373. *The Dipole Moments of Vapours. Part V. Aromatic Compounds.*

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Observations are recorded of the dipole moments of 16 aromatic compounds in the vapour state. In two series of *o*-, *m*-, and *p*-isomerides it is found that the observed moments for the *m*-compounds agree with the values calculated by the simple vector addition of group moments, whilst the *o*-compounds show large discrepancies.

In this paper we record measurements of the dipole moments of a number of aromatic compounds. Most of these substances have high boiling points, and observations on the vapour can only be made over a restricted range of temperature. It has been shown in Part IV (preceding paper), however, that the atomic polarisation, P_A, can be assumed with a high degree of accuracy to be 5% of P_E, so observations at one temperature are sufficient to obtain an accurate value of the dipole moment. The data so obtained are collected in the table below.

Substance.	μ.	Substance.	μ.
o-Dichlorobenzene	2·16	*p*-Nitroanisole	5·22
m-Dichlorobenzene	1·67	Phenol	1·40
p-Dichlorobenzene	0	Anisole	1·35
o-Chloronitrobenzene	4·59	Phenetole	1·40
m-Chloronitrobenzene	3·69	*cyclo*Hexyl methyl ether	1·29
p-Chloronitrobenzene	2·78	Diphenyl ether	1·35
o-Nitroanisole	4·77	Aniline	1·48
m-Nitroanisole	4·51	Dimethylaniline	1·61

A full discussion of these results requires a detailed consideration of induction within the molecule: this discussion we shall defer to Part VI of this series. Meanwhile, it is of interest to compare the moments found for *o*-, *m*-, and *p*-isomerides with those predicted by adding vectorially the group moments acting at angles of 60°, 120°, and 180° respectively. Using for the moments of the chloro- and the nitro-group the moments recorded in Part II (J., 1935, 972) for chlorobenzene (1·73) and nitrobenzene (4·24), we have calculated the following figures:

	μ, calc.	μ, obs.		μ, calc.	μ, obs.
o-Dichlorobenzene	3·00	2·16	*o*-Chloronitrobenzene	5·32	4·59
m- ,, ...	1·73	1·67	*m*- ,, ...	3·69	3·69
p- ,, ...	0	0	*p*- ,, ...	2·51	2·78

It will be seen that the meta-compounds show substantial agreement between the observed and the calculated values. Both the ortho-compounds have moments which are considerably smaller than the calculated values, and *p*-chloronitrobenzene has a moment which is appreciably larger. *p*-Dichlorobenzene would be expected to have zero moment, and the experimental results agree with this conclusion.

Experimental.

The polarisations were measured with the apparatus described in Part I (J., 1934, 1094). In the tables below, T is the absolute temperature, p the pressure of the vapour in mm., P the measured polarisarion in c.c., and μ the dipole moment deduced on the assumption that P_A is 5% of P_E. All the values given for P_E refer to the sodium-D line.

o-Dichlorobenzene was purified by fractional distillation. The best fraction was frozen out three times and finally distilled; b. p. 179—181°/755 mm., $d_{4°}^{25°}$ 1·2965; $P_E = 36·0$.

T.	p.	P.	μ.	T.	p.	P.	μ.
420°	140	107·0	2·17	448°	101	101·6	2·15
,,	150	106·9	2·17	,,	145	101·8	2·16
						Mean	2·16

m-Dichlorobenzene prepared from 2 : 4-dichloroaniline had b. p. 172·8°, $d_{4°}^{20°}$ 1·287 (" International Critical Tables " gives 1·288); $P_E = 36·0$.

413	63	79·0	1·66	458	98	75·7	1·68
,,	79	79·4	1·67	,,	113	75·9	1·68
						Mean	1·67

p-*Dichlorobenzene*. The specimen used had m. p. 53·0°; $P_E = 36·0$. Two observations at $T = 434°$ and $p = 110$ and 120 gave $P = 38·1$, 38·1. Since $1·05P_E = 37·8$, the moment is zero within the limits of the experimental error.

o-*Chloronitrobenzene*. The specimen used had m. p. 32·7°; $P_E = 36·9$.

