ethyl nitrite (2·20). The solubility is dependent on the dielectric constant of a liquid rather than on the electric moment, and it happens that in this case the moments are paralleled by the dielectric constants of the pure materials, as shown by the following data :

Compound.	Temp.	ϵ.	$\mu \times 10^{18}$.
Nitroethane	18°	30·6	3·21
Ethyl nitrate	20	19·7	2·91
*iso*Propyl nitrite	19	*ca.* 11·5	2·28 (*n*-compound)

Summary.

The dipole moments of methyl (2·85), ethyl (2·91), *n*-propyl (2·98), and *n*-butyl (2·96) nitrates are approximately constant, as are those of ethyl (2·20) and *n*-propyl (2·28) nitrites. The results are contrasted with those for the nitro-compounds, in which induction along the hydrocarbon chain occurs.

Part IX. The Dipole Moments of some Nitrosoamines, *p*-Nitrosophenol, Ethylaniline, Hydrazobenzene, and Benzaldehydephenylhydrazone.

The following measurements relate to alkyl and aryl nitrosoamines, $R_2N{\cdot}NO$, and to hydrazo-compounds.

Experimental.

Preparation of Materials.—The nitrosoamines were prepared by the action of a cold concentrated solution of sodium nitrite on the secondary amine dissolved in excess of dilute hydrochloric acid. They were separated, washed, dried (calcium chloride), and purified by vacuum fractionation until some physical property was constant. Diphenylnitrosoamine was recrystallised.

Nitrosoamine.	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	M. p.	B. p.
Dimethyl	1·0061	1·4368	—	154°/760 mm.
Diphenyl	—	—	66·5°	—
Phenylmethyl	1·1288	1·5769	14·7	—
Phenylethyl	1·0874	1·5598	—	—

Recorded values for these compounds are :

Dimethylnitrosoamine : $D_{4^\circ}^{20^\circ}$ 1·0059 (Turner and Merry, J., 1910, **97**, 2074).
Diphenylnitrosoamine : m. p. 66·5°.
Phenylmethylnitrosoamine : $D_{4^\circ}^{20^\circ}$ 1·1275; $n_D^{20^\circ}$ 1·57688 (Turner and Merry, *loc. cit.*).
Phenylethylnitrosoamine : $D_{4^\circ}^{20^\circ}$ 1·0874; $n_D^{20^\circ}$ 1·5598 (Schmidt, *Z. physikal. Chem.*, 1907, **58**, 519).

Hydrazobenzene, benzaldehydephenylhydrazone, and nitrosophenol were all recrystallised until their m. p.'s were constant, *viz.*, 127°, 156°, and 126°, respectively. Ethylaniline was dried and fractionated : $D_{4^\circ}^{20^\circ}$ 0·9628; $n_D^{20^\circ}$ 1·5560 (Kahlbaum, *Z. physikal. Chem.*, 1906, **26**, 646, gives $D_{4^\circ}^{20^\circ}$ 0·9630; $n_D^{20^\circ}$ 1·5559). Except for nitrosophenol, the solvent is benzene in the following measurements.

Nitrosodimethylamine.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8790	2·280	26·55
0·0392	0·8836	3·245	37·73
0·0632	0·8861	3·851	42·79
0·0749	0·8875	4·155	44·90

$P_{2\infty}$ = 355 c.c.; P_E = 19 c.c.; $P_{2\infty} - P_E$ = 336 c.c.; μ = 3·98.

Nitrosodiphenylamine.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8787	2·279	26·55
0·0082	0·8830	2·427	28·85
0·0115	0·8853	2·485	29·70
0·0202	0·8877	2·642	32·10
0·0256	0·8928	2·736	33·59

$P_{2\infty}$ = 302 c.c.; P_E = 59 c.c.; $P_{2\infty} - P_E$ = 243 c.c.; μ = 3·39.

N-*Nitrosomethylaniline.*

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8787	2·279	26·55
0·0127	0·8822	2·525	30·10
0·0212	0·8844	2·687	32·26
0·0300	0·8875	2·866	34·39
0·0375	0·8910	3·014	36·15

$P_{2\infty}$ = 318 c.c.; P_E = 40 c.c.; $P_{2\infty} - P_E$ = 278 c.c.; μ = 3·62.

