

368. *Physical Properties and Chemical Constitution. Part XXII.* *Some Primary, Secondary, and Tertiary Amines.*

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New determinations have been made of the refractivities at 20° and the parachors of a series of primary aliphatic amines, secondary aliphatic and aromatic amines, and tertiary aliphatic and aromatic amines. By combining the new data with the constants for the alkyl groups (Part XI, this vol., p. 611) and for phenyl (Part XV, this vol., p. 654), the following new constants have been evaluated :

	P.	R _C .	R _D .	R _F .	R _{G'} .	Mn _D ^{20°} .
NH ₂ (primary aliphatic amine).....	44.0	4.414	4.438	4.507	4.570	22.64
NH (secondary aliphatic amine) ...	28.4	3.572	3.610	3.667	3.732	23.34
NH (secondary aromatic amine) ...	27.1	4.548	4.678	5.000	5.273	29.52
N (tertiary aliphatic amine).....	7.2	2.698	2.744	2.820	2.914	24.37
N (tertiary aromatic amine).....	?	4.085	4.243	4.675	5.155	30.23

The corresponding values for N in primary and secondary amines, deduced by subtracting the constants for H in CH₂ (Part IX, *J.*, 1946, 133), are :

	P.	R _C .	R _D .	R _F .	R _{G'} .	Mn _D ^{20°}
N (primary aliphatic amine).....	12.6	2.356	2.376	2.414	2.482	27.80
N (secondary aliphatic amine)	12.7	2.546	2.582	2.624	2.692	25.90
N (secondary aromatic amine)	11.4	3.522	3.550	3.957	4.223	32.08

THE different contributions of nitrogen to the molecular refractivity according to the state of combination have long been recognised. For instance, Brühl (for review, see Eisenlohr, " Spektrochemie organischer Verbindungen : Molekularrefraktion und -dispersion ", Ferdinand Enke, 1912, pp. 55, 62) has computed values for nitrogen in primary, secondary, and tertiary aliphatic and aromatic amines as well as in many other states of combination. Eisenlohr (in Landolt-Börnstein, " Tabellen ", 1923, II, 985) gives the following constants for nitrogen :

	R _C .	R _D .	R _F .	R _{G'} .
N (in primary amines)	2.309	2.322	2.368	2.397
N (in secondary amines)	2.478	2.502	2.561	2.605
N (in tertiary amines)	2.808	2.840	2.940	3.000
N (in tertiary imides)	3.740	3.776	3.877	3.962
N (in cyanides)	3.102	3.118	3.155	3.173

In the original table of atomic and structural parachors, Sugden (*J.*, 1924, 125, 1180) gave " N = (12.5) " and stated (*loc. cit.*, p. 1179) : " Certain figures which are deduced from one or two compounds only, or which are based on somewhat doubtful data, are enclosed in brackets and can only be regarded as provisional values ". The data from which this value was deduced are not stated, but this " provisional value " was widely employed in various tables in that paper.

Presumably the figure 12·5 was subsequently adopted but no additional evidence seems to have been published (see, e.g., Sugden, Reed, and Wilkins, *J.*, 1925, 127, 1526; Henley and Sugden, *J.*, 1929, 1060; Sugden, "The Parachor and Valency", 1930, p. 38).

New determinations of the refractivities at 20° and the parachors of a series of primary alkylamines have now been made, and the NH₂ contributions computed by subtraction of the constants for alkyl groups (Part XI, *loc. cit.*). Only one polymethylene diamine (ethylenediamine) has so far been investigated : this, coupled with the constants for CH₂ (Part IX, *J.*, 1946, 133), provides an independent determination of the NH₂ constants. All the results are collected in Table I, and the mean values have been deduced from all the alkylamines except sec.-butylamine.

TABLE I.
Values for NH₂ from primary amines.

