560. *Molecular Polarisation and Molecular Interaction. Part II. The Apparent Dipole Moments of* p-*Chloro-,* 2 : 4 : 6-*Tribromo-, and* 2 : 4 : 6-*Tribromodimethyl-aniline,* n- *and* tert.-*Butylamine in Benzene and Dioxan. The Mesomeric Effect in Substituted Anilines.*

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From measurements of the dielectric constants, refractive indices, and specific volumes of dilute solutions, the apparent molecular polarisations at infinite dilution ($P_{2\infty}$), and molecular refractions ($[R_D]$) of these amines in benzene and dioxan at 25° have been determined. For *p*-chloro- and 2 : 4 : 6-tribromo-aniline the values of $P_{2\infty}$ are much greater in dioxan than in benzene, whilst with the other compounds named in the title the differences are very small. These results support the view that the higher values observed with certain amines in dioxan are attributable to interaction between the amino-hydrogen atoms and the oxygen atoms of the dioxan molecule. If the total distortion polarisations are assumed to be $1{\cdot}05[R_D]$, the apparent dipole moments in benzene and dioxan, respectively, are : *p*-chloro- 2·994 and 3·372, 2 : 4 : 6-tribromo- 1·693 and 1·972, and 2 : 4 : 6-tribromodimethyl-aniline 1·048 and 1·029; *n*- 1·322 and 1·305, and *tert.*-butylamine 1·322 and 1·322 D.

The value of the moment for 2 : 4 : 6-tribromodimethylaniline in benzene indicates that the mesomeric effect of the amino-group is strongly repressed by steric influences, whereas no such influences appear to operate with 2 : 4 : 6-tribromoaniline.

In Part I (this vol., p. 753) it was confirmed that the apparent molecular polarisation of aniline is much higher in dioxan than in benzene solution, and it was found that the difference between the values, in the two solvents, was smaller for methylaniline and quite small for dimethylaniline. These results support the view that the high values observed for aniline and methylaniline in dioxan are due to molecular interaction involving the formation of hydrogen bonds between the amino-hydrogen atoms and one of the oxygen atoms of the dioxan molecule.

With the aim of confirming the validity of these conclusions, derivatives of aniline and dimethylaniline were studied, so as to ascertain whether the effect was always associated with the presence of an amino-hydrogen atom. It was also of interest to ascertain whether the effect is common to all primary amines or occurs only when the amino-group is linked directly to an aromatic nucleus. In the latter case the mesomeric effect of the amino-group would be expected to facilitate the bonding of the amino-hydrogen atoms to oxygen atoms of the dioxan molecule. This could be tested by measurements on primary alkylamines. Studies have therefore been made of the molecular polarisations of *p*-chloro-, 2 : 4 : 6-tribromo-, 2 : 4 : 6-tribromodimethyl-aniline and *n*- and *tert.*-butylamine in benzene and dioxan. The measurements on the two tribromo-compounds were of particular interest in view of the possible steric-hindrance effects similar to those reported for aminodurene, mesidine, and dimethylmesidine (Birtles and Hampson, *J.*, 1937, 10; Ingham and Hampson, *J.*, 1939, 981).

The two butylamines were chosen as the simplest alkylamines of sufficiently low volatility to permit easy and accurate manipulation, and as representing compounds with the amino-group linked to a primary and tertiary carbon atom, respectively.

Experimental.

Materials.—Benzene and dioxan were purified as described in Part I.

p-Chloroaniline (commerical " pure " grade) was freed from products due to superficial oxidation by being washed with cold ethyl alcohol, and was then recrystallised from aldehyde-free methyl alcohol until of constant m. p. It was dried in an atmosphere of nitrogen and stored under that gas in a tightly stoppered bottle; it had m. p. 69·9°.

2 : 4 : 6-Tribromoaniline, prepared by the direct bromination of commercially pure aniline, was recrystallised from ethyl alcohol until of constant m. p. (121·7°) and stored under nitrogen.

