

251. *Studies in Dielectric Polarisation. Part XVII. The Dipole Moments of Some Aromatic Acid Halides.*

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IN Part XVI (this vol., p. 158) the dipole moments of some aliphatic acid halides were recorded. The work has now been extended to the aromatic series, the following compounds having been investigated (values of moment in Debye units in benzene solution at 20°):

Benzoyl chloride	3.33	<i>p</i> -Nitrobenzoyl chloride	1.11
Phenylacetyl chloride	2.54	3 : 5-Dinitrobenzoyl chloride	1.20
<i>p</i> -Chlorobenzoyl chloride	2.00	<i>p</i> -Toluoyl chloride.....	3.81
<i>p</i> -Bromobenzoyl chloride.....	2.03	Benzoyl bromide	3.37

The first result of interest is that the moment of benzoyl chloride (3.33) is very much larger than that of acetyl chloride (2.45) or of propionyl chloride (2.61, both in benzene solution, Part XVI, *loc. cit.*). Nespital (*Z. physikal. Chem.*, 1932, B, 16, 178, footnote) gives $P_{2\infty}$ for benzoyl chloride in benzene solution as 270 c.c., which agrees with the value 271.5 c.c. now found, but he assumes the value 50 c.c. for P_{E+A} , whilst we have found P_E to be 37.1 c.c. Nespital thus obtains the incorrect value of 3.23 for the moment of benzoyl chloride. Since the sign of the COCl moment is negative, the difference between the aromatic and aliphatic group moments is therefore negative, which is in agreement with the well-known meta-directing properties of the group. In this respect COCl resembles the CHO group, the moment of benzaldehyde, 2.75 (Williams, *Physikal. Z.*,

1928, **29**, 683), being greater than that of propaldehyde, 2.04 (Herold and Wolf, *Z. physikal. Chem.*, 1930, *B*, **12**, 170; both in benzene solution).

The moment of phenylacetyl chloride would be expected to be much less than that of benzoyl chloride. It is actually found to be between those of acetyl and propionyl chlorides. A comparison of the moments of some methyl, ethyl, and benzyl compounds (all in benzene solution) is made in the following table :

Group.	Methyl.	Ethyl.	Benzyl.
CN	3.44 ¹	3.57 ¹	3.47 ²
Cl	1.67 ³	1.91 (C ₃ H ₇) ⁴	1.84 ⁵
COCl.....	2.45 ⁶	2.61 ⁶	2.54 ⁷

¹ Cowley and Partington, J., 1935, 604. ² Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 1860. ³ Calculated from the results of Morgan and Lowry, *J. Physical Chem.*, 1930, **34**, 2385.

⁴ Calculated from the results of Müller, *Physikal. Z.*, 1933, **34**, 701. ⁵ Parts, *Z. physikal. Chem.*, 1931, *B*, **12**, 323. ⁶ Part XVI, *loc. cit.* ⁷ Present work.

In all three cases the value of the moment of the benzyl compound lies between those of the methyl and ethyl compounds.

The moments of the *p*-substituted benzoyl chlorides can be calculated by simple vector addition, since rotation of the COCl group about the bond joining it to the ring cannot alter the value of the resultant moment. For 3 : 5-dinitrobenzoyl chloride the same argument holds, since the resultant moment of the two nitro-groups acts in the same direction as the moment of a single group in the para-position.

The moment of benzoyl chloride can be considered to be made up of the moment of the COCl group (taken as 2.61, the value for the aliphatic series; Part XVI, *loc. cit.*) acting at 16° to the line joining the group to the ring, and an "electromeric" moment acting in the direction of the line joining the para-positions. From the value 3.33 for the resultant, the value 2.61 for the COCl moment, and the angle 16°, solving the vector triangle gives a value 0.92 for the "electromeric" moment, and an angle 12° 29' to the line joining the para-positions for the direction of the resultant moment.