Amine.	P.	R _O .	R _D .	R _F .	R _G ·	Mn _D ^{20*} .
NH ₂ Pr ⁿ	44·1	4·46	4·48	4·56	4·61	22·81
NH ₂ Bu ⁿ	43·3	4·35	4·37	4·44	4·49	22·65
NH ₂ Bu ^t	42·8	4·34	4·36	4·42	4·56	22·64
NH ₂ Bu ^s *.....	46·9	4·66	4·68	4·75	4·81	21·69
NH ₂ Am ⁿ	44·5	4·44	4·47	4·53	4·58	22·56
NH ₂ Am ^t	44·4	4·41	4·44	4·52	4·56	22·54
NH ₂ C ₆ H ₁₃ ⁿ	44·4	4·41	4·43	4·51	4·56	22·39
NH ₂ C ₇ H ₁₅ ⁿ	—	4·39	4·41	4·47	4·53	22·38
NH ₂ C ₈ H ₁₇ ⁿ	—	4·47	4·49	4·57	4·64	22·28
NH ₂ C ₃ H ₅	43·2	4·43	4·46	4·52	4·58	23·51
NH ₂ CH ₂ ·CH ₂ ·NH ₂	45·5	4·44	4·47	4·53	4·59	22·68
Mean NH ₂ (excluding *)	44·0	4·414	4·438	4·507	4·570	22·64
C ₆ H ₅ ·NH ₂	41·8	5·13	5·20	5·40	—	25·63
C ₆ H ₆ ·CH ₂ ·NH ₂	45·1	4·26	4·26	4·32	4·34	21·05
C ₆ H ₁₁ ·NH ₂	47·1	4·63	4·68	4·75	4·80	21·70

The figures deduced from aniline and benzylamine are given at the end of the table for purposes of comparison : the constants for phenyl were those from Part XV (this vol., p. 654) and for benzyl from C₆H₅·CH₂Cl — Cl (XIV, 281). The constants from cyclohexylamine, C₆H₁₁·NH₂, deduced with the aid of the data for dicyclohexyl (XIX, 445), are not regarded as very trustworthy in view of the difficulties attending the manipulation of this strongly fuming compound.

The constants for the secondary amine group, >NH, have been deduced by two independent methods : (1) From dialkylamines and alkyl groups in aliphatic hydrocarbons : under this heading must be included dicyclohexylamine, *i.e.*, C₆H₁₁·NH·C₆H₁₁ — C₆H₁₁·C₆H₁₁ (XIX, 445). (2) From ethyl N-alkylcarbamates and esters, *e.g.*, CH₃·NH·CO₂C₂H₅ — CH₃·CO₂C₂H₅ (XIII, 189). It will be noted that the constants for CH₂ are not involved. The results are summarised in Table II ; in the calculation of the mean values, the figures for secondary aliphatic amines containing secondary alkyl groups have been omitted. The values for NH computed from secondary aromatic amines C₆H₅·NHALkyl — C₆H₅·Alkyl (Part X, this vol., p. 607) are given in Table III ; the parachor contribution agrees within about 1 unit, but the refractivities are uniformly higher. The measurements of n_G for secondary aromatic amines with a Pulfrich refractometer are difficult because of the faintness of the line and in consequence the values for R_G for these compounds are somewhat less trustworthy.

TABLE II.
Values for NH from secondary aliphatic amines.

	P.	R _O .	R _D .	R _F .	R _G ·	Mn _D ^{20*} .
NHET ₂	29·5	3·66	3·70	3·77	3·86	23·96
NHPr ₂ ⁿ	28·0	3·57	3·62	3·66	3·72	23·68
NHPr ₂ ^t	29·0	3·67	3·69	3·75	5·84	24·00
NHBu ₂ ⁿ	28·2	3·61	3·65	3·70	3·78	23·61
NHBu ₂ ^t	28·1	3·57	3·59	3·66	3·72	23·03
NHBu ₂ ^s *.....	31·7	3·73	3·74	3·81	3·88	21·92
NHAM ₂ ⁿ	28·7	3·46	3·49	3·55	3·61	23·57
NHAM ₂ ^t	28·4	3·58	3·63	3·69	3·74	23·30
C ₆ H ₁₁ ·NH·C ₆ H ₁₁	30·4	3·66	3·69	3·76	3·81	23·11
CH ₃ ·NH·CO ₂ C ₂ H ₅	27·6	3·44	3·49	3·55	3·60	25·44 *
CH ₃ ·CH ₂ ·NH·CO ₂ C ₂ H ₅	27·0	3·60	3·63	3·69	3·75	25·19 *
Mean NH (excluding *).....	28·4	3·572	3·610	3·667	3·732	23·34

