571. *Molecular Interaction: Molecular Polarisation of Amines in Benzene and Carbon Tetrachloride.*

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Evidence of weak interaction between amines and carbon tetrachloride has been obtained from studies of dipole moments. Interaction depends both on the basicity of the amine and on steric factors. Its extent is detected by the difference in total polarisation or dipole moment of the solute in carbon tetrachloride and benzene. Similar interaction occurs with pyridine 1-oxides.

CONSIDERABLE qualitative evidence [1-4] indicates that amines can interact with polyhalogenated methanes. Polarisation studies [5,6] of ethers in tri- and tetra-halogenated methanes have indicated the formation of 1 : 1 complexes in solution, the bonding of the trihalogenated being stronger than that of the tetrahalogenated methanes. Similar results were found for acetone and quinoline.[6] In addition, studies have been made on chloroform–triethylamine mixtures in benzene.[5] It seems that the trihalogenated complexes are held together mainly by hydrogen bonding, whereas in the tetrahalogenated complexes the halogen atoms act as electron acceptors. Pentachloroethane shows as much tendency as chloroform to combine with ether, whereas hexachloroethane behaves in a similar manner to carbon tetrachloride.[6]

In phase equilibrium studies of systems containing pyridine and polyhalogenated methanes VanderWerf and his co-workers [7] detected solid compounds having ratios of base to halogenated methane 3 : 1, 2 : 1, 1 : 1, and 1 : 2. 2,6-Lutidine appears to form only 1 : 1 solid addition compounds. The compounds other than those containing equimolecular proportions seem to be " lattice compounds."

Whilst Raman spectra [8] show that the doublet at 790 cm.$^{-1}$ of carbon tetrachloride shifts in frequency and intensity when liquid ammonia is added, the relaxation time of aniline in carbon tetrachloride solution indicates that any association can be at the most only very weak.[9] The bands corresponding to the symmetric and antisymmetric amino-stretching frequencies of butylamine in carbon tetrachloride and dioxan solution are

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[1] Collins, *Chem. and Ind.*, 1957, 704.

[2] Davies, Evans, and Whitehead, *J.*, 1939, 644.

[3] Sharada and Murthy, *Current Sci.*, 1960, **5**, 179.

[4] Cromwell, Foster, and Wheeler, *Chem. and Ind.*, 1959, 228.

[5] Hammick, Norris, and Sutton, *J.*, 1938, 1755.

[6] Earp and Glasstone, *J.*, 1935, 1709, 1720.

[7] Davidson, VanderWerf, and Boatwright, *J. Amer. Chem. Soc.*, 1947, **69**, 3045; VanderWerf, Davidson, and Michaelis, *ibid.*, 1948, **70**, 908.

[8] Kinumaki and Aida, *Sci. Reports Res. Inst. Tohôku Univ.*, 1954, *A*, **6**, 636.

[9] Fischer, *Z. Naturforsch.*, 1954, **9a**, 904.

considerably reduced in intensity in the former solvent, suggesting some form of interaction between the amine and carbon tetrachloride.[10] Partington and Middleton [11] found the dipole moment of pyridine to be abnormally high in carbon tetrachloride and ascribed this to the presence of an interaction between the solvent and solute. Le Fèvre and his co-workers [12] also found an increase in dipole moment of 0·12 D relative to benzene for pyridine and rather smaller differences for quinoline and isoquinoline, but they attributed the difference to an increase in atomic polarisation as a result of solvation rather than to formation of a polar adduct.

EXPERIMENTAL

Apparatus.—Dielectric constants were measured by using a heterodyne capacitance meter based on a circuit described by Weissberger [13] but modified by addition of an oscilloscope to detect the balance point. The apparatus was calibrated with benzene (dielectric constant 2·2725). Capacity changes were followed with a Sullivan Precision Variable Air Condenser, and variations in dielectric constant of 0·0001 could be detected. With the cell in a draught-proof holder, and temperature controlled at 25° ± 0·01°, the maximum drift during at least 0·5 hr. was generally undetectable on the scale of the variable condenser.

Specific volumes were measured in a pyknometer of the type described by Cumper, Vogel, and Walker,[14] the specific volume of benzene being assumed to be 1·14445.

Refractive indices were measured on a Pulfrich refractometer which was supplied with water at 25° from the thermostat-bath.

Preparation and Purification of Materials.—Thiophen-free, crystallisable benzene was shaken with concentrated sulphuric acid, until no browning of the acid layer occurred, washed, shaken with sodium hydroxide solution, and dried (KOH). The benzene was then distilled from sodium in a 70-cm. column packed with glass helices, the middle fraction being collected and refractionated from potassium in a 14-plate column packed with glass helices, a middle fraction again being taken. This fraction was stored in the dark over sodium wire for at least a week before use.

" AnalaR " carbon tetrachloride was refluxed for several hours with 5% sodium hydroxide solution, washed with water, dried ($CaCl_2$; then P_2O_5), and fractionated from phosphoric oxide in a 1-m. column packed with Dixon gauze rings. There was no change in b. p. between the first and the last fraction, but a middle fraction, comprising about two-thirds of the total, was always taken and stored for at least a week in the dark over phosphoric oxide before use.