2 : 4 : 6-Tribromodimethylaniline was prepared by the method of Clarke, Gillespie, and Weisshaus (*J. Amer. Chem. Soc.*, 1933, **55**, 4571). 2 : 4 : 6-Tribromoaniline (0·5 mol.) was heated under reflux during 3 hours with a mixture of 98% formic acid (15 mols.) and 40% aqueous formaldehyde (1·3 mols.). After addition of hydrochloric acid (0·5 mol.) the remaining formic acid and formaldehyde were removed by distillation under reduced pressure. The residue was made alkaline with 20% sodium hydroxide solution and extracted with ether. The heavy oil recovered from this extract was dried (KOH pellets) and distilled under reduced pressure with acetic anhydride. The base was then dried again (KOH pellets) and distilled from freshly prepared barium oxide at 0·4 mm. It had b. p. 208°/24 mm., 110°/0·4 mm., d_4^{25} 1·9959.

n-Butylamine. A pure commercial sample was distilled at atmospheric pressure, dried (P_2O_5), and distilled from this reagent through a 15-plate column. The middle fraction of boiling range 0·1° was collected; b. p. 77·3°, d_4^{25} 0·73265.

tert.-Butylamine. As attempts to prepare this amine from *tert.*-butyl alcohol led to small yields only, it was made by the method of Campbell, Sommers, and Campbell (*Org. Synth.*, **27**, 12).

2 : 2-Dimethylethyleneimine, produced from 2-amino-2-methylpropanol by the action of sulphuric acid, was fractionated, the fraction boiling at 71—72° being collected. It was then dissolved in dioxan and hydrogenated at 80 atmospheres during 1½ hours, using dioxan-wetted Raney nickel as catalyst. The *tert.*-butylamine was fractionally distilled through the column, the fraction, b. p. 43·7—43·8°, being collected. This was dried (crushed KOH) and redistilled; b. p. 43·7—43·8°, d_4^{25} 0·68670, n_4^{25} 1·3750.

TABLE I.