TABLE III.

Values for NH from secondary aromatic amines.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G'.</i>	<i>Mn_D^{20°}</i> .
NHMePh	27.9	4.46	4.57	4.90	5.19	30.43
NHEtPh	27.2	4.56	4.70	5.02	5.24	29.50
NHPr ⁿ Ph	26.2	4.57	4.72	5.03	5.32	29.22
NHBu ⁿ Ph	27.0	4.60	4.72	5.05	5.34	28.91
Mean NH.....	27.1	4.548	4.678	5.000	5.273	29.52

New determinations have also been made of the refractivities at 20° and the parachors of a number of tertiary amines. The data for trialkylamines have been employed in the evaluation in the usual manner of the contributions of the N atom. The results are presented in Table IV :

TABLE IV.

Values for N from tertiary aliphatic amines.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}</i> .
NET ₃	10.6	2.84	2.89	2.99	3.10	28.61
NPr ₃ ⁿ	6.7	2.75	2.78	2.87	2.98	25.29
NBu ₃ ⁿ	6.0	2.70	2.74	2.82	2.90	25.57
NAm ₃ ⁿ	6.4	2.52	2.57	2.61	2.70	25.36
NAm ₃ ⁱ	6.4	2.68	2.74	2.81	2.89	25.02
Mean N	7.2	2.698	2.744	2.820	2.914	24.37
C ₆ H ₅ ·CH ₂ ·NET ₂	7.0	2.65	2.68	2.76	2.86	22.59

the values deduced from benzyl diethylamine are also included (the constants for the benzyl group were computed from C₆H₅·CH₂Cl — Cl) and are in moderate agreement with the mean constants. For tertiary aromatic amines, NPhAlk₂, the constants for N have been computed by subtracting {Ph (Part XV, *loc. cit.*) + 2Alkyl (Part XI, *loc. cit.*)}. All the results are collected in Table V. It will be noted that the parachor for N appears to decrease as the molecular weight of the alkyl group increases; it is hoped to confirm the surface-tension results by the method of maximum bubble pressure in order to rule out the possibility that the decreasing parachor values are due to slight departures from zero contact angles.

TABLE V.

Values for N from tertiary aromatic amines.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G'.</i>	<i>Mn_D^{20°}</i> .
NMe ₂ Ph	11.5	3.99	4.15	4.50	4.95	29.48
NET ₂ Ph	7.9	4.08	4.24	4.68	5.20	30.61
NPr ₂ Ph	3.8	4.12	4.27	4.73	5.22	30.49
NBu ₂ Ph	2.3	4.15	4.31	4.79	5.25	30.32
Mean N	?	4.085	4.243	4.675	5.155	30.23

The results deduced from ethyl nitrilotri-carboxylate, N(CO₂Et)₃, are of interest. If the CO₂Et constants are calculated from ethyl oxalate (XIII, 236), the following values for N are obtained : *P* 13.2; *R_C* 2.41; *R_D* 2.44; *R_F* 2.48; *R_{G'}* 2.51; *Mn_D^{20°}* 24.12. The use of the mean constants for COO (esters), deduced in Part XIII (this vol., p. 624), leads to abnormal results.