" Spectroscopic-grade " cyclohexane was passed through silica gel to remove any traces of unsaturated compounds and then fractionated from potassium. A middle fraction was taken, although no change in b. p. occurred. The sample was stored for a week over sodium wire before use.

The following compounds were commercial samples, purified by drying (K_2CO_3) and fractionation from phosphoric oxide in a high-efficiency, low-hold-up column (recorded b. p.s and m. p.s are given in parentheses): piperidine, b. p. 106°/760 mm. (105·6° [15]), butylamine, b. p. 76·5°/765 mm. (76·2° [16]), triethylamine, b. p. 88·5°/755 mm. (89·4° [17]), 2,6-dimethylpyridine (fractionated from boron trifluoride [18]), b. p. 144·5° (144—145° [19]) [picrate, m. p. 163° (163° [19])]. Aniline was a synthetic sample purified as described by Smith [20] and had b. p. 184° (184·4° [17]).

8-Hydroxyquinoline was recrystallised several times from light petroleum (b. p. 60—80°) and had m. p. 75° (75—76° [19]).

[10] Richards and Walker, *Trans. Faraday Soc.*, 1961, **57**, 399.

[11] Partington and Middleton, *Nature*, 1938, 141, 516.

[12] Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.

[13] Weissberger, " Physical Methods of Organic Chemistry," Interscience Publ., Inc., New York, 1949, p. 1638.

[14] Cumper, Vogel, and Walker, *J.*, 1956, 3621.

[15] Davies and McGee, *J.*, 1950, 678.

[16] Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 457.

[17] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[18] Brown, Johnson, and Podall, *J. Amer. Chem. Soc.*, 1954, **76**, 5556.

[19] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1957, Vol. IVa.

[20] Few and Smith, *J.*, 1949, 753.

The following compounds were prepared by standard methods and purified by fractionation or crystallisation: 4-methylpyridine 1-oxide [21] (from benzene), m. p. 183° (185—186°,[21] 181° [22]) unchanged by further recrystallisation, 4-phenylpyridine [23] (from water), m. p. 77° (77—78° [19]) [picrate, m. p. 196° (195—196° [23])], 4-nitropyridine, m. p. 52° (50° [24]), 3-isopropylpyridine, b. p. 179°/750 mm. (179·3° [25]) [picrate, m. p. 138·5° (138·1—138·6° [25])], 4-t-butylpyridine, b. p. 197°/765 mm. (196·3° [25]) [picrate, m. p. 131° (130·9—131·4° [25])], 2-phenylpyridine,[26] b. p. 270°/760 mm. (268—269° [19]) [picrate, m. p. 175—176° (174—175° [19])], 2,6-diphenylpyridine, m. p. 80—81° (81° [27]) [picrate, m. p. 171° (171° [27])].

4-Methylpyridine, b. p. 144·2°/750 mm. (145·4°/760 mm.[28]) [picrate, m. p. 168—169° (165°, 167°, 168° [19])], and 3-methylpyridine, b. p. 143·5°/755 mm. (144°/755 mm.[28]) [picrate, m. p. 153°

TABLE 1.

Piperidine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1264	2·2745	1·14449	2·24352
2560	2·2762	1·14453	2·24343
3992	2·2781	1·14455	2·24305
5425	2·2802	1·14459	2·24292
6402	2·2816	1·14462	2·24274
10,284	2·2874	1·14474	2·24215
10,698	2·2880	1·14474	2·24224

$\varepsilon_{12} = 2{\cdot}2725 + 1{\cdot}4400w_2$;
$v_{12} = 1{\cdot}14445 + 0{\cdot}0273w_2$;
$n_{12}^2 = 2{\cdot}24370 - 0{\cdot}1440w_2$;
${}_2P_\infty = 52{\cdot}78$ c.c.;
$R_D = 26{\cdot}90$ c.c.; $\mu = 1{\cdot}13$ D.

Piperidine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1115	2·2318	0·63091	2·12463
1575	2·2338	0·63113	2·12466
2317	2·2362	0·63181	2·12477
2938	2·2385	0·63181	2·12483
3506	2·2404	0·63211	2·12489
4144	2·2432	0·63242	2·12497
6087	2·2501	0·63341	2·12518

$\varepsilon_{12} = 2{\cdot}2276 + 3{\cdot}7266w_2$;
$v_{12} = 0{\cdot}63035 + 0{\cdot}5039w_2$;
$n_{12}^2 = 2{\cdot}12447 + 0{\cdot}1200w_2$;
${}_2P_\infty = 61{\cdot}62$ c.c.
$R_D = 27{\cdot}46$ c.c.; $\mu = 1{\cdot}29$ D.

Butylamine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
569	2·2304	0·63081	2·12332
1809	2·2371	0·63170	2·12302
2011	2·2387	0·63185	2·12291
2871	2·2431	0·63253	2·12279
3362	2·2458	0·63284	2·12262
4951	2·2545	0·63398	2·12232
6313	2·2620	0·63497	2·12200

$\varepsilon_{12} = 2{\cdot}2272 + 5{\cdot}5377w_2$;
$v_{12} = 0{\cdot}63040 + 0{\cdot}7256w_2$;
$n_{12}^2 = 2{\cdot}12343 - 0{\cdot}2298w_2$;
${}_2P_\infty = 71{\cdot}65$ c.c.;
$R_D = 25{\cdot}15$ c.c.; $\mu = 1{\cdot}51$ D.