From this it can be found whether there is any "interaction" moment in the *p*-substituted benzoyl chlorides. From the moment of benzoyl chloride and that of a *p*-substituted compound, the component acting in the *p*-position is calculated, and the result compared with the moment of the group substituted in the *p*-position. These are taken as the values for the corresponding phenyl compounds, measured in benzene solution. The values, taken from the "Table of Dipole Moments" (*Trans. Faraday Soc.*, 1934, Appendix), and usually obtained by several different workers, are as given in the table below in column B. The values calculated for the moment acting in the *p*-position (A) and the corresponding "interaction" moments (C) are also given in the table, the "interaction" moment being taken as positive when it acts towards the COCl group.

Compound.	A.	B.	C.
<i>p</i> -Chlorobenzoyl chloride	1.38	1.56	+0.18
<i>p</i> -Bromobenzoyl chloride	1.35	1.53	+0.18
<i>p</i> -Nitrobenzoyl chloride.....	4.11	3.96	-0.15
<i>p</i> -Toluoyl chloride	0.49	0.40	+0.09

A similar calculation for 3 : 5-dinitrobenzoyl chloride gives a value of -0.25 or -0.43, according to whether the group moment is taken as that of nitrobenzene (3.96) or of *m*-dinitrobenzene (3.78). In this compound the nitro-groups are in meta-positions to the COCl group so that no definite conclusion can be reached, but it is interesting to note that the "interaction" moment has the same sign as in the *p*-nitro-compound. For the four compounds given in the table, the "interaction" moments are all small, but while that for the methyl group is less than those for the halogens, the "interaction" moment for the nitro-group is opposite in sign. The result for benzoyl bromide may be slightly in error on account of the pronounced action which this compound had on the silver plates of the dielectric cell, even in very dilute solution.

EXPERIMENTAL.

The apparatus and method of calculation were the same as described previously (Part XVI, *loc. cit.*). In connexion with the results described in Part XII and subsequent papers of this series, it should be noted that the values of the dielectric constants are given only to 4 significant figures, which, for the values used, correspond to an accuracy of about 0.025–0.04%. The capacities measured by the apparatus used by us, which is as accurate as any at present in use for the measurement of the dielectric constants of solutions, are accurate to $\pm 0.02 \mu\mu\text{F}$, which corresponds to 0.04% for a capacity of 50 $\mu\mu\text{F}$ and 0.01% for a capacity of 200 $\mu\mu\text{F}$. Since the dielectric constant is obtained from values for two capacities, it involves the errors of both measurements, and thus cannot be of greater accuracy than either. Results for high dielectric constants given to the same number of figures as smaller ones must be accepted with caution, since the measurement involves the use of a dielectric cell of much smaller capacity, causing a considerable reduction of accuracy if the same standard variable condenser is used.

Benzoyl chloride, phenylacetyl chloride, and benzoyl bromide were obtained from Kahlbaum; all the other compounds were from Fraenkel and Landau, except *p*-nitrobenzoyl chloride, obtained from Schuchardt.

Phenylacetyl chloride was fractionated under reduced pressure. Benzoyl chloride and bromide were fractionated at atmospheric pressure, and *p*-chlorobenzoyl and *p*-toluoyl chlorides under reduced pressure, all these four compounds then being fractionally frozen. *p*-Bromo- and *p*-nitro-benzoyl chlorides were twice distilled in a vacuum and twice crystallised from light petroleum. 3 : 5-Dinitrobenzoyl chloride was twice distilled under reduced pressure and twice crystallised from carbon disulphide. The crystals were then heated just below the m. p. in a vacuum desiccator for several hours, being powdered from time to time. In this way crystals melting at 71° were obtained. This compound crystallises with the solvent, the product obtained by crystallising from benzene melting at 52° after drying at ordinary temperature.

The benzene used was the same as before.