It is instructive to calculate the constants for N by subtracting the values for H in CH₂ (Part IX, J., 1946, 133) from the mean values for NH₂ and NH. The results are given below.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}</i> .
N (in primary aliphatic amines) ...	12.6	2.362	2.382	2.421	2.490	27.76
N (in secondary aliphatic amines) ...	12.7	2.546	2.582	2.624	2.692	25.90
N (in secondary aromatic amines) ...	11.4	3.522	3.550	3.957	4.233	32.08
N (in cyanides)	15.4	0.900	0.891	0.851	0.822	23.31

The following conclusions may be drawn from these figures : (1) The parachor for N is approximately the same in primary and in secondary amines but differs from that in tertiary amines (compare Sugden who gives, and uses, one value for N in all nitrogen compounds). (2) The refractivities for N differ according to the state of combination * and at least five values for N in amines (primary aliphatic; secondary aliphatic; secondary aromatic; tertiary aliphatic; and tertiary aromatic) are necessary. This view would agree with that originally expressed by

* A sufficient number of primary aromatic amines has not yet been investigated by the author to decide whether N in these differs from that in primary aliphatic amines.

Bruhl but differs from that of Eisenlohr; the refractivities deduced by Eisenlohr (compare *Z. physikal. Chem.*, 1912, **79**, 129; Landolt-Bornstein, "Tabellen", 1923, II, 985) for N in primary, secondary, and tertiary amines, which are widely quoted (see, e.g., Ostwald-Luther, "Hilfsbuch zur Ausführung physiko-chemischer Messungen", Akad. Verlag, 5th Edition, 1931, p. 910; Fajans, in Weissberger, "Physical Methods of Organic Chemistry", Interscience, 1945, I, 673), are consequently meaningless and definitely misleading. The constants for N in cyanides have been computed from CN — (C + \equiv , terminal) (Part XVII, this vol., p. 674).

The question of the refraction of the various electron groups involving nitrogen will form the subject of a future communication (compare Smyth, "Dielectric Constant and Molecular Structure", Chemical Catalog Co., 1931, p. 152; Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 397).

EXPERIMENTAL.

Primary aliphatic amines. 25—50 G. samples of the pure commercial products were dried over potassium hydroxide pellets and fractionated, with adequate precautions against the entrance of moisture, in an all-glass apparatus, and three middle fractions were collected for the physical measurements. The purified specimens were kept in Pyrex test-tubes, closed with corks covered with tin or platinum foil, and used immediately after distillation. Precautions were taken as far as possible to prevent the entrance of moisture during the measurements. The b. p.s are given under the physical measurements below. The sources of the various amines were as follows:—*n*-propyl, allyl, *n*-butyl, *isobutyl*, *sec.-butyl*, *n*-amyl, and *isoamyl*, from Eastman Kodak; *n*-hexyl, *n*-heptyl, and *n*-octyl from Sharples; *cyclohexyl* from Light; ethylenediamine from Eastman Kodak.

Aniline. A.R. Aniline (Hopkin and Williams) was dried with potassium hydroxide pellets and distilled from an all-glass apparatus; b. p. 184.5°/750 mm.

Benzylamine. A pure B.D.H. sample was dried over potassium hydroxide pellets and twice distilled from an all-glass apparatus; b. p. 185°/767 mm.

Secondary aliphatic amines. The pure commercial products were purified and manipulated as detailed for primary aliphatic amines. Diethylamine and di-*n*-butylamine were presented by Sharples; di-*n*-propyl-, di*isopropyl*-, di*isobutyl*-, di-*sec.-butyl*-, di-*n*-amyl-, and di*isoamyl*-amine were purchased from Eastman Kodak.

Dicyclohexylamine. The commercial product (Light) was distilled, and the fraction, b. p. 251.5°/760 mm., collected; this had a very pale green colour, which was removed upon distillation under reduced pressure; b. p. 113.5°/9 mm.

N-Nitrosomethylaniline. This was prepared from B.D.H. pure monomethylaniline according to *Org. Synth.*, 1933, **13**, 82, except that a 1-l. beaker replaced the 3-l. flask, the extraction with benzene was omitted, and the compound was dried with anhydrous calcium sulphate; the yield was not appreciably affected. The *N*-nitrosomethylaniline had b. p. 120°/13 mm. The b. p. of 135—137°/13 mm. recorded in *Organic Syntheses* would appear to be in error.