Triethylamine in carbon tetrachloride *

10^6w_2	ε_{12}	v_{12}	n_{12}^2
833	2·2280	0·63091	—
1824	2·2290	0·63169	—
2950	2·2304	0·63243	—
4592	2·2327	0·63368	—
6491	2·2351	0·63503	—
7959	2·2368	0·63610	—

$\varepsilon_{12} = 2{\cdot}2268 + 1{\cdot}2617w_2$;
$v_{12} = 0{\cdot}63035 + 0{\cdot}0177w_2$;
${}_2P_\infty = 53{\cdot}16$ c.c.;
$R_D = 33{\cdot}74$ c.c.; $\mu = 0{\cdot}98$ D.

* Because crystals of triethylamine hydrochloride appear within an hour of mixing, the dielectric constant and specific volume of each solution were measured immediately after mixing and the molar refractivity was calculated from bond data. The dielectric constant of a mixture of triethylamine and carbon tetrachloride did not alter by a significant factor during the total time taken for each set of measurements.

4-Methylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
759	2·2391	0·63069	2·12365
1311	2·2476	0·63094	2·12384
2006	2·2584	0·63119	2·12401
3015	2·2747	0·63159	2·12428
3414	2·2815	0·63179	2·12448
4271	2·2945	0·63209	2·12474
6582	2·3307	0·63305	2·12538

$\varepsilon_{12} = 2{\cdot}2270 + 15{\cdot}8017w_2$;
$v_{12} = 0{\cdot}63038 + 0{\cdot}4064w_2$;
$n_{12}^2 = 2{\cdot}12342 + 0{\cdot}3015w_2$;
${}_2P_\infty = 183{\cdot}77$ c.c.;
$R_D = 29{\cdot}43$ c.c.; $\mu = 2{\cdot}75$ D.

4-Methylpyridine in cyclohexane

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1416	2·0220	1·29375	2·02479
3274	2·0330	1·29338	2·02490
4700	2·0419	1·29310	2·02510
5661	2·0487	1·29296	2·02541
6771	2·0557	1·29275	2·02558
7970	2·0627	1·29249	2·02575
10,866	2·0805	1·29192	2·02610

$\varepsilon_{12} = 2{\cdot}0128 + 6{\cdot}2695w_2$;
$v_{12} = 1{\cdot}29402 - 0{\cdot}1916w_2$;
$n_{12}^2 = 2{\cdot}02445 + 0{\cdot}1594w_2$;
${}_2P_\infty = 166{\cdot}66$ c.c.;
$R_D = 29{\cdot}69$ c.c.; $\mu = 2{\cdot}59$ D.

4-t-Butylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
923	2·2365	0·63076	2·12372
1726	2·2473	0·63115	2·12387
2675	2·2588	0·63158	2·12434
4127	2·2755	0·63220	2·12469
5916	2·2971	0·63303	2·12524
8828	2·3311	0·63432	2·12571
10,610	2·3530	0·63513	2·12626

$\varepsilon_{12} = 2{\cdot}2266 + 11{\cdot}8692w_2$;
$v_{12} = 0{\cdot}63035 + 0{\cdot}4517w_2$;
$n_{12}^2 = 2{\cdot}12343 + 0{\cdot}2822w_2$;
${}_2P_\infty = 212{\cdot}33$ c.c.;
$R_D = 44{\cdot}10$ c.c.; $\mu = 2{\cdot}87$ D.

3-Methylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1039	2·2413	0·63079	2·12353
1679	2·2497	0·63107	2·12404
2896	2·2662	0·63154	2·12436
3850	2·2793	0·63193	2·12471
5344	2·2998	0·63253	2·12530
5400	2·3007	0·63256	2·12533
7677	2·3306	0·63348	2·12606

$\varepsilon_{12} = 2{\cdot}2270 + 13{\cdot}5769w_2$;
$v_{12} = 0{\cdot}63038 + 0{\cdot}4031w_2$;
$n_{12}^2 = 2{\cdot}12342 + 0{\cdot}3367w_2$;
${}_2P_\infty = 161{\cdot}75$ c.c.;
$R_D = 29{\cdot}71$ c.c.; $\mu = 2{\cdot}54$ D.

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[21] Boeckelheide and Linn, *J. Amer. Chem. Soc.*, 1954, **76**, 1286.
[22] Ochiai, *J. Pharm. Soc. Japan*, 1944, **64**, 72.
[23] Haworth, Heilbron, and Hey, *J.*, 1940, 349.
[24] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.
[25] Brown and Murphey, *J. Amer. Chem. Soc.*, 1951, **73**, 3308.
[26] Gilman and Blatt, *Org. Synth.*, Coll. Vol. II.
[27] Heilbron, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1936.
[28] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.