N-*Nitrosoethylaniline.*

0	0·8787	2·279	26·55
0·0093	0·8806	2·452	29·15
0·0190	0·8838	2·645	31·83
0·0277	0·8861	2·812	34·05
0·0490	0·8928	3·222	38·88

$P_{2\infty}$ = 320 c.c.; P_E = 45 c.c.; $P_{2\infty} - P_E$ = 275 c.c.; μ = 3·61.

Nitrosophenol.
(Moment determined in dioxan)

0	1·0340	2·244	24·94
0·0070	1·0347	2·482	28·22
0·0113	1·0361	2·611	29·76
0·0163	1·0370	2·751	31·50
0·0202	1·0392	2·905	33·18

$P_{2\infty}$ = 503 c.c.; P_E = 29 c.c.; $P_{2\infty} - P_E$ = 474 c.c.; μ = 4·72.

Ethylaniline.

0	0·8787	2·279	26·55
0·0171	0·8790	2·346	27·77
0·0274	0·8806	2·395	28·56
0·0441	0·8822	2·464	29·66
0·0505	0·8830	2·487	30·05

$P_{2\infty}$ = 100 c.c.; P_E = 40 c.c.; $P_{2\infty} - P_E$ = 60 c.c.; μ = 1·68.

Hydrazobenzene.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8789	2·279	26·56
0·0092	0·8816	2·316	27·33
0·0124	0·8830	2·330	27·61
0·0160	0·8853	2·342	27·85
0·0197	0·8875	2·361	28·18

$P_{2\infty}$ = 118 c.c.; P_E = 60 c.c.; $P_{2\infty} - P_E$ = 58 c.c.; μ = 1·66.

Benzaldehydephenylhydrazone.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8787	2·275	26·55
0·0082	0·8822	2·328	27·45
0·0139	0·8844	2·362	28·08
0·0176	0·8861	2·386	28·50
0·0205	0·8875	2·404	28·81

$P_{2\infty}$ = 137 c.c.; P_E = 62 c.c.; $P_{2\infty} - P_E$ = 75 c.c.; μ = 1·89.

Discussion of Results.

The moments, $\mu \times 10^{18}$, found are tabulated below :

Nitrosodimethylamine	3·98	*p*-Nitrosophenol	4·72
Nitrosodiphenylamine	3·39	Hydrazobenzene	1·66
Nitrosomethylaniline	3·62	Benzaldehydephenylhydrazone	1·89
Nitrosoethylaniline	3·61		

The moments of the corresponding amines are :

Dimethylamine (gas)	0·96 (Steiger, *Helv. Phys. Acta*, 1930, **3**, 161; *Physikal. Z.*, 1931, **32**, 425; Ghosh and Chatterjee, *Physical Rev.*, 1931, **37**, 427, give 0·90).
Diphenylamine	1·3 (Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 134).
Methylaniline	1·64 (Williams and Fogelberg, *Physikal. Z.*, 1931, **32**, 27).
Ethylaniline	1·68 (Present paper).

The results indicate that the nitroso-group possesses a large moment, in agreement with the result for nitrosobenzene, 3·14 (Hammick, New, and Sutton, J., 1932, 742, where the assumed connexion with electromeric effects is discussed), and the *p*-nitroso-substituted anilines (Le Fèvre and Smith, *ibid.*, p. 2239).

The results for the three aromatic nitrosoamines indicate that the nitroso-group has the same moment in each, since there is probably no appreciable change in the inclination of the groups to one another in these compounds. That ethyl- and methyl-aniline should have the same moments, within the limit of experimental error, is not surprising, since the moments of dimethyl- and diethyl-amine are also equal. These results suggest that no change in angle, or induction, occurs on substituting an ethyl for a methyl group in an amine. The corresponding nitrosoamines have a constant moment. Nitrosodiphenylamine has a lower moment than the nitroso-compounds of methyl- and ethyl-anilines, but the moment of dimethylamine is higher.

The nitroso-group has a larger moment in the aromatic than in the aliphatic series (Hammick, New, and Sutton, *loc. cit.*). Thus, nitrosobenzene has a moment of 3·14 and 2-nitroso-2 : 5-dimethylhexane one of 2·51. In this case the relation is quite different from that found with the nitrosoamines, since in the latter the phenyl group of the aliphatic chain is subject to the action of the nitroso-group. In the nitrosoamines the nitroso-group, the moment of which is inclined at an angle to the N–N bond, is situated at the corner of a probably irregular tetrahedron. The angles between the sides will vary with the substituted groups, and in the dimethyl compound, containing smaller groups, the angles will be smaller, with the result that the moment should be larger, as is the case. The differences between the N–R moment in aliphatic and aromatic compounds must, of course, also be allowed for.