$100w_2$.	ε.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
p-Chloroaniline in benzene.									
0·0000	2·2725	1·14456	0·34089	—	1·4982	0·33559	—	—	—
1·0719	2·3575	1·14098	0·35545	216·80	1·4991	0·33505	36·39	7·93	−0·334
1·6195	2·4018	1·13915	0·36277	215·86	1·4994	0·33473	36·04	7·984	−0·334
2·3380	2·4595	1·13675	0·37203	213·43	1·4999	0·33429	35·72	7·998	−0·334
3·8438	2·5822	1·13171	0·39077	209·06	1·5010	0·33342	35·61	8·057	−0·3343
5·6249	2·7297	1·12576	0·41170	204·11	1·5024	0·33248	35·76	8·128	−0·3342
7·2468	2·8653	1·12036	0·42953	199·56	1·5037	0·33159	35·77	8·180	−0·3339
8·2352	2·9498	1·11706	0·44003	197·09	1·5045	0·33103	35·75	8·225	−0·3339
9·6641	3·0724	1·11235	0·45447	193·45	1·5055	0·33023	35·74	8·277	−0·3333
p-Chloroaniline in dioxan.									
0·0000	2·2037	0·97282	0·27856	—	1·4201	0·24623	—	—	—
0·8256	2·2988	0·97144	0·29350	266·43	1·4214	0·24654	36·21	11·52	−0·167
1·2531	2·3483	0·97072	0·30100	264·03	1·4222	0·24676	36·81	11·54	−0·167
1·8378	2·4164	0·96974	0·31101	260·83	1·4230	0·24697	36·55	11·57	−0·167
2·8419	2·5337	0·96808	0·32749	255·22	1·4248	0·24744	36·87	11·61	−0·1667
4·0899	2·6806	0·96599	0·34684	248·55	1·4266	0·24784	36·31	11·660	−0·1670
5·3965	2·8356	0·96382	0·36587	241·97	1·4287	0·24830	36·31	11·709	−0·1668
6·0602	2·9145	0·96273	0·37504	238·67	1·4298	0·24860	36·41	11·729	−0·1664
6·8116	3·0046	0·96147	0·38512	235·14	1·4312	0·24896	36·53	11·758	−0·1666
2 : 4 : 6-Tribromoaniline in benzene.									
0·0000	2·2725	1·14458	0·34090	—	1·4982	0·33559	—	—	—
1·4159	2·2879	1·13447	0·34108	116·65	1·4992	0·33322	55·48	1·21	−0·714
2·3023	2·3005	1·12808	0·34114	115·88	1·4999	0·33175	55·68	1·22	−0·717
3·6825	2·3178	1·11823	0·34129	115·94	1·5007	0·32926	54·00	1·230	−0·716
4·3863	2·3267	1·11320	0·34134	115·74	1·5014	0·32821	55·18	1·236	−0·7155
5·0571	2·3352	1·10838	0·34137	115·51	1·5020	0·32712	55·45	1·240	−0·7158
7·3010	2·3644	1·09234	0·34149	115·12	1·5039	0·32343	55·75	1·259	−0·7155
7·7505	2·3702	1·08912	0·34148	114·92	1·5043	0·32266	55·71	1·261	−0·7156
2 : 4 : 6-Tribromoaniline in dioxan.									
0·0000	2·2040	0·97282	0·27861	—	1·4199	0·24612	—	—	—
1·5503	2·2326	0·96428	0·28081	138·71	1·4219	0·24500	57·35	1·84	−0·551
2·0761	2·2426	0·96138	0·28158	138·09	1·4227	0·24468	58·30	1·86	−0·551
2·6912	2·2544	0·95798	0·28246	139·09	1·4234	0·24415	57·04	1·87	−0·551
3·3374	2·2606	0·95439	0·28332	138·52	1·4243	0·24371	57·36	1·876	−0·552
4·7975	2·2951	0·94635	0·28535	138·24	1·4263	0·24263	57·19	1·899	−0·552
5·2373	2·3037	0·94387	0·28592	137·87	1·4271	0·24239	57·69	1·904	−0·553
6·1353	2·3214	0·93893	0·28711	137·60	1·4283	0·24171	57·47	1·914	−0·5524
7·5378	2·3499	0·93121	0·28898	137·28	1·4301	0·24063	57·16	1·936	−0·5520
2 : 4 : 6-Tribromodimethylaniline in benzene.									
0·0000	2·2725	1·14458	0·34090	—	1·4982	0·33559	—	—	—
1·5633	2·2809	1·13452	0·33946	89·05	1·4990	0·33312	63·56	0·537	−0·6435
2·1904	2·2843	1·13048	0·33888	89·02	1·4993	0·33210	63·08	0·539	−0·6437
3·9309	2·2938	1·11928	0·33726	88·88	1·5003	0·32937	63·48	0·542	−0·6436
4·4793	2·2967	1·11577	0·33673	88·70	1·5006	0·32850	63·46	0·540	−0·6432
6·1407	2·3061	1·10508	0·33519	88·73	1·5015	0·32585	63·35	0·547	−0·6433
7·3160	2·3130	1·09750	0·33411	88·81	1·5022	0·32400	63·41	0·554	−0·6435
9·6381	2·3264	1·08254	0·33189	88·56	1·5034	0·32022	63·03	0·559	−0·6437
12·2106	2·3420	1·06601	0·32948	88·54	1·5049	0·31613	63·07	0·569	−0·6435
2 : 4 : 6-Tribromodimethylaniline in dioxan.									
0·0000	2·2039	0·97289	0·27861	—	1·4199	0·24613	—	—	—
1·3467	2·2126	0·96660	0·27823	89·61	1·4213	0·24525	64·71	0·646	−0·4670
2·0949	2·2178	0·96307	0·27807	90·49	1·4221	0·24481	65·54	0·664	−0·4688
3·1687	2·2250	0·95797	0·27775	90·00	1·4234	0·24415	65·73	0·666	−0·4680
3·7197	2·2288	0·95547	0·27763	90·28	1·4239	0·24378	65·48	0·673	−0·4683
5·4216	2·2404	0·94747	0·27715	90·08	1·4261	0·24279	66·04	0·679	−0·4689
6·7183	2·2495	0·94129	0·27677	89·92	1·4275	0·24192	65·66	0·681	−0·4690
8·2839	2·2609	0·93403	0·27640	90·17	1·4293	0·24094	65·61	0·688	−0·4691
10·0755	2·2738	0·92564	0·27589	90·05	1·4315	0·23982	65·68	0·694	−0·4690

TABLE I (*continued*).