TABLE 1. (*Continued.*)

3-Methylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
2181	2·2872	1·14426	2·24276
3424	2·2956	1·14413	2·24274
5834	2·3116	1·14387	2·24274
6438	2·3163	1·14385	2·24280
7108	2·3213	1·14377	2·24276
11,181	2·3478	1·14335	2·24281
12,455	2·3571	1·14320	2·24284

ε_{12} = 2·2725 + 6·7749w_2;
v_{12} = 1·14447 − 0·1000w_2;
n_{12}^2 = 2·24271 + 0·0082w_2;
$_2P_\infty$ = 147·63 c.c.;
R_D = 28·50 c.c.; μ = 2·41 D.

3-Isopropylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
614	2·2334	0·63063	2·12305
1143	2·2388	0·63086	2·12337
2683	2·2540	0·63151	2·12372
3573	2·2641	0·63192	2·12396
4263	2·2714	0·63224	2·12431
5075	2·2801	0·63263	2·12448
5885	2·2884	0·63298	2·12483

ε_{12} = 2·2266 + 10·5012w_2;
v_{12} = 0·63035 + 0·4442w_2;
n_{12}^2 = 2·12296 + 0·3013w_2;
$_2P_\infty$ = 172·49 c.c.;
R_D = 39·53 c.c.; μ = 2·55 D.

3-Isopropylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1429	2·2796	1·14437	2·24247
2963	2·2880	1·14428	2·24242
4509	2·2957	1·14417	2·24233
6002	2·3034	1·14408	2·24230
7218	2·3101	1·14399	2·24224
8723	2·3183	1·14390	2·24221
12,408	2·3372	1·14366	2·24207

ε_{12} = 2·2723 + 5·2300w_2;
v_{12} = 1·14446 − 0·0638w_2;
n_{12}^2 = 2·24253 − 0·0386w_2;
$_2P_\infty$ = 158·20 c.c.;
R_D = 37·45 c.c.; μ = 2·43 D.

2,6-Dimethylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1081	2·2332	0·63086	2·12358
2330	2·2402	0·63141	2·12375
3599	2·2477	0·63199	2·12401
6033	2·2617	0·63305	2·12454
7673	2·2712	0·63378	2·12504
11,176	2·2911	0·63539	2·12576
15,129	2·3139	0·63716	2·12661

ε_{12} = 2·2270 + 5·7421w_2;
v_{12} = 0·63035 + 0·4507w_2;
n_{12}^2 = 2·12326 + 0·2227w_2;
$_2P_\infty$ = 98·74 c.c.;
R_D = 34·21 c.c.; μ = 1·78 D.

2,6-Dimethylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1549	2·2769	1·14438	2·24326
3707	2·2825	1·14426	2·24331
5662	2·2879	1·14416	2·24352
7752	2·2938	1·14405	2·24364
9144	2·2977	1·14397	2·24375
11,085	2·3028	1·14386	2·24382
13,450	2·3096	1·14373	2·24391

ε_{12} = 2·2725 + 2·7450w_2;
v_{12} = 1·14446 − 0·0537w_2;
n_{12}^2 = 2·24318 + 0·0564w_2;
$_2P_\infty$ = 90·13 c.c.;
R_D = 35·39 c.c.; μ = 1·64 D.

4-Phenylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1007	2·2368	0·63061	2·12407
2383	2·2498	0·63095	2·12518
2446	2·2500	0·63097	2·12515
4220	2·2665	0·63143	2·12661
5346	2·2773	0·63172	2·12754
6312	2·2862	0·63197	2·12810
9255	2·3133	0·63272	2·13017

ε_{12} = 2·2273 + 9·3255w_2;
v_{12} = 0·63035 + 0·2557w_2;
n_{12}^2 = 2·12342 + 0·7388w_2;
$_2P_\infty$ = 193·07 c.c.;
R_D = 50·22 c.c.; μ = 2·64 D.

4-Phenylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1008	2·2772	1·14427	2·24227
1617	2·2806	1·14412	2·24240
3216	2·2881	1·14369	2·24278
4682	2·2948	1·14339	2·24326
5353	2·2984	1·14317	2·24349
7781	2·3097	1·14260	2·24427
8688	2·3147	1·14238	2·24433

ε_{12} = 2·2725 + 4·8230w_2;
v_{12} = 1·14446 − 0·2350w_2;
n_{12}^2 = 2·24192 + 0·2745w_2;
$_2P_\infty$ = 182·81 c.c.;
R_D = 50·16 c.c.; μ = 2·55 D.

2-Phenylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1332	2·2330	0·63076	2·12355
2596	2·2399	0·63111	2·12436
3894	2·2464	0·63150	2·12547
5656	2·2557	0·63195	2·12687
6444	2·2605	0·63219	2·12743
8781	2·2718	0·63279	2·12961
10,385	2·2808	0·63331	2·13093

ε_{12} = 2·2260 + 5·2728w_2;
v_{12} = 0·63040 + 0·2766w_2;
n_{12}^2 = 2·12250 + 0·7859w_2;
$_2P_\infty$ = 127·48 c.c.;
R_D = 51·88 c.c.; μ = 1·92 D.

