110. *Steric Inhibition of Resonance. Part II. The* m-*Xylidines and* N-*Dimethyl*-m-*xylidines.*

By George Thomson.

Corroboration of views expressed in Part I is given by the observation that the atomic refractivity of nitrogen in *N*-dimethyl-*m*-2-xylidine is lowered to nearly the value observed in aliphatic tertiary amines, whereas in *N*-dimethyl-*m*-5-xylidine it has the normal value for aromatic tertiary amines. An intermediate value is found in *N*-dimethyl-*m*-4-xylidine, in which one methyl group is ortho to the dimethylamino-group.

The molecular solution volume of *N*-dimethyl-*m*-2-xylidine is higher than that of *N*-dimethyl-*m*-5-xylidine but indistinguishable from that of *N*-dimethyl-*m*-4-xylidine.

The parachors of the *N*-dimethyl-*m*-xylidines decrease in the order *m*-5 > *m*-4 > *m*-2.

In Part I (preceding paper) the view is expressed that inhibition of the resonance between a nitro-group and a benzene nucleus is accompanied by a lowering of molecular refractivity and that even a single bulky substituent ortho to a nitro-group will to some extent inhibit resonance. Since Hampson and his collaborators (J., 1937, 10; 1939, 981) have shown that steric inhibition of resonance by vicinal methyl groups is more marked in dimethylamino- than in amino-compounds, it becomes of interest to investigate the molecular refractivities of such compounds. Brühl (*Z. physikal. Chem.*, 1895, **16**, 497) noted that the atomic refractivity of nitrogen in *N*-dimethyl-*o*-toluidine was abnormally low, and this was confirmed by Ley and Pfeiffer (*Ber.*, 1921, **54**, 369), who found abnormalities in the absorption spectra and low molecular refractivities of ortho-substituted *N*-dimethylanilines and of *N*-dimethylxylidines in which methyl groups occupied one or both of the ortho-positions to the dimethylamino-group; when both ortho-positions were substituted the absorption spectrum was profoundly altered. On the other hand, no anomalies were found in the optical properties of ortho-substituted primary or secondary amines.

The present paper records a remeasurement of the molecular refractivities of *m*-4- and *m*-2-xylidines and their *N*-dimethyl derivatives, and measurements of the molecular refractivities of *m*-5- and *N*-dimethyl-*m*-5-xylidine and of the parachors of all six compounds, for it was desirable that these physical constants should be measured for all the compounds under the same conditions.

In Table I are recorded the values at 25° of densities, surface tensions (in dynes/cm.), and refractive indexes for five wave-lengths (mercury 4358 A. and 5461 A., hydrogen 4861 A. and 6563 A., and sodium 5893 A.). Table II contains the values of parachors and molecular refractivities calculated from the data of Table I together with some values from the literature, also the molecular solution volumes measured in benzene solution at 25°.

From Ley and Pfeiffer's measurements (*loc. cit.*) at 20° on *m*-2-xylidine and the *N*-dimethyl derivatives of *m*-2- and *m*-4-xylidines and those made by Brühl (*Z. physikal. Chem.*, 1895, **16**, 218) at 19·4° on *m*-4-xylidine, it would appear that *m*-2- has a higher density and higher refractive indexes than *m*-4-xylidine, whereas on

TABLE I.

Substance.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{100^\circ}$.	γ^{25°.	γ^{100°.	$n_{4358}^{25^\circ}$.	$n_{4861}^{25^\circ}$.	$n_{5461}^{25^\circ}$.	$n_{D}^{25^\circ}$.	$n_{6563}^{25^\circ}$.
Benzene	0·87368	—	—	—	1·51979	1·50987	1·50210	1·49818	1·49340
m-Xylene	0·86010	—	—	—	1·5154	1·5061	1·4987	1·4949	1·4906
Dimethylaniline	0·95241	—	—	—	1·5900	1·5741	1·5621	1·5562	1·5496
m-2-Xylidine	0·97763	—	37·91	—	1·58662	1·57434	1·56369	1·55855	1·55273
m-4-Xylidine *	0·97185	—	36·49	—	1·5856	1·5725	1·5622	1·5570	1·5512
m-5-Xylidine	0·97038	—	36·38	—	1·58470	1·57150	1·56153	1·55635	1·55047
Dimethyl-*m*-2-xylidine	0·91507	0·8493	29·74	24·06	1·53552	1·52640	1·51762	1·51365	1·50920
Dimethyl-*m*-4-xylidine	0·91269	0·8474	30·88	24·15	1·54032	1·53070	1·52230	1·51808	1·51325
Dimethyl-*m*-5-xylidine	0·92751	0·8651	35·17	26·73	1·57272	1·55659	1·54772	1·54236	1·53631

* Buehler, Wood, Hull, and Erwin (*J. Amer. Chem. Soc.*, 1932, **54**, 2398) give d^{25° 0·9723, γ^{25° 36·75.