$100w_2$.	ε.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
n-Butylamine in benzene.									
0·0000	2·2725	1·14457	0·34090	—	1·4982	0·33559	—	—	—
1·1033	2·2973	1·14725	0·34634	61·02	1·4969	0·33568	25·06	2·25	0·2429
1·7068	2·3111	1·14870	0·34934	62·14	1·4960	0·33555	24·33	2·26	0·2420
3·1706	2·3443	1·15218	0·35653	60·99	1·4941	0·33548	24·27	2·265	0·2400
4·3997	2·3724	1·15509	0·36256	60·94	1·4925	0·33538	24·18	2·271	0·2391
6·4198	2·4189	1·15982	0·37242	60·85	1·4900	0·33532	24·23	2·280	0·2376
7·1388	2·4357	1·16152	0·37595	60·84	1·4891	0·33528	24·22	2·286	0·2374
8·8174	2·4746	1·16548	0·38407	60·75	1·4870	0·33520	24·21	2·292	0·2368
10·7310	2·5203	1·16988	0·39346	60·76	1·4847	0·33513	24·23	2·309	0·2359
n-Butylamine in dioxan.									
0·0000	2·2038	0·97288	0·27859	—	1·4201	0·24623	—	—	—
0·9458	2·2284	0·97671	0·28375	60·28	1·4197	0·24700	23·96	2·60	0·4049
1·4520	2·2412	0·97871	0·28642	59·82	1·4195	0·24741	23·95	2·58	0·4015
2·2635	2·2628	0·98199	0·29090	60·15	1·4192	0·24807	23·95	2·60	0·4025
3·3060	2·2896	0·98617	0·29648	59·96	1·4188	0·24895	24·03	2·595	0·4020
4·9376	2·3320	0·99274	0·30525	59·87	1·4184	0·25038	24·15	2·596	0·4022
5·7141	2·3534	0·99582	0·30943	59·85	1·4182	0·25102	24·14	2·601	0·4015
7·1842	2·3901	1·00170	0·31718	59·66	1·4177	0·25227	24·17	2·593	0·4012
8·6457	2·4275	1·00769	0·32490	59·55	1·4172	0·25354	24·19	2·587	0·4026
tert.-Butylamine in benzene.									
0·0000	2·2725	1·14458	0·34090	—	—	—	—	—	—
1·4543	2·3024	1·14943	0·34795	60·40	—	—	—	2·06	0·3335
1·9700	2·3130	1·15113	0·35044	60·35	—	—	—	2·056	0·3325
3·1087	2·3354	1·15473	0·35568	59·71	—	—	—	2·023	0·3265
3·3661	2·3403	1·15554	0·35683	59·55	—	—	—	2·014	0·3256
4·2566	2·3574	1·15833	0·36084	59·20	—	—	—	1·995	0·3230
5·1958	2·3748	1·16108	0·36487	58·68	—	—	—	1·969	0·3176
9·3203	2·4466	1·17281	0·38155	56·83	—	—	—	1·868	0·3029
tert.-Butylamine in dioxan.									
0·0000	2·2038	0·97280	0·27857	—	—	—	—	—	—
1·8581	2·2504	0·98170	0·28880	60·64	—	—	—	2·508	0·4790
2·3369	2·2619	0·98398	0·29135	60·37	—	—	—	2·486	0·4784
3·3088	2·2855	0·98848	0·29651	60·03	—	—	—	2·468	0·4739
4·3226	2·3094	0·99321	0·30178	59·65	—	—	—	2·443	0·4696
5·5872	2·3389	0·99891	0·30824	59·22	—	—	—	2·418	0·4673
6·2585	2·3538	1·00192	0·31154	58·91	—	—	—	2·397	0·4653
6·7483	2·3649	1·00410	0·31398	58·75	—	—	—	2·385	0·4638

TABLE II.

Polarisation data.

	α.	α'.	β.	$P_{2\infty}$.	$[R_D]$.	P_μ.	μ (D.).
p-Chloroaniline in benzene ...	7·909	3·84	−0·3338	220·60	35·77	183·04	2·994
,, in dioxan	11·503	3·74	−0·1667	271·82	36·43	233·57	3·372
2 : 4 : 6-Tribromoaniline in benzene	1·202	0·77	−0·7156	116·72	55·50	58·45	1·693
2 : 4 : 6-Tribromoaniline in dioxan	1·832	1·37	−0·5520	139·54	57·39	79·28	1·972
2 : 4 : 6-Tribromodimethyl-aniline in benzene	0·527	0·33	−0·6435	88·90	63·30	22·40	1·048
2 : 4 : 6-Tribromodimethyl-aniline in dioxan	0·658	0·41	−0·4688	90·56	65·57	21·61	1·029
n-Butylamine in benzene	2·249	5·0	0·2408	61·13	24·22	35·64	1·322
,, in dioxan	2·594	0	0·4022	60·14	24·10	34·70	1·305
tert.-Butylamine in benzene ...	2·101	−2·5	0·3393	61·23	24·38 *	35·63	1·322
,, in dioxan ...	2·548	−2·4	0·4836	61·28	24·38 *	35·68	1·322

* Value calculated from n_D^{25} and d_4^{25} for the pure liquid.

