387. *The Preparation and Physical Properties of the Pure Lutidines.*

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The preparation and purification of 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-lutidine are described. The purities of the samples have been established by melting-point measurements. Properties which have been measured or computed are: freezing points and cryscopic constants, vapour pressure-temperature relationships, boiling points, latent heats of vaporization, densities, coefficients of expansion, refractive indices, and infrared absorption spectra.

MEASUREMENTS of certain physicochemical properties of pure 2 : 6-lutidine were recorded earlier.[1] We now give results for the less accessible 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dimethylpyridines. These all occur in shale-oil or coal-tar, although only the 2 : 4- and 2 : 5-lutidines are sufficiently plentiful in a commercial tar-base lutidine fraction for this to be a convenient source for their extraction on the kilogram scale.[2] The extraction of 2 : 3-lutidine is tedious and this base is perhaps more readily secured by synthesis. For the remaining 3 : 4- and 3 : 5-lutidine, there are no feasible alternatives to synthesis as a method for their preparation in quantity.

Batches of 2 : 4- and 2 : 5-lutidine were therefore prepared from a commercial " lutidine fraction, b. p. 155—161°," the first through its hydrochloride, the second through the phenol complex.[3] Some 2 : 3-lutidine was secured as a by-product of these operations through the urea complex [4] but more was synthesised by Wibaut and Kooyman's method.[5] 3 : 4-Lutidine was also synthesised by their route. The starting material for both syntheses was ethyl acetoacetate and by various improvements in the successive stages it was possible to work on a much greater scale and to increase the overall yields.

In the course of our work a commercial specimen of 3 : 5-lutidine became available. It contained non-basic and aldehydic contaminants and was probably the result of a thermal treatment of propionaldehyde–ammonia. Pure 3 : 5-lutidine obtained from it was supplemented with synthetic material made from diethyl acetonedicarboxylate by a five-stage process.[6]

An essential step in the purification of all five bases was the removal of non-basic impurities. The standard of purity required, *ca.* 99·9 moles %, was reached by fractional

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[1] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.
[2] Coulson, Hales, Holt, and Ditcham, *J. Appl. Chem.*, 1952, **2**, 71.
[3] Coulson, B.P. 715,680/1954.
[4] Milner and Y.T.D., B.P. 584,148/1947.
[5] Wibaut and Kooyman, *Rec. Trav. chim.*, 1944, **63**, 231.
[6] Coulson and Ditcham, *J.*, 1957, 356.

distillation, fractional freezing, and treatment with calcium hydride to remove traces of water, followed by distillation *in vacuo*.

The physicochemical properties which have been measured on samples of these highly purified bases or computed from measurements, are given in the Tables, and provide a basis for the characterization of pure or mixed specimens and for setting up analytical and separation techniques. Although we have compared our results with published data no useful purpose would be served by presenting a detailed collation. Many previous measurements are of lower precision, and all were made on materials of which the purity was quantitatively unknown. In general the most reliable previous values are due to Eguchi.[7]

Certain physicochemical measurements on specimens of some of these bases have already been reported from this laboratory: heats of combustion and formation;[8] solubilities in water and in deuterium oxide;[9] activity coefficients;[9] ultraviolet absorption spectra and dissociation constants;[10] vapour pressures;[11] second virial coefficients;[12] and critical temperatures.[13]

EXPERIMENTAL

Preparation of Pure 2 : 5-, 2 : 4-, *and* 2 : 3-*Lutidine from Tar Base Fractions*.—2 : 5-*Lutidine*. Commercial " 2 : 4–2 : 5-lutidine " contains somewhat more than 50% of the 2 : 4-isomer along with about 30—40% of 2 : 5-lutidine and smaller proportions of 2 : 3-lutidine and 2-ethyl-6-methylpyridine. The separation of a kilogram of 2 : 5-lutidine, purity 95%, from a commercial lutidine fraction was effected through the phenol complex.[2,3] Final purification was by fractional freezing, the base being kept at such a temperature that at least 24 hr. were required after seeding before 90—95% was frozen. The liquid was poured off, the crystals were melted and the process repeated until estimation showed that the required purity had been reached. The best sample of 2 : 5-lutidine so secured (593 g.) was dried by slowly distilling off about 10% in a fore-cut and the remaining portion had a purity of 99·85 moles % after distillation *in vacuo* from calcium hydride.