TABLE II.

Substance.	$[P]^{25^\circ}$.	$[P]^{100^\circ}$.	$[R_L]_{4358}$.	$[R_L]_{4861}$.	$[R_L]_{5461}$.	$[R_L]_{D}$.	$[R_L]_{6563}$.	M.S.V.
Benzene	—	—	27·14	26·64	26·36	26·17	25·97	—
Dimethylaniline	—	—	42·88	41·93	41·21	40·85	40·45	—
m-Xylene	—	—	37·19	36·62	36·17	35·93	35·67	—
m-2-Xylidine	307·1	—	41·57	40·86	40·24	39·94	39·59	—
				(40·90)[1]		(40·01)[1]	(39·66)[1]	
m-4-Xylidine	306[2]	—	41·76	40·99	40·39	40·08	39·74	—
						(40·04)[3]	(39·68)[3]	
m-5-Xylidine	306·2	—	41·77	41·00	40·41	40·10	39·75	—
Dimethyl-*m*-2-xylidine	380·2	388·4	50·73	50·01	49·31	48·99	48·64	164·0
				(49·96)[1]		(49·01)[1]	(48·65)[1]	
Dimethyl-*m*-4-xylidine	384·8	389·8	51·32	50·56	49·90	49·55	49·17	164·2
				(50·49)[1]		(49·48)[1]	(49·13)[1]	
Dimethyl-*m*-5-xylidine	391·2	391·3	52·91	51·68	51·01	50·58	50·11	161·8

[1] Ley and Pfeiffer (*loc. cit.*). [2] Buehler, Wood, Hull, and Erwin (*loc. cit.*) give 307·2. [3] Brühl (*Z. physikal. Chem.*, 1895, **16**, 218).

dimethylation the position is reversed, *N*-dimethyl-*m*-2- having a lower density and lower refractive indexes than *N*-dimethyl-*m*-4-xylidine. The present density measurements agree with this conclusion in regard to *m*-2- and *m*-4-xylidine but not in regard to their dimethyl compounds. If we consider the difference of density between the xylidine and its *N*-dimethyl derivative we have the series *m*-5 < *m*-4 < *m*-2, *i.e.*, dimethylation of the vicinal xylidine results in the greatest lowering of density. The change in b. p. on dimethylation shows a similar regularity; whereas dimethylation *raises* the b. p. of aniline and of *m*-5-xylidine by 9° and 6°, respectively, it *lowers* the b. p. of *m*-4- and of *m*-2-xylidine by 9° and 22°, respectively. Such behaviour seems general: whenever a methyl group occupies a position ortho to the amino-group, dimethylation of the amine results in a lowering of b. p., whereas if the ortho-positions are unsubstituted a rise of b. p. results: *o*-toluidine (— 13°), *m*-toluidine (+ 8°), *p*-toluidine (+ 11°), *p*-xylidine (— 10°), *o*-xylidine (— 22°), mesidine (— 14°).

For each wave-length for which measurements have been made, the refractive indexes of the *m*-xylidines show only differences in the third decimal figure between the isomers, but they increase in the order *m*-5 < *m*-4 < *m*-2. On dimethylation the differences become greater (now affecting the second decimal figure); the order is reversed and becomes *m*-5 > *m*-4 > *m*-2. The molecular refractivities of *m*-5- and *m*-4-xylidines are indistinguishable; the value for *m*-2-xylidine is a little lower. The values for the dimethylxylidines are best discussed by reference to Table III, from which it is evident that the molecular refractivity of dimethyl-*m*-5-xylidine is normal as compared with dimethylaniline and dimethyl-*m*- and -*p*-toluidines, that whenever methyl or chlorine is substituted ortho to the dimethylamino-group it results in a reduction of approximately 1 c.c. in molecular refractivity, and that when both ortho-positions are occupied by methyl groups the molecular refractivity is lowered by about 1·6 c.c.

