278. *Indicator Measurements with Amines in Anisole and Chlorobenzene Solution.*

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The basic strengths of 21 amines have been compared in anisole and chlorobenzene solutions by measuring their equilibria with the indicators 2 : 6-dinitrophenol and bromophenol-blue. The data are best interpreted quantitatively by assuming that the binary complexes of base and indicator are not associated further in solution, and do not dissociate into ions. The indicator constants in chlorobenzene differ very little from those in anisole. The values obtained provide a more rational account of the effect of alkyl substitution on basic strength than do dissociation constants in water, and it is concluded that the anomalies in the latter are largely due to hydrogen-bonding with the solvent. The indicator constants for amines in anisole bear a close relationship to their catalytic constants in the decomposition of nitramide in the same solvent.

If dissociation constants in water are used as a measure of the basic strengths of amines there are many apparent anomalies in the relations between structure and strength (cf., *e.g.*, the numerous data given by Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469). In particular, it appears that the dissociation constants of primary, secondary, and tertiary amines are not directly comparable, and this effect has been attributed to hydrogen-bonding between water molecules and either the amine molecules (Moore and Winmill, *J.*, 1912, **101**, 1635) or their cations (Trotman-Dickenson, *J.*, 1949, 1293; Evans and Hammann, *Trans. Faraday Soc.*, 1951, **47**, 34). It is therefore desirable to obtain data for the basic strengths of amines in non-hydroxylic solvents, and this is most readily done by means of indicator measurements. It is well known that there are often difficulties in the quantitative interpretation of indicator measurements in non-aqueous solvents (cf., *e.g.*, LaMer and Downes, *J. Amer. Chem. Soc.*, 1931, **53**, 888; Baggesgaard-Rasmussen and Reimers, *Dansk Tidsskr. Farm.*, 1933, **7**, 225; Griffiths, *J.*, 1938, 818), and our aim in the present investigation has been to obtain approximate comparable values for a large number of amines rather than to make an exact quantitative study of any one system. The solvents used were chlorobenzene and anisole, since these are devoid of any acidic properties and have been used previously in kinetic work on acid–base catalysis.

EXPERIMENTAL

Chlorobenzene and anisole were distilled, dried over phosphoric oxide, and redistilled through a column. The indicators used were 2 : 6-dinitrophenol and bromophenol-blue: the former was recrystallized from alcohol (m. p. 63·0°), and both were dried *in vacuo* over phosphoric oxide. Most of the amines were dried over potassium hydroxide for several days and then distilled. Their b. p.s were within 1° of the accepted values. *p*-Toluidine was dissolved in ligroin and shaken with activated alumina. It was then recrystallized twice and dried over phosphoric oxide *in vacuo* (m. p. 45°). Quinoline was precipitated as dichromate, which was decomposed by potassium hydroxide, and the amine separated by steam distillation, drying, and distilling *in vacuo*. *iso*Quinoline was partially frozen, distilled, and then fractionally frozen three times (m. p. 23—23·5°). All the amines were colourless, and gave colourless solutions in chlorobenzene and anisole.

The glass-ware and optical cells used for solutions were baked for at least 2 hours at 150—170° before use, and left in a vacuum-desiccator over pellets of potassium hydroxide. If these precautions were not taken some of the bromophenol-blue was liable to be adsorbed as a yellow film on the glass surfaces. This adsorption was particularly strong with soda-glass, and all cells and other vessels used were of Pyrex or Hysil glass. The absorption of the solutions was measured with a Hilger Spekker absorptiometer, 1-cm. cells and the mercury 4047 Å line being used. In making a measurement, the cell was warmed slightly above 25°, and the reading taken when it had cooled to 25° after a few minutes in the instrument.