2-Phenylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
2281	2·2788	1·14392	2·24355
4655	2·2855	1·14334	2·24430
6878	2·2920	1·14284	2·24513
9375	2·2988	1·14221	2·24613
10,042	2·3007	1·14207	2·24619
11,959	2·3060	1·14158	2·24679
15,443	2·3160	1·14077	2·24813

ε_{12} = 2·2725 + 2·8087w_2;
v_{12} = 1·14445 − 0·2378w_2;
n_{12}^2 = 2·24277 + 0·3478w_2;
$_2P_\infty$ = 123·88 c.c.;
R_D = 51·52 c.c.; μ = 1·88 D.

2,6-Diphenylpyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
578	2·2289	0·63060	2·12469
1102	2·2301	0·63068	2·12489
1560	2·2310	0·63079	2·12521
2554	2·2335	0·63102	2·12591
4053	2·2375	0·63137	2·12704
4606	2·2388	0·63151	2·12740
5290	2·2406	0·63167	2·12798

ε_{12} = 2·2271 + 2·5679w_2;
v_{12} = 0·63042 + 0·2381w_2;
n_{12}^2 = 2·12410 + 0·7304w_2;
$_2P_\infty$ = 121·17 c.c.;
R_D = 73·53 c.c.; μ = 1·53 D.

2,6-Diphenylpyridine in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1941	2·2755	1·14391	2·24445
3052	2·2770	1·14359	2·24475
4768	2·2797	1·14315	2·24541
5893	2·2814	1·14279	2·24592
7744	2·2842	1·14228	2·24676
8486	2·2853	1·14207	2·24703
9473	2·2867	1·14180	2·24730

ε_{12} = 2·2725 + 1·5064w_2;
v_{12} = 1·14445 − 0·2795w_2;
n_{12}^2 = 2·24364 + 0·3903w_2;
$_2P_\infty$ = 125·11 c.c.;
R_D = 75·83 c.c.; μ = 1·55 D.

4-Nitropyridine in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
805	2·2305	0·63049	2·12334
2079	2·2356	0·63065	2·12390
2826	2·2388	0·63074	2·12413
3918	2·2433	0·63090	2·12469
4815	2·2467	0·63101	2·12489
5406	2·2491	0·63110	2·12533
7292	2·2567	0·63133	2·12582

ε_{12} = 2·2273 + 4·0379w_2;
v_{12} = 0·63038 + 0·1312w_2;
n_{12}^2 = 2·12302 + 0·4038w_2;
$_2P_\infty$ = 80·47 c.c.;
R_D = 31·32 c.c.; μ = 1·55 D.

8-Hydroxyquinoline in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
665	2·2325	0·63053	2·12422
1039	2·2366	0·63061	2·12445
1784	2·2438	0·63077	2·12495
1954	2·2450	0·63080	2·12504
2616	2·2521	0·63093	2·12538
2739	2·2532	0·63096	2·12556
3548	2·2615	0·63112	2·12614

ε_{12} = 2·2260 + 9·9614w_2;
v_{12} = 0·63040 + 0·2036w_2;
n_{12}^2 = 2·12378 + 0·6469w_2;
$_2P_\infty$ = 188·24 c.c.;
R_D = 43·43 c.c.; μ = 2·66 D.

Aniline in carbon tetrachloride

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1629	2·2352	0·63099	2·12530
3409	2·2438	0·63167	2·12620
5271	2·2534	0·63236	2·12743
6982	2·2620	0·63302	2·12839
8197	2·2679	0·63347	2·12924
10,072	2·2782	0·63420	2·13029
10,966	2·2826	0·63452	2·13093

ε_{12} = 2·2265 + 5·1068w_2;
v_{12} = 0·63038 + 0·3776w_2;
n_{12}^2 = 2·12427 + 0·5995w_2;
$_2P_\infty$ = 77·59 c.c.;
R_D = 31·79 c.c.; μ = 1·50 D.

Pyridine 1-oxide in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1209	2·2964	1·14398	2·24385
2069	2·3129	1·14368	2·24415
3639	2·3452	1·14313	2·24478
3648	2·3467	1·14312	2·24454
6607	2·4048	1·14203	2·24553
7442	2·4245	1·14172	2·24577
9841	2·4726	1·14084	2·24661

ε_{12} = 2·2720 + 20·2318w_2;
v_{12} = 1·14444 − 0·3651w_2;
n_{12}^2 = 2·24350 + 0·3114w_2;
$_2P_\infty$ = 383·95 c.c.;
R_D = 27·36 c.c.; μ = 4·18 D.

TABLE 1. (*Continued.*)

Pyridine 1-oxide in cyclohexane †

10^6w_2	ε_{12}	v_{12}	n_{12}^2
0	2·0130	1·29374	—
70	2·0141	1·29371	—
258	2·0171	1·29366	—
328	2·0183	1·29363	—
556	2·0217	1·29355	—

$\varepsilon_{12} = 2{\cdot}0130 + 15{\cdot}84w_2$;
$v_{12} = 1{\cdot}29374 - 0{\cdot}338w_2$;
${}_2P_\infty = 386{\cdot}0$ c.c.;
$\mu = 4{\cdot}19 \pm 0{\cdot}03$ D.

† Several other solutions which were prepared gave precipitates before measurement was complete. The R_D value obtained for benzene solution was used in calculating μ.