N-Nitrosoethylaniline. This was prepared similarly to the methyl compound from B.D.H. pure monoethylaniline; b. p. 131°/20 mm.

Monomethylaniline. 78 G. of pure *N*-nitrosomethylaniline were reduced with 150 g. of tin and 300 ml. of concentrated hydrochloric acid, affording 46 g. of pure, colourless monomethylaniline, b. p. 193°/738 mm.

Monoethylaniline. 75 G. of pure *N*-nitrosoethylaniline were similarly reduced and yielded 43 g. of pure, almost colourless monoethylaniline, b. p. 202.5°/750 mm.

Mono-n-propylaniline. 230 G. of A.R. aniline were heated with 123 g. of *n*-propyl bromide for 8 hours and the excess of aniline was removed by precipitation with 50% zinc chloride solution (Hickinbottom, J., 1930, 993). The secondary amine was isolated by several extractions with light petroleum (b. p. 60—80°), the solvent removed, and the product fractionated. The crude amine (85 g.) distilled at 218—222°. Redistillation from a little zinc dust gave pure *n*-propylaniline, b. p. 219°/758 mm., d_4^{20} 0.9460, n_D^{20} 1.54375. For the physical measurements, the compound was distilled under reduced pressure; b. p. 96°/9 mm.

Mono-n-butylaniline. A commercially pure sample, kindly presented by Sharples Chemicals Inc. was fractionated from a little zinc dust, and the fraction, b. p. 237—238°/760 mm., collected. Redistillation gave a colourless product, b. p. 105°/3 mm.

Ethyl N-methylcarbamate. This was prepared from 33% aqueous methylamine solution, ethyl chloroformate, and sodium hydroxide solution, but the product was distilled under normal pressure and not under reduced pressure (cf. *Org. Synth.*, 1932, **12**, 38). The ester distilled as a colourless liquid, b. p. 169.5°/769 mm., and there was no sign of decomposition.

Ethyl N-ethylcarbamate. This compound was prepared from 110 ml. of ether, 90 g. of 33% aqueous ethylamine solution, 72.5 g. of ethyl chloroformate, and 26.5 g. of A.R. sodium hydroxide dissolved in 40 ml. of water (see *Org. Synth.*, 1932, **12**, 38). The yield of pure, colourless ester, b. p. 175°/748 mm., was 64 g.

Tertiary aliphatic amines. The pure commercial products (triethylamine, tri-*n*-butylamine, and benzyltriethylamine from Sharples; tri-*n*-propylamine, tri-*n*-amylamine, and tri*isoamyl*amine from Eastman Kodak) were shaken mechanically with about half the volume of A.R. potassium hydroxide pellets, filtered, and distilled from sodium in a flask with a fractionating side arm, due precautions being taken to prevent access of moisture. The b. p.s are given under the physical properties.

Ethyl nitrilotricarboxylate. This was prepared from urethane, dry ether, sodium, and ethyl chloroformate (*Org. Synth.*, 1944, **24**, 60) and was twice distilled under reduced pressure; b. p. 143°/10 mm.

Dimethylaniline. A mixture of 50 g. of A.R. dimethylaniline and 25 g. of redistilled acetic anhydride was refluxed for 3 hours and then distilled until about 10 ml. remained; the residue contained any acetyl derivatives which might have been present (compare Brand and Franz, *J. pr. Chem.*, 1927, **115**,

540. Ethyl nitrilotricarboxylate. B. p. 143°/10 mm.; M 233.22; n_C 1.42665, n_D 1.42897, n_F 1.43456, n_G 1.43877; R_G 52.53, R_D 52.88, R_F 53.38, R_G 53.82; $Mn_D^{20^\circ}$ 333.51. Densities determined: $d_4^{20^\circ}$ 1.1392, $d_4^{40.0^\circ}$ 1.1198, $d_4^{60.9^\circ}$ 1.0994, $d_4^{86.1^\circ}$ 1.0749. Apparatus E.