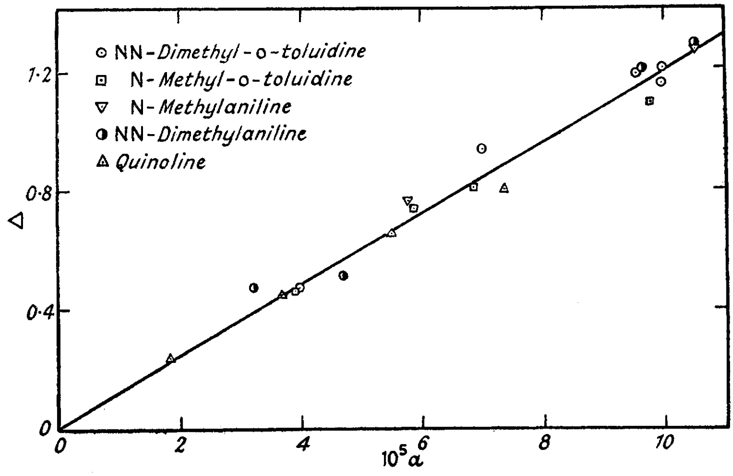
Dry solutions of both indicators are colourless, but on adding amine solution a yellow colour is produced and reaches a constant absorption when a large excess of base is added. Typical figures are given in Table 1. The negligible absorption found at 5780 Å shows that the change yellow ⟶ blue (normally used in aqueous solution) is not involved, and the same is true for all the aromatic and heterocyclic amines studied. With strong aliphatic amines, on the other hand, bromophenol-blue gives a red or purple colour (cf. Davis, Schuhmann, and Lovelace, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 27) and was therefore not used for studying these amines. Similarly, 2 : 6-dinitrophenol with some aromatic bases gives a brown colour which differs from the usual yellow colour of the basic form. It is thought that this phenomenon is due to complex formation of the same type which occurs between nitro-compounds and a variety of aromatic hydrocarbons, and 2 : 6-dinitrophenol was therefore only used with aliphatic amines.

TABLE 1. *Addition of* NN-*dimethyl*-o-*toluidine to bromophenol-blue in chlorobenzene.*

(Δ = change produced in drum reading by addition of amine; indicator concentration = $0{\cdot}952 \times 10^{-4}$ mole/litre.)

[Amine] ……	$3{\cdot}65 \times 10^{-5}$	$1{\cdot}82 \times 10^{-4}$	$9{\cdot}12 \times 10^{-4}$	$1{\cdot}82 \times 10^{-3}$	$9{\cdot}12 \times 10^{-2}$	$1{\cdot}0 \times 10^{-1}$	$2{\cdot}0 \times 10^{-1}$
Δ(4047 Å) …	0·23	0·64	0·08	1·14	1·18	1·22	1·22
Δ(5780 Å) …	$0{\cdot}00_2$	$0{\cdot}00_6$	$0{\cdot}00_5$	$0{\cdot}00_7$	$0{\cdot}00_5$	0·02	0·01

FIG. 1. *Bromophenol-blue in chlorobenzene.*



With the above reservations the absorption at 4047 Å of the basic form of each indicator was proportional to the indicator concentration and approximately independent of the nature of the amine which had been added in excess. This is illustrated in Figs. 1—3, which give plots of the Spekker reading Δ (proportional to the extinction coefficient of the solution) against the indicator concentration a. It may therefore be assumed that the change observed represents a true acid–base reaction, and that any association phenomena which may occur have little effect on the validity of Beer's law. Similar results are obtained in other solvents, and Table 2 gives the molar extinction coefficients of the basic form of bromophenol-blue in various solvents. The variations are no greater than would be expected from the changes of medium involved.