2 : 4-*Lutidine*. A lutidine fraction containing a known amount of the 2 : 4-isomer was diluted with twice its volume of benzene, and dry hydrogen chloride was bubbled through the mixture until the increase of weight corresponded to the transformation of the 2 : 4-isomer content into hydrochloride. The precipitated hydrochloride was filtered off and washed with benzene. The crude hydrochloride obtained in this way from commercial " 2 : 4–2 : 5-lutidine " contained hydrochlorides of other bases which were removed by recovering the bases and repeating the precipitation process, and there was some advantage in first removing the 2 : 5-isomer as the phenol complex. When hydrochloride was precipitated from a base mixture containing more than 70% of 2 : 4-isomer it could be further purified without difficulty by crystallization from alcohol to constant m. p. 214—214·5°.

Base recovered from this hydrochloride was finally purified by fractional freezing and dried by slowly distilling off a fore-cut which contained most of the water. The best specimen (500 g.) had a purity of 99·92 moles % after being dried (CaH_2).

2 : 3-*Lutidine*. As the content of 2 : 3-lutidine in tar-base lutidine fractions may be as low as 3% it is convenient to concentrate it by fractional distillation and by separation of 2 : 4- and 2 : 5-lutidine as described. To such an enriched fraction (300 g.) were added urea (340 g.) and water (300 g.) and the mixture was heated until it formed a single liquid phase. This was cooled and the 2 : 3-lutidine–urea complex which separated was crystallised twice from about one-fourth of its weight of water. It decomposed when steam-distilled and the base was recovered from the aqueous condensate. Crude 2 : 3-lutidine (80 to 90% pure) from several

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[7] Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 227.

[8] Cox and Gundry, *J.*, 1958, 1019.

[9] Andon and Cox, *J.*, 1952, 4601; Cox, *J.*, 1952, 4606; *J.*, 1954, 3183; Andon, Cox, and Herington, *J.*, 1954, 3188; *Discuss. Faraday Soc.*, 1953, No. **15**, 168; *Trans. Faraday Soc.*, 1957, **53**, 410; Cox and Herington, *Trans. Faraday Soc.*, 1956, **52**, 926.

[10] Andon, Cox, and Herington, *Trans. Faraday Soc.*, 1954, **50**, 918.

[11] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.

[12] Andon, Cox, Herington, and Martin, *Trans. Faraday Soc.*, 1957, **53**, 1074. Cox and Andon, *Trans. Faraday Soc.*, 1958, **54**, 1622.

[13] Ambrose and Grant, *Trans. Faraday Soc.*, 1957, **53**, 771.

batches was purified by again forming and crystallizing the urea complex. When the purity had reached 95% fractional freezing was resorted to for the final purification (as with the synthetical sample, below).

Synthesis of Pure 3 : 4- *and* 2 : 3-*Lutidine.*—3 : 4-*Lutidine*. By allowing concentrated ammonia solution to react with ethyl α-methylacetoacetate, Wibaut and Kooyman [5] obtained a mixture of α-methylacetoacetamide and ethyl β-amino-α-methylcrotonate. The former, which remained in the aqueous ammonia, served for the preparation of 3 : 4-lutidine; the latter, which crystallized was filtered off and used for the preparation of 2 : 3-lutidine. It is preferable to avoid forming these two intermediates simultaneously, otherwise there is cross-contamination of products and loss and difficulty in succeeding stages of the two synthetic routes When ethyl α-methylacetoacetate reacted with a mixture of ammonia and ethyl cyanoacetate in aqueous solution the formation of the diammonium salt of 5-cyano-2 : 6-dihydroxy-3 : 4-dimethylpyridine (required for the further stages in the preparation of 3 : 4-lutidine) was quicker and more complete than when the reactions with ammonia and ethyl cyanoacetate were successive.