<i>t.</i>	<i>H.</i>	d_4° .	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4° .	γ .	<i>P.</i>
18.9°	13.11	1.1403	34.82	496.8	60.2°	11.84	1.1101	30.35	497.3
20.5	13.03	1.1387	34.81	497.5	86.8	11.15	1.0742	27.89	498.9
40.2	12.52	1.1196	32.65	497.9	Mean 497.7				

541. Dimethylaniline. B. p. 194°/760 mm.; M 121.18; n_C 1.55110, n_D 1.55776, n_F 1.57051, n_G 1.59132 (line very faint); R_G 40.40, R_D 40.81, R_F 41.84, R_G 42.80; $Mn_D^{20^\circ}$ 188.77. Densities determined: $d_4^{20^\circ}$ 0.9571, $d_4^{62.0^\circ}$ 0.9255, $d_4^{86.2^\circ}$ 0.9055, $d_4^{119.7^\circ}$ 0.8783. Apparatus B.

19.5°	16.11	0.9575	36.17	310.4	86.8°	13.65	0.9050	28.97	310.6
66.3	14.39	0.9222	31.12	310.4	121.7	12.37	0.8768	25.43	310.4
Mean 310.5									

542. Diethylaniline. B. p. 214.5°/748 mm. and 86.5°/6 mm.; M 149.23; n_C 1.53578, n_D 1.54178, n_F 1.55773, n_G 1.57227 (line faint); R_G 49.74, R_D 50.20, R_F 51.42, R_G 52.52; $Mn_D^{20^\circ}$ 230.08. Densities determined: $d_4^{20^\circ}$ 0.9353, $d_4^{40.8^\circ}$ 0.9195, $d_4^{61.3^\circ}$ 0.9042, $d_4^{85.6^\circ}$ 0.8851. Apparatus C.

19.9°	15.55	0.9354	34.53	386.7	60.7°	14.10	0.9047	30.28	386.9
40.9	14.81	0.9194	32.33	387.0	86.8	13.13	0.8837	27.55	386.9
Mean 386.9									

543. Di-n-propylaniline. B. p. 242°/758 mm. and 95°/4 mm.; M 177.28; n_C 1.52333, n_D 1.52873, n_F 1.54292, n_G 1.55539 (line very faint); R_G 59.05, R_D 59.56, R_F 60.89, R_G 62.05; $Mn_D^{20^\circ}$ 271.01. Densities determined: $d_4^{20^\circ}$ 0.9176, $d_4^{41.2^\circ}$ 0.9021, $d_4^{61.1^\circ}$ 0.8879, $d_4^{85.8^\circ}$ 0.8695. Apparatus C.

22.0°	15.08	0.9160	32.79	463.1	60.4°	13.67	0.8884	28.83	462.4
24.3	14.95	0.9145	32.46	462.7	87.5	12.84	0.8683	26.47	463.1
42.4	14.39	0.9012	30.79	463.4	Mean 463.0				

544. Di-n-butylaniline. B. p. 269—270°/760 mm.; M 205.33; n_C 1.51444, n_D 1.51929, n_F 1.53246, n_G 1.54349 (line very faint); R_G 68.29, R_D 68.84, R_F 70.30, R_G 71.51; $Mn_D^{20^\circ}$ 311.96. Densities determined: $d_4^{20^\circ}$ 0.9058, $d_4^{41.3^\circ}$ 0.8905, $d_4^{61.0^\circ}$ 0.8763, $d_4^{85.4^\circ}$ 0.8581. Apparatus C.

15.1°	15.22	0.9083	32.82	541.1	61.6°	13.61	0.8759	28.30	540.7
40.7	14.35	0.8901	30.32	541.3	87.8	12.80	0.8567	26.03	541.4
Mean 541.1									