The physical constants of the compounds were as follows :

Compound.	B. p.	M. p.	$D_4^{20^\circ}$.	$n_D^{20^\circ}$.	$[R_L]_D$.
Benzoyl chloride	197.3°/754 mm.	-0.5°	1.2113	1.5536	37.14
Phenylacetyl chloride	105.1/23	—	1.1685	1.5333	41.06
<i>p</i> -Chlorobenzoyl chloride.....	99.6/11	13.5	1.3621	1.5790	42.72
<i>p</i> -Bromobenzoyl chloride	104.5/6	41	—	—	44.90
<i>p</i> -Nitrobenzoyl chloride	136.1/4	73	—	—	43.29
3 : 5-Dinitrobenzoyl chloride	201.2/17	71	—	—	50.56
<i>p</i> -Toluoyl chloride	102.7/14	-3.9	1.1686	1.5449	41.80
Benzoyl bromide	215.0/741	8.1	1.5461	1.5900	40.37

The refractivities of *p*-bromo-, *p*-nitro-, and 3 : 5-dinitro-benzoyl chlorides were calculated from those of benzoyl chloride and the substituted groups.

The following figures are available for comparison :

Benzoyl chloride : b. p. 197.2°/760 mm. (Perkin, J., 1896, **69**, 1205); m. p. -1° (Lieben, *Annalen*, 1875, **178**, 43); $D_4^{20^\circ}$ 1.2122, $n_D^{20^\circ}$ 1.5537 (Brühl, *ibid.*, 1886, **235**, 11); $D_4^{20.9^\circ}$ 1.2105, $n_D^{20.9^\circ}$ 1.5538 (von Auwers and Schmidt, *Ber.*, 1913, **46**, 482); b. p. 197.9°, m. p. -0.6°, $n_D^{20^\circ}$ 1.5535 (Smyth and Kamerling, *J. Amer. Chem. Soc.*, 1933, **55**, 463). Phenylacetyl chloride : b. p. 104–105°/23 mm. (Schott, *Ber.*, 1896, **29**, 1986); $D_4^{20^\circ}$ 1.1682 (Anschütz and Berns, *ibid.*, 1887, **20**, 1390). *p*-Chlorobenzoyl chloride : b. p. 111.5°/18 mm. (Montagne, *Rec. trav. chim.*, 1900, **19**, 61); m. p. 14–16° (Meyer, *Monatsh.*, 1901, **22**, 415); D 1.377 (Emmerling, *Ber.*, 1875, **8**, 881). *p*-Bromobenzoyl chloride : b. p. 154–155°/50 mm., m. p. 41° (Sudborough, J., 1895, **67**, 591). *p*-Nitrobenzoyl chloride : b. p. 154°/12 mm. (Benary, Reiter, and Soenderop, *Ber.*, 1917, **50**, 72); m. p. 73° ("Organic Syntheses," Vol. 3, p. 75). 3 : 5-Dinitrobenzoyl chloride : b. p. 196°/10–12 mm., m. p. 74° (Berend and Heymann, *J. pr. Chem.*, 1902, **65**, 291; 1904, **69**, 455); m. p. 66–68° (Cohen and Armes, J., 1906, **89**, 1481). *p*-Toluoyl chloride : b. p. 102°/15 mm. (Frankland and Aston, J., 1899, **75**, 494); b. p. 95–95.5°/10 mm., m. p. -2° to -1.5° (van Scherpenzeel, *Rec. trav. chim.*, 1901, **20**, 156); D 1.570 (Cahours, *Annalen*, 1858, **108**, 317). Benzoyl bromide : b. p. 218–219°/760 mm., m. p. 0°, D^{15° 1.570 (Claisen, *Ber.*, 1881, **14**, 2473).

Results.—Solvent, benzene. All measurements at 20°.