Ethyl α-methylacetoacetate, prepared [14] from ethyl acetoacetate (343 g.) but not distilled (and hence containing some ethyl acetoacetate), ethyl cyanoacetate (300 g.), and ammonia solution (1500 ml., s. g. 0·880) were mixed in a Winchester quart bottle which was stoppered and shaken for 4 or 5 days. The diammonium salt was filtered off and air-dried, the yield being 330 g. (58%). In all, 3·8 kg. of the salt were prepared and converted into 2·075 kg. of 2 : 6-dihydroxy-3 : 4-dimethylpyridine (77·8%) by Wibaut and Kooyman's method.[5] The conversion of the dihydroxy- into the dichloro-compound was effected in an autoclave on a scale one hundred times that of Wibaut and Kooyman, the yield from 2·075 kg. being 2·084 kg. (79%).

The reduction of 2 : 6-dichloro-3 : 4-dimethylpyridine to 3 : 4-lutidine was carried out with 110 g. batches of dichloro-compound, 8 g. of palladium chloride being added at the start and a further 5 g. when the reaction had slowed down after absorption of 2/3 of the stoicheiometric amount of hydrogen.

The crude 3 : 4-lutidine was freed from non-basic contaminants by blowing steam through a solution in 1·2 equiv. of 22·6% sulphuric acid.[1] The 3 : 4-lutidine (1·056 kg., 83·4% from the dichloro-derivative or 29·7% over the five stages from ethyl acetate) nevertheless still contained about 2% of γ-picoline (shown by the infrared spectrum) which was removed in a fore-cut boiling below 176°, with a fifty-plate column. The main bulk of base remaining was next subjected to a series of slow fractional freezings and a final distillation to reduce the water content.[1] The best material (775 g.) contained less that 0·05% by volume of water and after drying (CaH_2) was 99·88 moles % pure (by m. p. determination).

2 : 3-*Lutidine*. A better way of securing ethyl β-amino-α-methylcrotonate than that employed by Wibaut and Kooyman [5] is by heating ethyl α-methylacetoacetate on a steam-bath and passing in a stream of dry ammonia for 2 days. Water is formed and is separated from the reaction product which is then distilled. The fraction, b. p. 80—100°/2—3 mm., which crystallizes on cooling, is ethyl β-amino-α-methylcrotonate (77·3%). From 4·008 kg. there were obtained 4·459 kg. (68·2%) of the mono-sodium salt of ethyl 4 : 6-dihydroxy-2 : 3-dimethylpyridine-5-carboxylate following Wibaut and Kooyman's procedure.[5]

The hydrolysis and decarboxylation of the last-named compound were effected by boiling 200 g. batches with concentrated hydrobromic acid (460 ml.) for 15 hr. The reaction mixture was cooled and neutralized with aqueous sodium hydroxide; the 4 : 6-dihydroxy-2 : 3-dimethylpyridine which separated was filtered off, washed with cold water, and dried (92%).

Replacement of the two hydroxyl groups by chlorine (using $POCl_3$) is easier in 4 : 6-dihydroxy-2 : 3-dimethylpyridine than in the isomeric 2 : 6-dihydroxy-3 : 4-dimethylpyridine but the temperature must be more carefully controlled or charred by-products will result. Well-dried dihydroxy-compound (90 g.) and phosphorus oxychloride (120 ml.) in a flask fitted with a reflux condenser and guard tube were heated for 5 hr. in a metal-bath at 170—175°. The product was added to about 500 g. of crushed ice and after the exothermic reaction had subsided the mixture was warmed on the steam-bath and a small charred insoluble residue was removed by filtration. The dichloro-derivative was extracted from the filtrate with ether and the ethereal extract after being shaken with sodium carbonate solution was fractionally distilled. The

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[14] Michael, *Ber.*, 1905, **38**, 2083.