Methods.—The dielectric constants, specific volumes, and refractive indices were determined as in the previous investigation, and the same methods were used in the derivation of the apparent molecular polarisation at infinite dilution ($P_{2\infty}$) and the apparent dipole moment μ.

The results are recorded in Table I, whilst the parameters α and β, and the values of $P_{2\infty}$ and μ derived from them are given in Table II.

Owing to the volatility of *tert.*-butylamine the refractive indices of its solutions changed appreciably with time. In the case of this solute, therefore, the molecular refraction obtained from measurements on the pure liquid was used in the calculation of P_μ.

Previous measurements of the dipole moments of these compounds appear to be restricted to studies of *p*-chloro- and 2 : 4 : 6-tribromo-aniline in benzene solution only. The values of 2·97 D. and 3·00 D. for *p*-chloroaniline, reported respectively by Tiganik (*Z. physikal. Chem.*, 1931, **14**, *B*, 135) and Fogelberg and Williams (*Physikal. Z.*, 1931, **32**, 27), are in accord with the results now described, the dielectric constant and density values at 25° recorded by the latter authors all lying within 0·001 and 0·0001 unit, respectively, of the values predicted from the parameters in Table II. The lower figure (2·90 D.) recorded by Bergmann and Tschudnowsky (*Z. physikal. Chem.*, 1932, **17**, *B*, 301) is deduced from data which are less self-consistent than the other determinations. Eide and Hassel (*Tidsskr. Kjem. Berg.*, 1930, **10**, 93) record the value 2·93 D. for *p*-chloroaniline, and Hassel and Naeshagen (*Z. physikal. Chem.*, 1931, **12**, *B*, 79) give 1·80 D. for 2 : 4 : 6-tribromoaniline, but, owing to their concentrations being expressed in g.-mols. per l. and their measurement temperature not being stated, their results are difficult to compare with those now recorded.

The results for the butylamines are of the order to be expected from literature values for methylamine and ethylamine.

DISCUSSION.

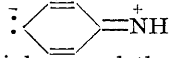
It is generally accepted that for measurements in benzene solution the higher dipole moment of aniline as compared with primary alkylamines is due to the mesomeric $(+M)$ effect of the amino-group, leading to resonance involving structures such as . Such structures produce a partial double-bond character in the C–N linkage and thereby cause the molecule to assume an approximately coplanar configuration. Exact analysis of the problem is difficult owing to the fact that the axis of the resultant molecule does not coincide with the axis of the N–C linkage, and attempts to calculate the angle of inclination are subject to considerable assumptions, but it may be inferred that similar effects are responsible for the higher moments of methyl- and dimethyl-aniline compared with secondary and tertiary alkylamines. Whereas for the aliphatic amines replacement of the amino-hydrogen atoms leads to a decrease in the moment, it leads to an increase for aniline. This may be ascribed to the inductive $(+I)$ effect of the methyl groups, which in the aromatic compounds increases the $+M$ effect of the amino-group (cf. Lucas, *J. Amer. Chem. Soc.*, 1923, **46**, 2475; 1925, **47**, 1459). Although the moment of dimethylaniline is not so great as that of methylaniline the increase from trimethylamine to dimethylaniline is greater than that from dimethylamine to methylaniline (Table III).

TABLE III.

Dipole moments of amines in benzene solution.

	D.		D.
Aniline	1·51 *	Dimethylaniline	1·58 *†
p-Chloroaniline	2·99	*p*-Chlorodimethylaniline	3·29 †
2 : 4 : 6-Tribromoaniline	1·69 ‡	2 : 4 : 6-Tribromodimethylaniline	1·05 ‡
p-Toluidine	1·27 §	Dimethyl-*p*-toluidine	1·29 †
Mesidine	1·40 ‖	Dimethylmesidine	1·03 ‖
Methylamine	1·46 ¶	Trimethylamine	0·86 ¶
n-Butylamine	1·32 ‡	Dimethylamine	1·17 ¶

* Part I. † Marsden and Sutton (*loc. cit.*). ‡ Present work.
§ Donle and Gehrckens (*Z. physikal. Chem.*, 1932, **18**, *B*, 316). ‖ Ingham and Hampson (*loc. cit.*).
¶ Le Fèvre and Russell (*Trans. Faraday Soc.*, 1947, **43**, 374).