The moment of the nitroso-group in these compounds will be inclined to the R–N moments, and thus little interaction will occur. Hammick, New, and Sutton (*loc. cit.*) calculate that the moment of the nitroso-group makes an angle of 157·7° in nitrosobenzene and 148° in the tertiary aliphatic compound, and this will be approximately the angle in the nitrosoamines. The calculation of the $-NH_2$ moment on the assumption that the ammonia molecule is tetrahedral (Hammick, New, and Sutton, *loc. cit.*) is, however, open to objection. Mecke (" Structure of Molecules," ed. P. Debye, 1932, 30) gives for ammonia the distances N–H = 0·977 Å.U., H–H = 1·43 Å.U., and the height of pyramid approximately 0·517 Å.U. The H–N–H angle deduced from these results is 94° 5′, which is decidedly smaller than the tetrahedral angle.

p-Nitrosophenol has a moment larger than the sum of the moments of its constituent groups. This is similar to the results found by Le Fèvre and Smith (*loc. cit.*), which show that the normal additivity rules are not valid for *p*-nitrosodimethylaniline and analogous compounds, a result explained as due to the large capacity of the nitroso-group for producing polarisation of the molecule as a whole. In *p*-nitrosophenol the moments of both groups do not lie in the line of the carbon valencies and the resultant moment depends on the relative position of the two groups. Since this compound is also tautomeric with quinonemonoxime, no definite conclusions are drawn at present.

The azo-compounds have been investigated by Bergmann, Engel, and Sandor (*Ber.*,

1930, **63**, 2572), who found that they possess the *trans*-configuration, since azobenzene is non-polar and *p*-chloroazobenzene has the same moment as chlorobenzene. It is improbable that hydrazo-compounds would exhibit similar relations, and we planned a systematic determination of the moments of derivatives of hydrazine. It was to be expected that free rotation could occur about the N–N bond, and if this was so, the hydrazo-compounds should possess large moments as contrasted with the azo-compounds, where the positions of the two nitrogen atoms are constrained by a double bond. It is clear that rotation occurs in hydrazobenzene, which has a moment of $1{\cdot}66 \times 10^{-18}$ e.s.u. If this compound was fixed in the *trans*-position, it would be non-polar. Only two of these compounds, hydrazobenzene and benzaldehydephenylhydrazone, had been measured when Audrieth, Nespital, and Ulich (*J. Amer. Chem. Soc.*, 1933, **53**, 673) published values for the moments of these and similar compounds. Their value of $P_{2\infty}$ for hydrazobenzene is identical with ours, but since we have left the atomic polarisation undetermined, whereas they quite arbitrarily assume it to be 15% of the electronic polarisation, their final value of the moment is slightly lower. Their value for benzaldehydephenylhydrazone is a little higher than ours.

We accept the conclusions of these experimenters with regard to the compounds, and as their results agree with ours, the moments of the other compounds have not been determined. All moments of hydrazo-compounds so far recorded lie between 1·5 and 1·9, with the exception of that of benzalazine, which is 0·8. The above authors suggest that this can be explained as due to preferential oscillation of the larger groups round the *trans*-position, and that completely free rotation does not occur.

Presumably in the nitrosoamines, rotation round the nitrogen bond can occur. Turner and Merry (*loc. cit.*) found that, although the aromatic nitrosoamines are unassociated in the pure state, yet the aliphatic compounds are associated. No values of the dielectric constants of the phenylnitrosoamines are available, but nitrosodimethylamine has the very high value of $\varepsilon = 54 \pm 1$ at 20°, has considerable conductivity and solvent power (Walden, *Z. physikal. Chem.*, 1903, **46**, 103), and differs from the other nitrosoamines in stability, in that it can be distilled at ordinary pressures, whereas the aromatic compounds decompose under similar treatment. The somewhat higher value for the electric moment, in view of these properties, is therefore not surprising.

Summary.

The moments of some nitrosoamines and nitrosophenol have been determined and compared with those of other nitroso-compounds previously recorded. The moments of the hydrazo-compounds are discussed.

Part X. The Dipole Moments of the Nitroanisoles.