477	91	314·3	4·61	477	87	310·5	4·58
475	68	313·0	4·59	,,	75	311·4	4·59
						Mean	4·59

m-*Chloronitrobenzene*. M. p. 44·5°; $P_E = 36·9$.

483	96	212·1	3·68	483	69	212·9	3·69
,,	114	212·8	3·69	,,	81	212·7	3·69
						Mean	3·69

p-*Chloronitrobenzene*. M. p. 83·5°; $P_E = 36·9$.

483	100	138·2	2·79	483	77	137·2	2·78
,,	63	138·6	2·80	,,	81	136·7	2·77
						Mean	2·78

o-*Nitroanisole*. The specimen used had b. p. 276·8°/757 mm., $d_{4°}^{20°}$ 1·266 (I.C.T. gives $d_{4°}^{20°}$ 1·268); $P_E = 39·6$.

477	55	338·5	4·79	477	53	337·4	4·78
,,	60	336·0	4·77			Mean	4·78

m-Nitroanisole, recrystallised from alcohol, had m. p. 38°; $P_E = 39·6$.

476	65	303·6	4·50	476	42	303·8	4·50
,,	59	306·0	4·52			Mean	4·51

p-*Nitroanisole*. The specimen used had m. p. 53·7°; $P_E = 39·6$.

478	50	391·2	5·21	478	58	397·3	5·25
,,	55	391·2	5·21			Mean	5·22

Phenol, distilled in a vacuum, had m. p. 41°; $d_{4°}^{40·6°}$ 1·058 (I.C.T. gives 1·0577); $P_E = 28·0$

T.	*p.*	*P.*	μ.	*T.*	*p.*	*P.*	μ.
449°	68	57·0	1·42	451°	103	56·2	1·40
,,	79	56·2	1·40	,,	112	55·3	1·38
451	90	56·7	1·41			Mean	1·40

At higher pressures and lower temperatures the value of μ varied with the pressure and was less than 1·40.

Anisole. The specimen used had b. p. 154°/759 mm., $d_{4°}^{20°}$ 0·9942 (I.C.T. gives 0·994) $P_E = 32·4$.

403	100	61·7	1·34	403	123	61·5	1·34
,,	125	62·5	1·36			Mean	1·35

Phenetole. The specimen used had b. p. 169°/739 mm., $d_{4°}^{20°}$ 0·9651 (I.C.T. gives 0·965); $P_E = 37·6$.

415	95	68·0	1·39	473	96	64·8	1·39
,,	55	68·1	1·39	,,	92	64·6	1·39
,,	94	69·2	1·41	,,	101	64·9	1·40
						Mean	1·40

*cyclo*Hexyl methyl ether, prepared from sodium, *cyclo*hexanol, and methyl iodide, had b. p. 135°/753 mm., $d_{4°}^{0°}$ 0·9012; $P_E = 33·9$.

406	107	60·9	1·29	438	104	58·7	1·28
,,	94	60·8	1·29	473	84	57·7	1·30
438	104	59·1	1·29	,,	99	57·6	1·30
,,	95	59·8	1·31	,,	61	57·3	1·29
						Mean	1·29

Diphenyl ether. The specimen used had m. p. 27·8°; $P_E = 52·8$.

486	109	78·7	1·36	486	105	78·3	1·34
,,	107	78·3	1·34			Mean	1·35

Aniline, purified by fractionation over zinc dust, had $d_{4°}^{20°}$ 1·0218 (I.C.T. gives 1·0217); $P_E = 30·6$.

459	76	61·7	1·48	459	106	61·7	1·48
,,	104	61·4	1·48	,,	110	61·4	1·48
						Mean	1·48

Dimethylaniline, distilled over zinc dust, had $d_{4°}^{20°}$ 0·9563 (Bramley, J., 1916, **109**, 434, found $d_{4°}^{20°}$ 0·9562); $P_E = 40·8$.

455	75	78·2	1·62	455	83	78·4	1·62
,,	60	77·3	1·60			Mean	1·61

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