TABLE 2. *Molar extinction coefficients* (ε) *of the basic form of bromophenol-blue.*

Solvent	$10^{-3}\,\varepsilon$	Solvent	$10^{-3}\,\varepsilon$	Solvent	$10^{-3}\,\varepsilon$
Chlorobenzene …………	11·1	Carbon tetrachloride ……	14·2	Dioxan ………………………	11·4
Anisole …………………	12·2	Chloroform ………………	12·5	Ethyl acetate ……………	14·2

Calculation of Equilibrium Constants.—The measurements of colour lead directly to the proportion of indicator in the basic form, but the further treatment of the results depends upon what assumption is made about the state of the reaction products, in particular whether the ions formed are free or are associated together in some way. We have calculated equilibrium constants on the assumption of association to form ion-pairs; *i.e.*, if B is the base and IH the indicator, the indicator constants are defined by

$$[BH^+,I^-]/[B][IH] = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This choice is supported by accurate work on the reaction between tribenzylamine and picric acid in benzene solution (Davis and McDonald, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 595) which agrees well with equation (1). The concentration of free ions in such solutions is negligible (Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3614), and measurements of dielectric constant indicate that the further association of the ion-pairs is small at the concentrations used here (Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 1). With some systems the values of K have a tendency to increase with increase in colour, as would be expected if further association of ion-pairs is taking place. However, in most cases the variations are random, and other methods of calculating the equilibrium constant (*e.g.*, assuming free ions, or binary association of ion pairs) give large systematic variations. If a is the total indicator concentration, b the concentration of base added, and r the ratio [coloured form of indicator]/[colourless form of indicator], then equation (1) becomes

FIG. 2. *Bromophenol-blue in anisole.*

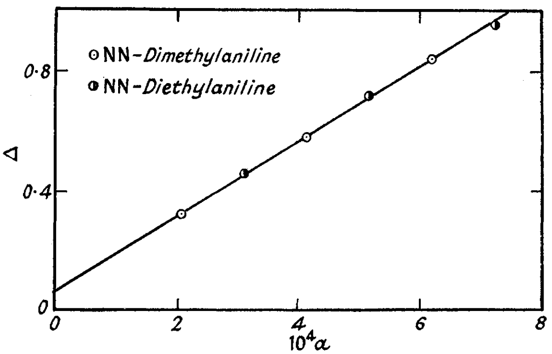
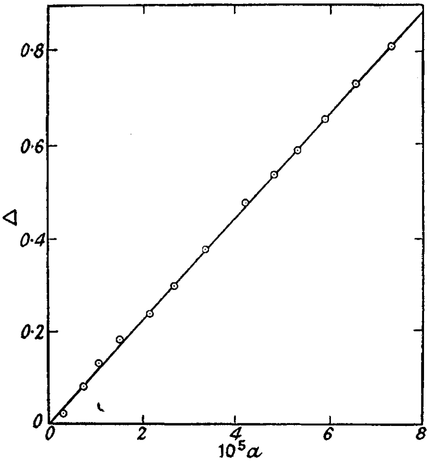


FIG. 3. *Excess of* n-*butylamine added to* 2 : 6-*dinitrophenol in chlorobenzene.*



$$r(1 + r)/[b(1 + r) - ar] = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation was used in calculating all the constants given in the following tables, r being derived directly from the Spekker reading and the absorption of the basic form of the indicator as shown in Figs. 1—3.

Tables of Results.—In the following tables all concentrations are expressed in moles per litre of solution, and the error attached to the mean values of the constants represents the probable error calculated from the usual statistical expressions.

TABLE 3. 2 : 6-*Dinitrophenol in chlorobenzene.*

10^4b	10^4a	r	$10^{-2}K$	10^4b	10^4a	r	$10^{-2}K$	10^4b	10^4a	r	$10^{-2}K$
	n-*Butylamine.*				*Di*-n-*butylamine.*				*Tri*-n-*butylamine.*		
0·974	1·06	0·122	14	0·293	1·06	0·213	200	0·335	1·06	0·393	990
2·82	1·06	0·422	17	0·677	1·06	0·515	160	0·658	1·06	0·937	650
3·70	1·06	0·581	18	0·971	1·06	0·852	180	0·978	1·06	1·77	590
5·35	1·06	0·852	19	1·57	1·06	1·60	170	1·27	1·06	2·81	580
8·32	1·06	1·17	15	2·44	1·06	2·71	160	1·83	1·06	5·03	530
		Mean	16 ± 1			Mean	690 ± 140			Mean	170 ± 10

TABLE 4. *Bromophenol-blue in chlorobenzene.*

Aniline.