TABLE 1. *Freezing constants for the six lutidines.*

Lutidine	Purity (moles %)	Depression produced by 1 mole % of impurity	Depression (K_f) for 1 mole of impurity in 1000 g.	F. p. of sample (t_f)	F. p. for 100% purity ($t_{f,0}$)
2 : 3	99·90 ± 0·02	0·467° ± 0·015°	4·95° ± 0·16°	−15·27° ± 0·02°	−15·22° ± 0·02°
2 : 4	99·92 ± 0·02	0·576 ± 0·020	6·11 ± 0·21	−64·00 ± 0·01	−63·96 ± 0·02
2 : 5	99·85 ± 0·02	0·469 ± 0·011	4·98 ± 0·12	−15·61 ± 0·01	−15·54 ± 0·02
2 : 6	99·89 ± 0·01	0·596 ± 0·026	6·32 ± 0·28	−6·16 ± 0·04	−6·10 ± 0·04
3 : 4	99·88 ± 0·01	0·710 ± 0·029	7·53 ± 0·30	−11·12 ± 0·04	−11·04 ± 0·04
3 : 5	99·91 ± 0·01	0·470 ± 0·003	4·99 ± 0·03	−6·54 ± 0·01	−6·50 ± 0·02

TABLE 2. *Vapour pressures.*

P, mm. Hg at 0° c and standard gravity; *t*, °c; Δ*t* = *t* (obs.) − *t* (calc.).

P	*t*	Δ*t*	*P*	*t*	Δ*t*
		2 : 3-Lutidine			
785·29	162·412	0·000	597·63	152·203	−0·001
778·48	162·077	−0·001	543·20	148·764	−0·002
770·32	161·672	−0·001	499·93	145·829	−0·003
760·85	161·199	−0·001	444·45	141·757	+0·002
750·29	160·668	+0·002	394·32	137·704	0·000
739·67	160·125	0·000	346·46	133·429	+0·001
729·20	159·586	+0·001	298·22	128·606	0·000
720·70	159·141	0·000	248·37	122·909	+0·004
710·48	158·603	+0·001	199·57	116·337	0·000
698·06	157·940	0·000	148·25	107·822	−0·001
650·82	155·326	−0·004	109·38	99·543	−0·024
		2 : 4-Lutidine			
788·89	159·825	+0·003	570·78	147·860	−0·007
773·86	159·092	+0·003	564·25	147·450	−0·006
758·50	158·333	+0·004	540·28	145·909	−0·006
748·00	157·801	0·000	463·91	140·601	−0·004
746·21	157·712	+0·001	385·60	134·371	−0·002
736·16	157·202	+0·002	339·32	130·192	+0·001
726·30	156·693	+0·001	285·18	124·673	+0·008
726·23	156·690	0·000	235·84	118·836	+0·009
715·08	156·107	−0·002	196·25	113·387	+0·018
711·07	155·900	+0·001	139·86	103·767	−0·001
708·01	155·739	+0·001	83·93	90·305	−0·018
698·46	155·232	+0·001	70·68	86·054	0·000
653·85	152·789	−0·002	46·78	76·246	−0·031
612·21	150·386	−0·004			
		3 : 4-Lutidine			
783·49	180·349	0·000	599·13	169·891	−0·001
773·99	179·860	−0·001	549·14	166·617	−0·001
765·09	179·401	+0·003	500·53	163·196	0·000
762·64	179·274	+0·003	449·74	159·324	0·000
756·18	178·933	0·000	400·62	155·228	−0·001
747·75	178·487	0·000	349·24	150·485	−0·003
737·34	177·931	−0·002	300·32	145·423	+0·006
727·20	177·384	0·000	247·51	139·127	+0·001
720·78	177·035	−0·001	199·36	132·352	+0·002
707·89	176·327	+0·002	148·61	123·572	+0·005
697·77	175·761	−0·001	98·86	112·101	−0·012
651·65	173·104	−0·001			
		3 : 5-Lutidine			
776·02	172·729	+0·001	546·21	159·412	−0·002
767·76	172·307	−0·002	483·05	154·971	−0·001
761·03	171·961	−0·002	449·97	152·456	−0·001
747·62	171·265	−0·004	395·94	148·007	−0·002
739·87	170·862	−0·001	344·88	143·329	−0·001
729·32	170·306	+0·001	295·09	138·193	+0·001
719·67	169·790	+0·001	248·60	132·720	+0·006
711·39	169·344	+0·002	199·77	125·975	+0·001
698·15	168·620	+0·002	152·75	118·063	+0·004
650·87	165·941	0·000	112·80	109·544	−0·014
599·51	162·850	−0·002	73·97	98·423	−0·017