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
Benzoyl chloride.				
0·00000	0·8784	2·276	26·52	—
0·01386	0·8842	2·502	29·78	262·0
0·02576	0·8893	2·699	32·39	254·5
0·03499	0·8934	2·854	34·29	248·8
0·04758	0·8988	3·066	36·76	241·8

$$P_{2\infty} = 271·5 \text{ c.c.}; P_E = 37·1 \text{ c.c.}; \mu = 3·33.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
<i>p</i> -Chlorobenzoyl chloride.				
0·00000	0·8791	2·279	26·54	—
0·01259	0·8878	2·356	27·79	126·0
0·02292	0·8948	2·405	28·79	124·6
0·03349	0·9021	2·481	29·78	123·1
0·04401	0·9092	2·543	30·76	122·3

$$P_{2\infty} = 127·1 \text{ c.c.}; P_E = 42·7 \text{ c.c.}; \mu = 2·00.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
<i>p</i> -Nitrobenzoyl chloride.				
0·00000	0·8784	2·276	26·52	—
0·01327	0·8888	2·304	27·09	69·5
0·02643	0·8992	2·331	27·65	69·3
0·03900	0·9091	2·358	28·18	69·3
0·05074	0·9180	2·381	28·71	68·7

$$P_{2\infty} = 69·4 \text{ c.c.}; P_E = 43·3 \text{ c.c.}; \mu = 1·11.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
<i>p</i> -Toluoyl chloride.				
0·00000	0·8790	2·280	26·56	—
0·01359	0·8840	2·570	30·74	334·3
0·02654	0·8899	2·851	34·33	319·7
0·03859	0·8947	3·111	37·39	307·4
0·05175	0·9001	3·392	40·42	294·4

$$P_{2\infty} = 348·6 \text{ c.c.}; P_E = 41·8 \text{ c.c.}; \mu = 3·81.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
Phenylacetyl chloride.				
0·00000	0·8792	2·280	26·55	—
0·01479	0·8855	2·421	28·73	174·2
0·02675	0·8903	2·534	30·44	172·0
0·03867	0·8954	2·646	32·05	168·7
0·05114	0·9004	2·760	33·66	165·6

$$P_{2\infty} = 178·0 \text{ c.c.}; P_E = 41·03 \text{ c.c.}; \mu = 2·54.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
<i>p</i> -Bromobenzoyl chloride.				
0·00000	0·8792	2·280	26·55	—
0·01081	0·8915	2·348	27·68	130·9
0·02123	0·9034	2·416	28·76	130·7
0·03149	0·9149	2·480	29·79	129·4
0·04288	0·9275	2·551	30·91	128·2

$$P_{2\infty} = 132·0 \text{ c.c.}; P_E = 44·9 \text{ c.c.}; \mu = 2·03.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
3 : 5-Dinitrobenzoyl chloride.				
0·00000	0·8789	2·281	26·58	—
0·01242	0·8938	2·315	27·25	81·0
0·02463	0·9081	2·347	27·92	80·9
0·03550	0·9205	2·376	28·52	81·2
0·04551	0·9317	2·403	29·06	81·1

$$P_{2\infty} = 81·1 \text{ c.c.}; P_E = 50·5 \text{ c.c.}; \mu = 1·20.$$

f_2	D_4^{20}	ϵ	P_{12} , c.c.	P_2 , c.c.
Benzoyl bromide.				
0·00000	0·8790	2·282	26·58	—
0·00706	0·8852	2·401	28·35	277·0
0·01398	0·8914	2·524	30·06	275·8
0·02037	0·8971	2·635	31·54	270·2
0·02602	0·9024	2·737	32·85	267·5

$$P_{2\infty} = 281·4 \text{ c.c.}; P_E = 40·4 \text{ c.c.}; \mu = 3·37.$$

SUMMARY.

The dipole moment of benzoyl chloride has been found to be larger than that of propionyl chloride, while that of phenylacetyl chloride is smaller, in agreement with the values for other benzyl compounds. The moments found for a number of *p*-substituted benzoyl chlorides can be explained by the conclusion regarding the direction of the COCl group moment arrived at in Part XVI.

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