10^4b	10^4a	r	K
27·1	0·800	0·0236	8·7
56·4	0·996	0·0331	5·9
56·4	0·996	0·0490	8·7
113	0·996	0·134	12
82·2	1·15	0·0763	9·3
137	1·15	0·226	17
138	1·15	0·216	16
45·1	1·20	0·0292	6·5
116	1·44	0·210	18
96	1·73	0·057	16
24·1	2·78	0·0186	7·7
12·1	5·76	0·0153	13
5·50	6·42	0·0056	10
		Mean	11 ± 3

o-*Toluidine.*

10^4b	10^4a	r	K
403	0·599	0·667	17
58	0·996	0·059	10
173	0·996	0·250	15
289	0·996	0·567	20
532	0·996	1·46	27
115	1·60	0·211	18
		Mean	18 ± 4

N-*Ethyl*-o-*toluidine.*

10^4b	10^4a	r	K
3·86	0·50	0·120	310
15·4	0·50	0·49	320
3·26	1·00	0·086	230
7·72	1·00	0·170	230
9·65	1·00	0·27	280
11·6	1·00	0·312	270
15·4	1·00	0·43	280
19·3	1·00	0·54	290
3·86	2·00	0·080	220
11·6	2·00	0·25	220
		Mean	270 ± 20

NN-*Dimethyl*-p-*toluidine.*

10^4b	10^4a	r	K
1·32	0·50	0·33	2800
2·64	0·50	0·69	2800
0·33	1·00	0·089	3600
0·66	1·00	0·180	3500
1·32	1·00	0·36	3400
2·64	1·00	0·69	3100
0·33	2·00	0·075	4000
0·66	2·00	0·150	3700
1·32	2·00	0·30	3500
		Mean	3400 ± 300

Quinoline.

10^4b	10^4a	r	K
0·734	0·50	0·40	6700
1·00	0·50	0·73	9300
0·220	1·00	0·110	9200
0·430	1·00	0·235	9700
1·12	1·00	0·60	8100
2·15	1·00	1·03	6300
5·91	1·00	2·50	4800
1·00	2·00	0·35	7200
		Mean	7500 ± 400

N-*Methylaniline.*

10^4b	10^4a	r	K
5·54	0·288	0·0246	44
11·1	0·288	0·056	50
1·38	1·44	0·0099	73
2·77	1·44	0·0163	60
4·80	1·44	0·0315	66
		Mean	59 ± 7

NN-*Dimethylaniline.*

10^4b	10^4a	r	K
0·820	0·321	0·051	640
1·23	0·321	0·081	680
10·2	0·321	0·567	560
0·614	1·61	0·041	750
1·54	1·61	0·085	600
3·08	1·61	0·165	580
		Mean	630 ± 40

N-*Methyl*-o-*toluidine.*

10^4b	10^4a	r	K
107	0·390	0·725	70
67·0	0·585	0·350	52
84·4	0·683	0·480	57
6·70	0·975	0·050	75
18·1	0·975	0·102	57
26·8	0·975	0·151	57
67·0	0·975	0·469	70
121	0·975	0·781	65
		Mean	63 ± 5

p-*Toluidine.*

10^4b	10^4a	r	K
14·0	0·332	0·031	22
14·0	0·527	0·065	46
5·0	1·05	0·028	57
8·0	1·05	0·032	40
20·0	1·05	0·125	63
30·0	1·05	0·264	88
40·0	1·05	0·508	130
8·0	2·10	0·054	69
14·0	2·10	0·134	97
		Mean	65 ± 20