total yield (80%) from 2·426 kg. of dihydroxy-compound was 2·452 kg. of 4 : 6-dichloro-2 : 3-dimethylpyridine, b. p. 83—86°/2—3 mm. or 90—109°/4—5 mm. This dichloro-compound is dimorphic and can be obtained in an unstable crystalline form, m. p. *ca.* 20°, which is rapidly transformed on seeding into the stable form, m. p. 44·5°, described by Wibaut and Kooyman.

In the catalytic reduction of 4 : 6-dichloro-2 : 3-dimethylpyridine to 2 : 3-lutidine the method used for preparing 3 : 4-lutidine was followed. A total of 1·167 kg. of 2 : 3-lutidine was obtained (78·2%) and the yield of base over the five stages from acetoacetic ester was thus 30·3%. Its infrared spectrum showed that although it contained about 5% of α-picoline, no significant amount of any other pyridine homologue was present. This occurrence of α-picoline (and of γ-picoline in the impure synthetic 3 : 4-lutidine) was due to the ethyl α-methylacetoacetate's not being free from ethyl acetoacetate.

The final stages of purification were similar to those described for 3 : 4-lutidine, *i.e.*, removal of traces of non-basic material by blowing steam through a solution in sulphuric acid, removal of α-picoline in a fore-cut, b. p. up to 158°, with a 50-plate column, slow fractional freezing, and lastly a slow distillation with rejection of water-containing fore-cuts. The best material (628 g.) contained 0·088% v/v of water and the purity by m. p. measurements after further drying (CaH_2) was 99·90 moles %.

Purification of 3 : 5-*Lutidine.*—The commercial specimen was purified by passing steam through a boiling solution of the base in 1·2 equiv. of 22·6% sulphuric acid until samples of the base recovered from the aqueous condensate showed no traces of aldehyde in the infrared spectra. The main bulk of the purified base was then recovered from the aqueous sulphate solution and fractionally frozen until the liquid pourings showed identity in infrared spectra with the crystallized portion. The water content was then reduced to 0·07% v/v by slow distillation and removal of a water-containing fore-cut. The best specimen (850 g.) had a purity of 99·91 moles % after drying (CaH_2).

Physicochemical Measurements.—Freezing points, cryoscopic constants, and the quantitative determination of purity. The determination of purity and the measurement of the freezing point of these compounds is difficult because temperature equilibrium between liquid and solid is attained slowly. The techniques which were employed have been described elsewhere.[15, 16] The purities of all the samples except 2 : 6-lutidine[1] were determined by a melting-point procedure (ref. 15, p. 19; ref. 16, p. 117). The initial freezing points and the freezing-point depressions produced by adding known quantities of impurity, 2 : 2 : 4-trimethylpentane, were determined by means of an apparatus employing a U-tube.[16] The statistical treatment of the data obtained from replicate experiments has been described.[1] The results of the measurements on the six lutidines are summarized in Table 1. Data [1] on 2 : 6-lutidine are included to complete the series. Some evidence was obtained that 3 : 4-lutidine occurs in two crystalline forms.

Vapour pressure–temperature relationships, normal boiling points, values of $(dt/dP)_{760\,mm.}$, *and latent heats of vaporization.* The apparatus and techniques of measurement previously described[11, 17] were used for 2 : 4-, 2 : 5-, 2 : 6-, and 3 : 4-lutidine. Measurements on 2 : 3- and 3 : 5-lutidine were made by adjusting the pressure in the apparatus to the required value and isolating the apparatus from the pumps. The barostat was not used. The b. p. of sample and water were then measured simultaneously. The time required to obtain the experimental data was reduced and it was considered that the results so obtained were more precise than the values obtained with a barostat.