As the dipole of the aniline molecule is inclined to the axis of the N–C linkage, the moment of *p*-chloroaniline (2·99 D.) is in accord with the view that the presence of the chlorine atom increases the contribution of the double-bonded resonance structures. Thus Marsden and Sutton (*J.*, 1936, 599) deduce, from the moments of chlorobenzene and aniline, that if the mesomeric effect were not modified the moment of *p*-chloroaniline would be 2·87 D. Owing to the inclination of the dipole axis to the axis of the N–C linkage, the increase in the mesomeric moment will be rather greater than 0·12, the difference between the observed and calculated values. This can be attributed either to the diminished mesomeric effect of the chlorine atom or to the inductive $(-I)$ effect of this atom.

The data of Marsden and Sutton for the moment of *p*-chloro- and *p*-bromo-dimethylaniline in benzene show that this effect is increased in these compounds, where vector additivity would indicate that the moments should be 2·97 and 2·93 D., respectively.

For *p*-toluidine the effects of the two substituents act in opposition. The methyl group has a permanent electron-release effect, caused by hyperconjugation, which will tend to inhibit the resonance structures in which there is a N–C double bond, whilst the mesomeric effect of the amino-group will tend in turn to inhibit the hyperconjugation. The moments attributable to the amino- and methyl groups will, therefore, each be diminished. As they operate in opposite senses, although at an angle to one another, the resultant moment of molecule will not be very different from the value which would be expected if the electron-donation effects were both unhindered. The fact that there is a diminished resonance effect in *p*-toluidine is indicated by the extra resonance energies deduced from the dissociation constants of these amines as compared with methylamine (cf. Pauling, " The Nature of the Chemical Bond," Cornell University Press, 1940, p. 206), the value for *p*-toluidine being appreciably lower than for aniline. The values shown in Table IV are derived from pK_a data on the assumption that at 25° $K_w = 1{\cdot}008 \times 10^{-14}$. The extra resonance energies are calculated by comparison of the K_b values of the primary amines with that of methylamine, and of the figures for methyl- and dimethyl-aniline with those for di- and tri-methylamine, respectively.

TABLE IV.

" Extra " resonance energies of amines deduced from dissociation constant data.

	pK_a.	K_b.	Extra resonance energy (kcals. per g.-mol.).
Aniline	4·58 *	$3{\cdot}83 \times 10^{-10}$	8·3
Methylaniline	4·85 *	$7{\cdot}15 \times 10^{-10}$	8·2
Dimethylaniline	5·08 *	$1{\cdot}21 \times 10^{-9}$	9·2
p-Toluidine	5·10 †	$1{\cdot}26 \times 10^{-9}$	7·3
p-Chloroaniline	4·07 †	$1{\cdot}17 \times 10^{-10}$	9·1
Methylamine	—	$5{\cdot}01 \times 10^{-4}$ ‡	—
Dimethylamine	—	$7{\cdot}41 \times 10^{-4}$ ‡	—
Trimethylamine	—	$7{\cdot}40 \times 10^{-3}$ ‡	—

* Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469).
† James and Knox (private communication).
‡ Glasstone (" Textbook of Physical Chemistry," 1946, p. 981).

For the tri-substituted compounds it is significant that the dipole moment of 2 : 4 : 6-tribromoaniline is appreciably greater than that of aniline itself. This is surprising because, for mesidine, Ingham and Hampson (*loc. cit.*) found the value 1·40 D., intermediate between the moments of aniline and a primary alkylamine. This decrease in moment compared with that of aniline could be attributed either to an induction effect or to the steric effect of the *ortho*-alkyl groups in hindering the formation of resonance structures involving N–C double bonds in which the amino-hydrogen atoms become coplanar with the benzene ring. The moments which had been observed for durene derivatives (Birtles and Hampson, *loc. cit.*) led Ingham and Hampson to prefer the latter view. The value for mesidine was almost identical with that of aminodurene (1·39 D.), suggesting that the same factors were operating in each case to decrease the value relative to that for aniline. The moment of bromodurene (1·55 D.), however, differed little from that of bromobenzene (1·52 D.); steric factors would be ineffective in this case, whereas induction could occur as well in bromodurene as in aminodurene and would be expected to diminish the mesomeric effect of the bromine atom and increase the moment towards the value for an alkyl bromide (2·15 D.).