The measurements on the three nitroanisoles were undertaken with the object of investigating the relations with the nitrophenols, and also because of existing conflicting experimental values for the *p*-compound. Höjendahl had pointed out that, since the moment of anisole makes an angle with the CH–O– bond, simple vector addition does not apply to these compounds. The three results for *o*-nitroanisole are in good agreement, but Höjendahl's value for the *p*-compound is too low. The value for the *m*-compound has been determined for the first time.

Experimental.

Preparation of Materials.—*o*-, *m*-, and *p*-Nitroanisoles were purified by Mr. H. J. Moss, who kindly placed specimens at our disposal. The physical constants as determined by him were independently confirmed. The *p*-compound was recrystallised from hexane, but the m. p. and moment remained unchanged.

Compound.	F. p.	$D_{4^\circ}^{25^\circ}$.	$n_D^{25^\circ}$.
o-Nitroanisole	10·3°	1·2408	1·5597
m- ,, ...	35·7	—	—
p- ,, ...	52·0	—	—

Results.—The solvent is benzene throughout.

o-*Nitroanisole.*				m-*Nitroanisole.*				p-*Nitroanisole.*			
f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8787	2·279	26·55	0	0·8787	2·279	26·55	0	0·8788	2·279	26·55
0·0099	0·8836	2·607	31·11	0·0115	0·8865	2·542	30·23	0·0110	0·8830	2·656	34·77
0·0176	0·8875	2·862	34·25	0·0192	0·8883	2·724	32·66	0·0213	0·8883	3·005	35·90
0·0216	0·8899	3·005	35·88	0·0311	0·8945	3·002	35·96	0·0265	0·8908	3·183	37·84
0·0308	0·8951	3·341	39·35	0·0378	0·8976	3·179	37·86	0·0357	0·8959	3·521	41·15
0·0382	0·8982	3·614	41·95								

$P_{2\infty}$ = 532 c.c.; P_E = 39 c.c.; $P_{2\infty}$ − P_E = 493 c.c.; μ = 4·83. $P_{2\infty}$ = 356 c.c.; P_E = 39 c.c.; $P_{2\infty}$ − P_E = 317 c.c.; μ = 3·86. $P_{2\infty}$ = 514 c.c.; P_E = 39 c.c.; $P_{2\infty}$ − P_E = 475 c.c.; μ = 4·74.

Discussion of Results.

The values found for the moments × 10^{18} of the nitroanisoles are compared in the following table :

o-Nitroanisole	4·83*	4·80†	4·84 (4·81)‡
m-Nitroanisole	3·86*	—	—
p-Nitroanisole	4·74*	4·36†	4·78 (4·75)‡

* Present paper.

† Höjendahl, Thesis, Copenhagen, 1928.

‡ Donle and Gehrckens, *Z. physikal. Chem.*, 1932, *B*, **18**, 316 (the values in parentheses are corrected for P_A).

Wolf (*Z. physikal. Chem.*, 1929, *B*, **3**, 128), by assuming that the moment of the methoxy-group makes an angle of 110° (an assumed oxygen angle) with the Ph–O bond, and that the group moments of $-NO_2$ and $-OCH_3$ have the same sign, has calculated a value for the moment of *p*-nitroanisole in exact agreement with Höjendahl's value (4·35 × 10^{-18} e.s.u.). Wolf's assumptions, however, are obviously incorrect, and the values for *p*-nitroanisole and *p*-nitrophenol have therefore been recalculated. It is now assumed that the moment of anisole bisects the oxygen angle (taken as 90°), and that the groups $-NO_2$ and –Cl are negative, while –OH and $-OCH_3$ are positive. These moments in aromatic compounds are taken from phenol 1·7, anisole 1·2, nitrobenzene 3·9, and chlorobenzene 1·5.

On the assumption of complete freedom of rotation of the methoxy-group, its component moment perpendicular to the direction of the nitro-group is zero and the resultant moment is given by $\mu = (3{\cdot}9 + 1{\cdot}2 \cos 45^\circ) \times 10^{-18} = 4{\cdot}75 \times 10^{-18}$ e.s.u. The values are compared in the following table :

Compound.	Obs.	Calc.	Compound.	Obs.	Calc.	Compound.	Obs.	Calc.
p-Nitroanisole	4·74	4·75	*p*-Nitrophenol	5·05*	5·10	*p*-Chlorophenol	2·68*	2·72

* Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1536.