Detailed results for 2 : 5- and 2 : 6-lutidines have already been published.[11] Table 2 gives the data for the other four.

Table 3 presents constants for all six lutidines; those for 2 : 5- and 2 : 6-lutidine[11] are included to complete the series. This table gives the constants in the Antoine equation, the normal boiling point, d*t*/d*P*, and the latent heat of vaporization at 760 mm. uncorrected for deviations of the vapours from the ideal-gas laws and for the molar volume of the liquid; the thermochemical calorie used is equal to 4·1840 J (abs.). It is planned to measure the virial coefficients by studying the compressibilities of the vapours, and to present corrected values of latent heats later.

Densities. Measurements of densities at 20° and 30° were made by means of a Sprengel–Ostwald pycnometer and precautions to exclude water were taken.[1] Table 4 lists the results

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[15] Herington, *Analyt. Chim. Acta*, 1957, **17**, 15.

[16] Handley, *Analyt. Chim. Acta*, 1957, **17**, 115.

[17] Biddiscombe and Martin, *Trans. Faraday Soc.*, 1958, **54**, 1316.

TABLE 3. *Constants of Antoine equation,* $\log_{10} P = A - B/(C + t)$*; normal boiling points;* $(\mathrm{d}t/\mathrm{d}P)_{760\ \mathrm{mm.}}$*: and molar latent heats of vaporization.*

Lutidine	A	B	C	B. p. (760 mm.) (°c)	(dt/dP) at 760 mm. (°c/mm.)	Heat of vaporization at 760 mm. (uncorr.) (cal./mole)
2 : 3	7·05075 ± 0·0042	1528·935 ± 2·9	205·499 ± 0·34	161·157 ± 0·002	0·05025	9816 ± 1
2 : 4	7·11647 ± 0·0082	1564·800 ± 5·7	211·032 ± 0·62	158·403 ± 0·002	0·04984	9771 ± 3
2 : 5	7·05816 ± 0·0069	1524·016 ± 4·7	207·820 ± 0·52	157·008 ± 0·003	0·04991	9695 ± 2
2 : 6	7·05246 ± 0·0097	1467·362 ± 6·4	207·701 ± 0·72	144·045 ± 0·003	0·04818	9446 ± 3
3 : 4	7·06898 ± 0·0071	1607·874 ± 5·1	204·776 ± 0·58	179·132 ± 0·001	0·05238	10211 ± 2
3 : 5	7·08598 ± 0·0044	1593·028 ± 3·2	206·916 ± 0·36	171·910 ± 0·003	0·05148	10061 ± 1

TABLE 4. *Observed densities at 20° and 30° of the six lutidines, and calculated densities and coefficients of cubical expansion at 25°.*

$[d_{25} = 0{\cdot}5(d_{20} + d_{30});\ \alpha_{25} = 0{\cdot}2(d_{20} - d_{30})/(d_{20} + d_{30})]$

Lutidine	d_{20} (g./ml.)	d_{30} (g./ml.)	d_{25} (g./ml.)	α_{25}
2 : 3	0·94641 ± 0·00001	0·93783 ± 0·00000	0·94212	0·000911 ± 0·000001
2 : 4	0·93102 ± 0·00000	0·92226 ± 0·00000	0·92664	0·000945 ± 0·000000
2 : 5	0·92910 ± 0·00000	0·92024 ± 0·00000	0·92467	0·000958 ± 0·000000
2 : 6	0·92257 ± 0·00002	0·91355 ± 0·00002	0·91806	0·000983 ± 0·000003
3 : 4	0·95773 ± 0·00001	0·94928 ± 0·00000	0·95351	0·000886 ± 0·000001
3 : 5	0·94234 ± 0·00001	0·93377 ± 0·00000	0·93806	0·000914 ± 0·000001

TABLE 5. *Frequencies (cm.$^{-1}$) and estimates of the intensities of the main absorption peaks for liquid samples of the six lutidines.*