4-Methylpyridine 1-oxide in carbon tetrachloride ‡

10^6w_2	ε_{12}	v_{12}	n_{12}^2
16	2·2344	0·63039	
50	2·2494	0·63045	—
50	2·2497	0·63046	—
95	2·2695	0·63054	—
108	2·2759	0·63057	—
120	2·2804	0·63059	—
131	2·2851	0·63062	—

$\varepsilon_{12} = 2{\cdot}2272 + 44{\cdot}56w_2$;
$v_{12} = 0{\cdot}63036 + 0{\cdot}193w_2$;
${}_2P_\infty = 540{\cdot}7$ c.c.;
$\mu = 4{\cdot}97 \pm 0{\cdot}03$ D.

‡ The R_D value for benzene solution was used. The lines obtained show that quoting weight fractions to the accuracy expressed here is acceptable.

4-Methylpyridine 1-oxide in benzene

10^6w_2	ε_{12}	v_{12}	n_{12}^2
785	2·2882	1·14417	2·24421
1479	2·3033	1·14394	2·24445
1823	2·3101	1·14381	2·24451
2727	2·3292	1·14357	2·24495
2875	2·3317	1·14352	2·24505
3242	2·3388	1·14340	2·24517
4491	2·3644	1·14303	2·24565

$\varepsilon_{12} = 2{\cdot}2725 + 20{\cdot}5600w_2$;
$v_{12} = 1{\cdot}14442 - 0{\cdot}3163w_2$;
$n_{12}^2 = 2{\cdot}24384 + 0{\cdot}4052w_2$;
${}_2P_\infty = 448{\cdot}90$ c.c.;
$R_D = 34{\cdot}92$ c.c.; $\mu = 4{\cdot}50$ D.

TABLE 2. *Dipole moments at* 25°.

	μ_B (D)	μ_{CT} (D)	μ_{CH} (D)	Lit.
Butylamine	—	1·51		
Piperidine	—	1·29		
Triethylamine	—	0·98		
4-Methylpyridine	—	2·75	2·59	B 2·60 [a]
4-t-Butylpyridine	—	2·87		B 2·73 [a]
2,6-Dimethylpyridine	1·64	1·78		B 1·65,[b] 1·66 [a]
3-Methylpyridine	2·41	2·54		B 2·40 [a]
3-Isopropylpyridine	2·43	2·55		
4-Phenylpyridine	2·55	2·64		
2-Phenylpyridine	1·88	1·92		
4-Nitropyridine	—	1·55		
2,6-Diphenylpyridine	1·55	1·53		
8-Hydroxyquinoline	—	1·86		
Aniline	—	1·50		CT 1·48 [c]
4-Methylpyridine 1-oxide	4·50	4·97		B 4·74 [d]
Pyridine 1-oxide	4·18	—	4·19	B 4·24 [e]

[a] See ref. 14. [b] Goethals (*Rec. Trav. chim.*, 1935, **54**, 299. [c] Few and Smith's figures (*J.*, 1949, 3057) recalculated, with $P_E + P_A = R_D$. [d] Katritzky, Randall, and Sutton, *J.*, 1957, 1769. [e] Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.

(153° [29])], were prepared by reduction of the appropriate methylpyridine 1-oxide with phosphorus trichloride followed by drying and fractionation in the column mentioned.[30]

In all cases, solid samples were stored under a high vacuum in the dark and in the presence of phosphoric oxide and wax shavings for at least 2 days before use. For deliquescent compounds, the desiccator was refilled with dry nitrogen before opening. Liquids were used immediately after distillation, or, where this was not possible, stored in small Quickfit stoppered flasks with a minimum of air-space and in the dark.

Results.—At least six solutions varying in weight fraction between 0·001 and 0·015 were used in each determination of dipole moment. Solute–solute interactions have been assumed to be negligible in this concentration range, and in all cases the plots of dielectric constant (ε_{12}), specific volume (v_{12}), and squares of the refractive indices (n_{12}^2) against their weight fractions showed no deviation from linearity. The equations employed were $\varepsilon_{12} = \varepsilon_1 + \alpha w_2$, $v_{12} = v_1 + \beta w_2$, and $n_{12}^2 = n_1^2 + \gamma w_2$, where α, β, and γ were calculated from the quotients shown below in order to avoid giving undue weight to the results in the most dilute solutions:

$$\alpha = \sum(\varepsilon_{12} - \varepsilon_1)/\sum w_2, \qquad \beta = \sum(v_{12} - v_1)/\sum w_2, \qquad \gamma = \sum(n_{12}^2 - n_1^2)/\sum w_2$$

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[29] Coulson and Jones, *J. Soc. Chem. Ind.*, 1946, **65**, 169.
[30] Ray, *Rev. Sci. Instr.*, 1957, **28**, 200.