A lower value of 2·27 for *p*-chlorophenol is given by Donle and Gehrckens (*Z. physikal. Chem.*, 1932, *B*, **18**, 316), but as their value for phenol, 1·61, is also lower than those of Smyth (1·73), Williams (1·70), and Zahn (1·74), the results are not comparable with other values. In the case of the *p*-substituted methyl compounds, the values calculated by the above method are not in good agreement, but since experimental values for simple compounds like *p*-chlorotoluene do not agree with calculated values, no particular significance can be attached to this result.

For the *o*- and the *m*-compounds, it is impossible to calculate any value without a three-dimensional figure. Calculation made by this method on the assumption of complete freedom of rotation of the methoxy-group, gives values which are too high for both nitrophenol and anisole. This is no doubt due to interaction between groups having a large dipole, such as $-NO_2$, so that rotation is hindered. In the case of the *o*-compound, as the groups are very close together, it would not be expected that simple calculations would give satisfactory results.

It is of interest to compare the moments of nitroanisoles and nitrophenols :

Compound.	ortho-.	meta-.	para-.	Compound.	ortho-.	meta-.	para-.
Nitroanisole	4·83	3·86	4·74	Nitrophenol	3·10	3·90	5·05

The order in the two series is not the same, and the irregularity seems to be exhibited by the *o*-compounds, since the other isomerides show regularity.

Examination of the solubilities and b. p.'s of a series of *o*-, *m*-, and *p*-substituted phenols shows (Sidgwick and Callow, J., 1924, **125**, 527) that the *o*-compound is more volatile, less soluble in water, and more soluble in benzene than would be expected, a result easily explained by postulating a co-ordinate link between the oxygen of the nitro-group and the hydrogen of the hydroxyl, which leads to a closed ring. In the *m*- and the *p*-compounds donation is assumed to occur between groups attached to different molecules. When hydrogen is substituted by a methyl group, co-ordination is not possible, and there is no difference in properties between *o*- and *p*-nitroanisoles. Sidgwick and Bayliss (J., 1930, 2027), in fact, find evidence in favour of formation of a chelate ring in *o*-nitrophenol, while *o*-nitroanisole is normal.

In dilute solutions in non-polar solvents the number of complexes of the second type would be negligible, but for *o*-nitrophenol the co-ordinate link would partially cancel the moment of the nitro-group, with a considerable reduction in total moment. This agrees with the experimental figures. In the anisole, it seems that the groups are attracted by electrostatic forces to give a moment of the observed magnitude.

Summary.

The dipole moments of the three nitroanisoles have been measured and the results discussed in relation to the nitrophenols.

Part XI. Note on the Dipole Moment of Pyrrole.

Heterocyclic nitrogen compounds which have previously been measured include pyridine, quinoline, *iso*quinoline, and acridine. The dipole moment of pyrrole was determined to investigate the effect of the size of the ring on the moment. No other result is available.

Pyrrole : $D_{4^\circ}^{20^\circ}$ 0·9600; $n_D^{20^\circ} = 1·5208$.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.
0	0·8790	2·280	26·56	0·0582	0·8822	2·557	29·98
0·0287	0·8806	2·413	28·26	0·0843	0·8844	2·687	31·38

$P_{2\infty} = 92$ c.c.; $P_E = 21$ c.c.; $P_{2\infty} - P_E = 71$ c.c.; $\mu = 1·83$.

The moments of these nitrogen ring compounds are ($\mu \times 10^{18}$) :

Pyrrole	1·83 (Present work).
Pyridine	2·11 (Lange, *Z. Physik.*, 1925, **33**, 169).
Quinoline	2·18 (Le Fèvre and Smith, J., 1932, 2810).
*iso*Quinoline	2·52 (Le Fèvre and Smith, *ibid.*).

The moment of pyrrole is lower than that of pyridine and quinoline, which have approximately the same moment. Pyrrole is not really comparable with these compounds, as both the difference in position of the double bonds and the hydrogen attached to the nitrogen atom would cause a change in moment on passing from pyrrole to pyridine. The angle formed by the nitrogen atom in the ring will be larger in pyridine than in pyrrole.

Work is in progress on the fully reduced rings, and it will be possible to deduce more definite conclusions from these results, which will not be complicated by the effect of unsaturation.

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