2 : 3-Lutidine: 4950w, 4606w, 4350sh.w, 4306w, 4233sh.w, 4108w, 4042w, 3953sh.w, 3916w, 3845w, 3775w, 3719w, 3633w, 3591w, 3453w, 3043v.s, 2978v.s, 2937v.s, 2909v.s, 2869sh.v.s, 2738w, 2651sh.w, 2607w, 2554w, 2518w, 2489w, 2426w, 2407w, 2376w, 2353w, 2310w, 2248w, 2220w, 2193w, 2159w, 2116sh.w, 2101w, 2050w, 2033w, 2000w, 1957w, 1939w, 1901w, 1870w, 1826w, 1800w, 1747w, 1708w, 1658w, 1584sh.s, 1575v.s, 1537sh.w, 1465v.s, 1449v.s, 1432v.s, 1384s, 1369s, 1315w, 1276m, 1238m, 1222sh.w, 1180s, 1165sh.w, 1123s, 1070m, 1019s, 992s, 971s, 947sh.w, 853w, 787v.s, 728v.s.

2 : 4-Lutidine: 4950w, 4640sh.w, 4572w, 4396w, 4306w, 4149w, 4029w, 3953w, 3764w, 3582w, 3472w, 3397w, 3248w, 3043sh.v.s, 3007v.s, 2944v.s, 2916v.s, 2869s, 2768w, 2726w, 2685w, 2651w, 2635w, 2549w, 2524w, 2464w, 2402w, 2358w, 2310w, 2289w, 2252sh.w, 2228w, 2212w, 2186w, 2163w, 2144w, 2126w, 2112w, 2083w, 2027w, 2007w, 1991w, 1924w, 1856w, 1760w, 1721w, 1692w, 1664w, 1629sh.m, 1604v.s, 1562v.s, 1550v.s, 1513s, 1479v.s, 1449v.s, 1397v.s, 1376s, 1294s, 1232w, 1193sh.w, 1166m, 1112w, 1037s, 995s, 976m, 951sh.w, 912s, 879m, 815v.s, 753m, 727w.

2 : 5-Lutidine: 4970w, 4640w, 4589w, 4396w, 4321w, 4177w, 4069w, 3941w, 3845w, 3764w, 3665w, 3592w, 3511sh.w, 3472sh.w, 3434w, 3406w, 3370w, 3273w, 3198sh.w, 3166sh.w, 3089m, 3021sh.s, 2992v.s, 2950v.s, 2916v.s, 2862s, 2738w, 2685w, 2623w, 2597w, 2544w, 2524w, 2474w, 2445w, 2417w, 2380w, 2336w, 2302w, 2268w, 2220w, 2155w, 2112w, 2090w, 2063w, 2030w, 2001w, 1970w, 1951w, 1930w, 1880w, 1832w, 1773w, 1738w, 1678w, 1601v.s, 1567v.s, 1490v.s, 1450v.s, 1376v.s, 1294s, 1245s, 1235w, 1215w, 1204w, 1138s, 1130s, 1043sh.s, 1031v.s, 1007sh.w, 964m, 920w, 839m, 815v.s, 727v.s, 647v.s.

2 : 6-Lutidine: 4970w, 4623w, 4365sh.w, 4306w, 4219sh.w, 4144w, 4055w, 3953w, 3775w, 3719w, 3602w, 3462w, 3406w, 3256w, 3150w, 3060v.s, 3018v.s, 2985v.s, 2957v.s, 2920v.s, 2853v.s, 2726w, 2674w, 2629w, 2575sh.w, 2539w, 2503w, 2450w, 2426w, 2407w, 2380w, 2358w, 2315w, 2298w, 2285w, 2193w, 2170w, 2094w, 2067w, 2000w, 1970w, 1945w, 1933w, 1910w, 1875w, 1816w, 1770w, 1708w, 1664w, 1643w, 1591v.s, 1578v.s, 1533s, 1511s, 1470v.s, 1451v.s, 1411sh.s, 1369s, 1326sh.w, 1278m, 1263m, 1245m, 1222s, 1153s, 1093s, 1028s, 996m, 969m, 905w, 888w, 772v.s, 728m, 716m.