TABLE 3. *Polarisation, relative polarisation, and dipole-moment changes.*

	$_2P_\infty$ (B) (c.c.)	$_2P_\infty$(CT) (c.c.)	ΔP (c.c.)	$\Delta P/_2P_\infty$ (B)	μ_B (D)	μ_{CT} (D)	$\Delta\mu$ (D)	pK_a
Butylamine	61·13[b]	71·65[a]	+10·52	0·172	1·34	1·51	+0·17	10·6[i]
Piperidine	52·78[a]	61·62[a]	+8·84	0·167	1·13	1·29	+0·16	11·1[j]
Triethylamine	50·10[c]	53·16[a]	+3·06	0·061	0·91	0·98	+0·07	10·78[k]
4-Methylpyridine	167·88[d]	183·77[a]	+15·89	0·095	2·60	2·75	+0·15	6·02[l]
4-t-Butylpyridine	195·26[d]	212·33[a]	+17·07	0·087	2·73	2·87	+0·14	5·99[l]
2,6-Dimethylpyridine	90·13[a]	98·74[a]	+8·61	0·096	1·64	1·78	+0·14	6·75[l]
3-Methylpyridine	147·63[a]	161·75[a]	+14·12	0·096	2·41	2·54	+0·13	5·68[l]
3-Isopropylpyridine	158·20[a]	172·49[a]	+14·29	0·090	2·43	2·55	+0·12	5·72[l]
Pyridine	127·8[e]	138·8[e]	+11·0	0·086	2·25	2·37	+0·12	5·29[m]
4-Phenylpyridine	182·81[a]	193·07[a]	+10·26	0·056	2·55	2·64	+0·09	—
2-Phenylpyridine	123·88[a]	127·48[a]	+3·60	0·029	1·88	1·92	+0·04	—
4-Nitropyridine	82·00[f]	80·47[a]	−1·53	−0·019	1·58	1·55	−0·03	—
Isoquinoline	181·0[e]	184·4[e]	+3·4	0·019	2·61	2·65	+0·04	5·14[j]
Quinoline	144·4[e]	147·1[e]	+2·7	0·019	2·24	2·27	+0·03	4·94[j]
2,6-Diphenylpyridine	125·11[a]	121·17[a]	−3·94	−0·031	1·55	1·53	−0·02	—
8-Hydroxyquinoline	191·48[g]	188·24[a]	−3·24	−0·017	2·68	2·66	−0·02	—
Aniline	78·35[h]	77·59[a]	−0·76	−0·010	1·53	1·50	−0·03	4·58[l]
4-Methylpyridine 1-oxide	448·90[a]	540·71[a]	+91·81	0·205	4·50	4·97	+0·47	—

B = Benzene. CT = Carbon tetrachloride.

$\Delta P = {_2P_\infty}$ (in CT) $-$ $_2P_\infty$ (in B). $\Delta\mu = \mu$ (in CT) $- \mu$ (in B).

[a] This investigation. [b] Few and Smith's figures (*J.*, 1949, 2663) recalculated with $R_D = P_E + P_A$. Barclay, Le Fèvre, and Smythe (*Trans. Faraday Soc.*, 1950, **46**, 812). [d] Cumper, Vogel, and Walker.[14] [e] Buckingham, Le Fèvre, *et al.*[12] [f] Katritzky, Randall, and Sutton (*J.*, 1957, 1769). [g] Richards and Walker.[10] [h] Few and Smith, *J.*, 1949, 3057. [i] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469. [j] From Rodd.[20] [k] Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261. [l] Brown and Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723. [m] Jaffé and Doak, *ibid.*, p. 4441.

The molar polarisation ($_2P_\infty$) and R_D value at infinite dilution were calculated from the equations:

$$_2P_\infty = M_2[3\alpha v_1/(\varepsilon_1 + 2)^2 + (\varepsilon_1 - 1)(v_1 + \beta)/(\varepsilon_1 + 2)]$$

$$R_D = M_2[3\gamma v_1/(n_1^2 + 2)^2 + (n_1^2 - 1)(v_1 + \beta)/(n_1^2 + 2)]$$

where ε_1 was taken as 2·2725, n_1^2 as 2·24331, and v_1 as 1·14445. The dipole moment (μ) was obtained from the usual relation, $\mu = 0{\cdot}01281(P_0T)^{\frac{1}{2}}$. P_0 was calculated by assuming that $P_E + P_A = R_D$. In fact, R_D is less than $P_E + P_A$, and the true dipole moment values are inexact to this extent. If, however, the P_A values are not strongly solvent-dependent, then the resultant dipole-moment difference is not greatly in error.

Tables 1—3 give detailed results.

DISCUSSION

Table 3 shows that the difference in moment between carbon tetrachloride and benzene solution ($\Delta\mu$) varies from slightly negative to 0·17 D for the amines, and to 0·47 D for 4-methylpyridine 1-oxide. The differences in total polarisation range up to 17·1 c.c. for the amines. Changes in total polarisation of this magnitude are unlikely to be solely due to increases in atomic polarisation, as suggested by Le Fèvre and his co-workers. The change in total polarisation of 4-methylpyridine 1-oxide (91·8 c.c.) is nearly three times the R_D value of that compound in benzene. Further, the known P_A and P_E values for pyridine are 1·5 and 23·0 c.c. respectively.[31] An increment of 11·0 c.c. in P_A for this compound in carbon tetrachloride is hardly conceivable. The dipole moments can best be explained by a donor–acceptor type of interaction, a transient increase in polarisation occurring as carbon tetrachloride molecules approach the vicinity of the lone-pair electrons of the nitrogen atom. Such an interaction would increase the total polarisation of the system, partly by increasing the atomic polarisation of the interacting molecules and partly by a change in dipole moment. The alternative explanation of the dipole moment differences as being due to interaction of the amines with the π-electron clouds of benzene can be discounted because of the similarity of the dipole moments of 4-methylpyridine,