TABLE III.

	$[R_L]_D$.	Δ.		$[R_L]_D$.	Δ.
Dimethylaniline	40·85	14·68	Dimethyl-*p*-toluidine[1]	45·68	14·62
Benzene	26·17		Toluene[2]	31·06	
Dimethyl-*m*-5-xylidine	50·58	14·65	Dimethyl-*m*-toluidine[1]	45·68	14·62
m-Xylene	35·93		Toluene[2]	31·06	
Dimethyl-*m*-4-xylidine	49·55	13·62	Dimethyl-*o*-toluidine[1]	44·62	13·56
m-Xylene	35·93		Toluene[2]	31·06	
Dimethyl-*m*-2-xylidine	48·99	13·06	Dimethyl-*o*-chloroaniline[1]	44·95	13·57
m-Xylene	35·93		Chlorobenzene[2]	31·38	

[1] Ley and Pfeiffer (*loc. cit.*). [2] Landolt–Börnstein, "Tabellen."

By calculation from Brühl's values of atomic refractivities the introduction of a dimethylamino-group into a hydrocarbon should result in a change of molecular refractivity in the aromatic series of 14·62 c.c., in the aliphatic series of 13·25 c.c.; from Eisenlohr's figures the value in the aliphatic series should be 12·78 c.c. The atomic refractivity of nitrogen in dimethyl-*m*-2-xylidine must therefore approach very closely the value for nitrogen in a tertiary aliphatic amine. Hampson's dipole-moment measurements (J., 1939, 981) have indicated the almost complete suppression of the resonance of the dimethylamino-group by the vicinal methyl groups in dimethylmesidine and nitrodimethylaminodurene; the value 54·2 c.c. given by him for the molecular refractivity (λ 5461) of dimethylmesidine is in complete agreement with the results now recorded, for the difference between that value and the value of 41·06 c.c. for mesitylene (Part I) is 13·14 c.c., as compared with 14·85 c.c. for the difference between the molecular refractivities (λ 5461) of dimethylaniline and benzene and 13·14 c.c. for the difference between dimethyl-*m*-2-xylidine and *m*-xylene for the same wave-length. It is noteworthy that exaltation of molecular refractivity appears to be shown by *p*- (Marsden and Sutton, J., 1936, 599) and by *o*-nitrodimethylaniline (Ley and Pfeiffer, *loc. cit.*) : it is well known that in *p*-nitrodimethylaniline, *p*-nitroaniline, and *o*-nitroaniline reinforcement of resonance effects leads to increased dipole moments.

There is an increase in molecular solution volume on passing from *N*-dimethyl-*m*-5- to *N*-dimethyl-*m*-4-xylidine, but the value for the latter is indistinguishable from that for *N*-dimethyl-*m*-2-xylidine. The values of molecular solution volume are practically identical with the values of *M*/*d* for the pure liquids at the same temperature.

The parachors of the three *m*-xylidines are practically identical (306—307) but considerably lower than the sum of the atomic parachors (314·6); this low value is confirmed by Buehler, Wood, Hull, and Erwin (*loc. cit.*), who found the parachor of *m*-4-xylidine to be 307·2. For the *N*-dimethyl-*m*-xylidines the sum of the atomic parachors is 392·7 : *N*-dimethyl-*m*-5-xylidine (391·2) is practically normal, but the parachors of the three isomers decrease in the order *m*-5 > *m*-4 > *m*-2 (a sequence confirmed by measurements at 100°), thus reversing the sequence found in the dichloronitrobenzenes (cf. Part I). This contrasting behaviour raises the question of the physical conception of the parachor. Interpretation of it as a molecular volume has been adversely criticised by Ferguson (*Nature*, 1930, **125**, 597) and by Reilly and Rae (" Physico-chemical Methods," 3rd edn., 1940, vol. 1, p. 110), the latter contending that it cannot have the dimensions of volume since it is calculated by multiplying *M*/*d* (which has the dimensions of volume) by the fourth root of the surface tension (which is not dimensionless) measured at the same temperature as *d*. Now the molecular refractivity has undoubtedly the dimensions of volume : it is again *M*/*d* multiplied by a factor [in this case $(n^2 - 1)/(n^2 + 2)$], and the molecular solution volume when measured in benzene solution approximates closely to the value of *M*/*d* for the pure liquid at the same temperature; since the data for the dichloronitrobenzenes (cf. Part I) and the data now presented show that in a series of position isomers, although the molecular solution volume may increase, the molecular refractivity can decrease, there seems to be no reason why in such homologous series variations in the parachor should of necessity have always the same sign as variations in either of these other properties.