3 : 4-Lutidine: 4970w, 4572w, 4396w, 4306w, 4205w, 4082w, 3953w, 3904w, 3868w, 3764w, 3612w, 3541w, 3462w, 3370w, 3273sh.w, 3089m, 3055s, 3021v.s, 3010v.s, 2971v.s, 2947v.s, 2923v.s, 2876s, 2762w, 2732w, 2685w, 2657w, 2612w, 2570sh.w, 2549w, 2474w, 2426w, 2407w, 2389w, 2376w, 2336w, 2306w, 2264w, 2244w, 2216w, 2159w, 2140w, 2097w, 2080w, 2060w, 2017w, 1988w, 1939sh.w, 1927w, 1883w, 1834w, 1776w, 1741w, 1702w, 1635m, 1594v.s, 1560s, 1492v.s, 1447v.s, 1405v.s, 1384v.s, 1349sh.w, 1305m, 1244sh.m, 1237m, 1194v.s, 1176m, 1148w, 1066s, 1048m, 1020s, 1001m, 985m, 918w, 839v.s, 821v.s, 751m, 726v.s, 600v.s.

3 : 5-Lutidine: 4970w, 4589w, 4365w, 4306w, 4247sh.w, 4191w, 4042w, 3941w, 3719w, 3561w, 3443w, 3370w, 3239sh.w, 3174w, 3029v.s, 2985 v.s, 2971sh.v.s, 2930v.s, 2869s, 2738w, 2651w, 2629w, 2612w, 2591w, 2554w, 2494sh.w, 2479w, 2445w, 2402w, 2367w, 2310w, 2268w, 2252w, 2216w, 2174w, 2137w, 2101w, 2033sh.w, 1976w, 1887sh.w, 1862w, 1776w, 1747w, 1627sh.w, 1602s, 1581v.s, 1463v.s, 1426v.s, 1379s, 1358sh.m, 1320m, 1273w, 1232s, 1164v.s, 1138s, 1043sh.s, 1032s, 1011m, 944w, 929w, 857v.s, 727sh.m, 715v.s, 710v.s.

v.s = very strong, s = strong, m = medium, w = weak, sh. = shoulder.

The approximate strengths of the bands are given with respect to liquid samples in a 0·06 mm. cell.

Frequency measurements are accurate to ±7 cm.$^{-1}$ at 3000 cm.$^{-1}$, ±2 cm.$^{-1}$ at 1500 cm.$^{-1}$, and ±1 cm.$^{-1}$ at 750 cm.$^{-1}$.

of the measurements with their standard deviations. All the samples were dried (CaH_2), and the concentration of water in the base at the end of the experiment was determined by infrared spectroscopy.[18] The concentration of water so found never exceeded 0·04% v/v and hence the error in density due to the presence of water should be less than 0·00002 g./ml.

Refractive indices. A high-accuracy Abbé refractometer (Bellingham and Stanley Ltd., London) and a sodium light source were placed in a flexible poly(vinyl chloride) glove cabinet with the two eye-pieces of the instrument projecting through holes. The cabinet was flushed with dry air. All measurements were made at 25·0 ± 0·1°, maintained by circulating water from a constant-temperature bath through the water-jacket of the refractometer. A quartz test-piece was used to check frequently the adjustment of the instrument during the series of measurements. At least ten readings were taken for each filling of the refractometer and at least five fillings were made of each lutidine, which had been dried (CaH_2). A further check was provided by measuring the refractive index of a sample of benzene 99·99 moles % pure. The value found, $1{\cdot}4979_1$ for n_D^{25}, is in good accord with that given by Forziati,[19] *viz.*, 1·49792. The following values for n_D^{25} were found: 2 : 3-lutidine $1{\cdot}5062_6$; 2 : 4-lutidine, $1{\cdot}4983_9$; 2 : 5-lutidine, $1{\cdot}4979_7$; 2 : 6-lutidine, $1{\cdot}4952_4$; 3 : 4-lutidine, $1{\cdot}5104_1$; 3 : 5-lutidine, $1{\cdot}5037_6$.

Infrared absorption spectra. The spectra of the liquids were obtained with a double-beam prism-grating spectrometer, constructed in this laboratory.[20]

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