The result now obtained, however, indicates that such a steric effect can operate only slightly, if at all, for 2 : 4 : 6-tribromoaniline. On the contrary, the $-I$ effects of the bromine atoms seem to favour the double bonded structure, leading to a moment higher than that for aniline.

To explain the diminished moments of mesidine and aminodurene compared with aniline, it is therefore necessary to assume either that the effect is due to the opposing electron-donating tendencies of the groups, which diminish the mesomeric effect of the amino-group, and that the small increase in moment on passing from bromobenzene to bromodurene is also due to such an interaction, or that the methyl groups produce a more pronounced steric effect than do the bromine atoms. Such a difference between the effects of the bromine atoms and methyl groups could be explained as due either to the mutual repulsion of the hydrogen atoms or to the formation of hydrogen bonds between the methyl groups and the nitrogen atoms, as suggested by Watson (*Ann. Reports*, 1939, **36**, 219).

The moment for 2 : 4 : 6-tribromodimethylaniline, however, is much lower than that for dimethylaniline itself, and is approximately equal to the value for dimethylmesidine. This supports the view of Birtles and Hampson that in dimethylamino-compounds mesomerism is inhibited through the presence of *ortho*-substituents.

Comparison of the dipole-moment changes on passing from benzene to dioxan solution for

TABLE V.

Comparison of polarisation data for amines in benzene and dioxan solutions.

	$P_{2\infty}$. Benzene.	$P_{2\infty}$. Dioxan.	μ (D.). Benzene.	μ (D.). Dioxan.	ΔP_2.	$\Delta\mu$.
Aniline	78·35	95·11	1·505	1·750	16·76	0·245
Methylaniline	93·20	106·72	1·643	1·833	13·52	0·190
Dimethylaniline	94·06	97·79	1·577	1·633	3·73	0·056
p-Chloroaniline	220·60	271·82	2·994	3·372	51·22	0·378
2 : 4 : 6-Tribromoaniline	116·72	139·54	1·693	1·972	22·82	0·279
2 : 4 : 6-Tribromodimethylaniline	88·90	90·56	1·048	1·029	1·66	—
n-Butylamine	61·13	60·14	1·322	1·305	—	—
tert.-Butylamine	61·23	61·28	1·322	1·322	—	—

the amines so far investigated (Table V) shows that the increase for 2 : 4 : 6-tribromoaniline is slightly greater, and for *p*-chloroaniline is much greater, than for aniline. This suggests that the effect giving rise to the enhanced polarisation in dioxan is favoured by substituents which increase the contribution of polar resonance structures. The present data do not permit separate determination of the degree of association and of the moments of the association complexes in the three cases. The general effect, however, can be explained by supposing that the increase from aniline to *p*-chloroaniline is associated principally with the $-I$ effect of the halogen atom, which will not only favour the association phenomenon but also lead to an added increase in the moment of the molecule when the association occurs. The effect in the case of 2 : 4 : 6-tribromoaniline may reasonably be less, owing to the facts that the axes of the carbon–halogen dipoles are symmetrically arranged, and that any modifications in these will be less apparent in the overall moment of the molecule.

The pronounced difference in behaviour between aniline and the butylamines, for which the moments in benzene and dioxan are nearly equal, may be associated with the more basic character of the alkylamines and to the fact that there is no possibility of resonance structures which would facilitate the bonding of the hydrogen atoms. It cannot be inferred conclusively from these results that no hydrogen bonding occurs between the butylamines and dioxan, but this appears improbable, as even in the absence of mesomeric effects it would be expected to lead to a charge displacement which would be detectable as a change in the apparent dipole moment such as was observed, for instance, in chloroform solutions of triethylamine and of di*iso*propyl ether (Hammick, Norris, and Sutton, *J.*, 1938, 1755).

There is also a distinct difference between the molecular refractions of some of the amines in the two solvents. This was observed previously with aniline and methylaniline, but it becomes even more distinct with 2 : 4 : 6-tribromoaniline and 2 : 4 : 6-tribromodimethylaniline. This was previously attributed to the hydrogen bonding, as had been assumed by Curran (*J. Amer. Chem. Soc.*, 1945, **67**, 1835) for the cases of salicylaldehyde and *o*-hydroxyacetophenone. In view of the large difference for 2 : 4 : 6-tribromodimethylaniline, however, the effect does not now seem to be due solely to this cause, and no explanation can as yet be offered.

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