EXPERIMENTAL.

Refractive indexes were measured on a Hilger–Pulfrich refractometer, and surface tensions at 25° by Sugden's differential bubble-pressure method and at 100° by Ferguson's method (cf. Part I). In calculating the parachors the density of the saturated vapour has been neglected.

Materials.—*m*-Xylene, dimethylaniline, *m*-4- and *m*-2-xylidine were obtained by repeated fractionation of products supplied as these specific compounds by B.D.H. The b. p.'s of the fractions used were : *m*-xylene 139°, dimethylaniline 192·5°, *m*-4-xylidine 213·5—214°, *m*-2-xylidine 216·5—217°. The molecular refractivities are in good agreement with those recorded in the literature. *m*-5-Xylidine was prepared from *m*-4-xylidine by Haller and Adams's method (*J. Amer. Chem. Soc.*, 1920, **42**, 1840) and purified by crystallisation of the acetyl derivative. The fraction used boiled at 223°/774 mm.

The dimethylxylidines were prepared by methylation with methyl sulphate. Use of acetic anhydride to remove unchanged or monomethylated amine was unsatisfactory (since the *N*-acetomethyl-*m*-2- and -*m*-4-xylidides have b. p.'s very close to those of the *N*-dimethylxylidines), and in the methylation of *m*-2-xylidine it was replaced by *p*-toluenesulphonyl chloride. The *N*-dimethyl-*m*-2-xylidine had b. p. 194·5—195°/760 mm. (Found : C, 80·3; H, 9·9. Calc. for $C_{10}H_{15}N$: C, 80·5; H, 10·1%). For methylation of *m*-4- and *m*-5-xylidines the method of Evans and Williams (J., 1939, 1199) was adopted. *N*-Dimethyl-*m*-4-xylidine had b. p. 204·5—205°/747 mm. (Found : C, 80·3; H, 9·9%). *N*-Dimethyl-*m*-5-xylidine had b. p. 228·5—229°/772 mm. (Found : C, 80·8; H, 10·1%); picrate, m. p. 192° (Found : C, 50·9; H, 4·5. Calc. for $C_{16}H_{18}O_7N_4$: C, 50·8; H, 4·8%).

Reference has been made to the surprising similarity in b. p. of *N*-dimethyl- and *N*-acetylmethyl-xylidines. *N*-Acetomethyl-*m*-4-xylidide (Found : C, 74·5; H, 8·9. Calc. for $C_{11}H_{15}ON$: C, 74·6; H, 8·5%) boils at 205—205·5°/747 mm., only 0·5° higher than *N*-dimethyl-*m*-4-xylidine. The refractive indexes are also practically identical, but the densities differ considerably. Physical constants measured are as follows :

	$d_{4^\circ}^{14\cdot3^\circ}$.	$d_{4^\circ}^{20\cdot6^\circ}$.	$d_{4^\circ}^{21\cdot1^\circ}$.	$d_{4^\circ}^{25^\circ}$.	$n_{5461}^{25^\circ}$.	$n_{5893}^{25^\circ}$.	$n_{6563}^{25^\circ}$.
N-Dimethyl-*m*-4-xylidine	0·92124	0·91621	—	0·91269	1·52230	1·51809	1·51325
N-Acetomethyl-*m*-4-xylidide	0·92672	—	0·92023	0·91696	1·52239	1·51817	1·51334

Molecular solution volumes in benzene solution.

	f_2.	$d_{4^\circ}^{25^\circ}$.	M.S.V.	f_2.	$d_{4^\circ}^{25^\circ}$.	M.S.V.
(Benzene)	—	0·87342	—	—	—	—
N-Dimethyl-*m*-5-xylidine	0·082768	0·88013	161·8	0·097186	0·88114	161·8
N-Dimethyl-*m*-4-xylidine	0·08647	0·87838	164·3	0·13041	0·88077	164·2
N-Dimethyl-*m*-2-xylidine	0·087024	0·87863	164·1	0·13002	0·88107	163·9

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