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[31] Cartwright and Errera, *J. Proc. Roy. Soc.*, 1936, *A*, **154**, 138.

and also of pyridine 1-oxide, in benzene and cyclohexane. There are other cases to support this.[32]

The observed increase should depend on two factors: (i) The stability of the adduct, where the total polarisation might be expected to increase as the basicity of the amine increases. The $\Delta\mu$ values would then show some dependence on the pK_a of the amine. If $\Delta\mu$ or ΔP is plotted against pK_a an approximately straight line is obtained for those molecules where the steric factors in the 2- and the 6-position are small. (ii) Since the bonding cannot be very strong, the number of solvent molecules passing near the nitrogen atom should depend on the total volume of approach that is available. The effect should, thus, be very dependent on steric factors. The steric effect is lowest in pyridines having no 2-substituent; this may account for their $\Delta\mu$ values which are high in relation to basicity.

The steric effect is well illustrated by 2-substituted pyridines. A 2-phenyl group cuts off about half the approach that is available in pyridine itself, although the basicity can hardly alter greatly. The $\Delta\mu$ value (0·04 D) is considerably less than that of pyridine. A second phenyl group (in the 6-position) almost completely blocks the approach of carbon tetrachloride molecules: the $\Delta\mu$ value is then —0·02 D. A slightly negative value was also found for aniline and 8-hydroxyquinoline, in both of which interaction can be expected to be negligible. Although 2,6-dimethylpyridine has a higher pK_a than pyridine, the steric effect of the two methyl groups limits the increase in dipole moment which might be expected (0·14 D). The steric effect of the methyl groups in this compound has been previously reported.[33]

The $\Delta\mu$ value for 4-nitropyridine is —0·03 D, but since the total dipole moment acts in the opposite direction to the nitrogen lone-pair dipole, the value required for comparison is +0·03 D. A low value would be expected in view of the probable reduction in basic strength as a result of electron-withdrawal by the nitro-group. Similar $\Delta\mu$ values are found for quinoline and isoquinoline which have lower basicities than pyridine.

In aliphatic amines, the alkyl groups and the amino-hydrogen atoms considerably obstruct the approach of carbon tetrachloride molecules, reducing the effect of their high basicity. In butylamine ($\Delta\mu$ 0·17 D) there are a number of rotational configurations in which approach is blocked.

It is impossible for the three ethyl groups all to lie " behind " the nitrogen atom at the same time in triethylamine; one of the groups must project over the nitrogen atom, thus shielding it from the approach of carbon tetrachloride molecules. As was expected, the $\Delta\mu$ value (0·07 D) was less than that of butylamine. The effect of the three ethyl groups in hindering the formation of co-ordination compounds has been previously reported.[34]

Piperidine has the highest basicity of the amines considered here, but again approach to the nitrogen atom is considerably restricted, not only by the adjacent CH_2 groups and the amino-hydrogen atom, but also by the remainder of the molecule since the ring is puckered. The $\Delta\mu$ value (0·16 D) appears reasonable in view of this.

Physical evidence indicates that the interaction of aniline with carbon tetrachloride is negligible.[9] The basicity is low, and approach to the nitrogen atom is also hampered by the amino-hydrogen atoms. The $\Delta\mu$ value found was —0·03 D. Infrared [35] and dipole-moment work [10] indicates that 8-hydroxyquinoline is strongly intramolecularly hydrogen bonded. Formation of any complex involving the lone pair of the nitrogen atom is, thus, not feasible. The $\Delta\mu$ value was —0·02 D, in accord with the values obtained for aniline and 2,6-diphenylpyridine. In these cases, this small negative value appears to be the straightforward solvent effect.

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[32] See Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts, 1948.

[33] Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 640.

[34] Ref. 33, p. 642.

[35] Bellamy and Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220.

The dipole-moment values obtained for pyridine 1-oxide and 4-methylpyridine 1-oxide differ from reported values because of complete exclusion of water. The effect of traces of moisture on the dipole moments of the pyridine oxides will be discussed in a later paper. The result indicates that a large increase in dipole moment may occur in carbon tetrachloride solution. This is not unreasonable, since the compounds are basic and the oxygen atoms may act as donors in a number of co-ordination complexes.[36] Moreover, there are two sets of lone-pair electrons on the oxygen atom, which extend well away from the bulk of the molecule and so are more favourably placed for interaction with carbon tetrachloride molecules.

The results as a whole are consistent with the concept of donor–acceptor interaction where carbon tetrachloride is the acceptor. Such interaction should be exothermic, and the heats of mixing of a number of substituted pyridines with benzene and carbon tetrachloride are at present being measured. The results so far agree well with the conclusions from dipole moments, the heat of mixing with benzene being small and mainly negative, but with carbon tetrachloride appreciably positive; the quantity of heat evolved is higher for compounds with high $\Delta\mu$ values.

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[36] Katritzky and Lagowski, " Heterocyclic Chemistry," Methuen, London, 1960, p. 104.