N-*Ethyl*-p-*toluidine.*

10^4b	10^4a	r	K
1·57	0·50	0·23	1600
3·14	0·50	0·56	1900
0·785	1·00	0·089	1300
1·57	1·00	0·23	1600
3·14	1·00	0·56	2000
0·785	2·00	0·104	1700
1·57	2·00	0·25	2100
3·14	2·00	0·57	2400
		Mean	1800 ± 100

iso*Quinoline.*

10^4b	10^4a	r	K
0·290	0·50	0·22	11000
0·580	0·50	0·57	14000
0·870	0·50	0·93	15000
0·290	1·00	0·23	18000
0·290	1·00	0·21	18000
0·580	1·00	0·44	16000
0·870	1·00	0·65	14000
0·580	2·00	0·27	17000
		Mean	15000 ± 500

N-*Ethylaniline.*

10^4b	10^4a	r	K
6·36	0·50	0·190	300
12·7	0·50	0·326	260
3·18	1·00	0·089	290
6·36	1·00	0·173	280
12·7	1·00	0·452	360
1·59	2·00	0·043	280
3·18	2·00	0·089	300
6·36	2·00	0·202	340
		Mean	300 ± 20

NN-*Diethylaniline.*

10^4b	10^4a	r	K
0·323	0·50	0·386	21000
0·646	0·50	0·906	22000
0·323	1·00	0·312	37000
0·646	1·00	0·671	27000
0·646	2·00	0·394	49000
		Mean	29000 ± 3000

NN-*Dimethyl*-o-*toluidine.*

10^4b	10^4a	r	K
1·99	0·398	0·57	3100
4·07	0·398	1·23	3100
9·04	0·398	3·71	4300
3·98	0·697	1·10	3000
9·04	0·697	2·92	3400
0·994	0·995	0·27	3400
1·99	0·995	0·51	3100
3·98	0·995	1·01	2900
5·97	0·995	1·56	2900
9·04	0·995	2·46	3000
		Mean	3200 ± 300

N-*Methyl*-p-*toluidine.*

10^4b	10^4a	r	K
3·72	0·50	0·160	450
1·86	1·00	0·058	320
3·72	1·00	0·140	390
7·44	1·00	0·33	460
1·86	2·00	0·094	550
1·86	3·66	0·087	560
		Mean	460 ± 50

Pyridine.

10^4b	10^4a	r	K
1·34	0·50	0·36	3000
1·69	0·50	0·53	3500
3·38	0·50	1·03	3300
0·669	1·00	0·160	3000
0·845	1·00	0·244	3800
1·34	1·00	0·33	3000
1·69	1·00	0·45	3300
0·334	2·00	0·070	3500
0·669	2·00	0·133	3100
0·845	2·00	0·196	3800
		Mean	3300 ± 200

TABLE 5. *Bromophenol-blue in anisole.*

Aniline.

10^4b	10^4a	r	K
170	0·50	0·21	12
340	0·50	0·38	11
85	1·00	0·072	9
116	1·00	0·126	11
170	1·00	0·075	10
340	1·00	0·39	11
85	2·00	0·072	9
170	2·00	0·24	14

Mean 11 ± 1

N-*Methylaniline.*

10^4b	10^4a	r	K
54·6	0·50	0·23	43
137	0·50	0·73	53
27·3	1·00	0·143	53
54·6	1·00	0·35	64
137	1·00	0·70	51
13·7	2·00	0·076	56
27·3	2·00	0·150	56
54·6	2·00	0·34	63

Mean 55 ± 4

NN-*Dimethylaniline.*

10^4b	10^4a	r	K
2·45	0·50	0·169	710
4·90	0·50	0·35	740
9·80	0·50	0·64	670
1·23	1·00	0·098	860
2·45	1·00	0·165	710
2·45	1·00	0·174	760
4·90	1·00	0·34	730
1·23	2·00	0·089	840
4·09	2·00	0·30	680

Mean 740 ± 40

N-*Ethylaniline.*

10^4b	10^4a	r	K
10·3	0·50	0·28	270
20·6	0·50	0·53	260
41·2	0·50	1·03	250
5·15	1·00	0·145	290
10·3	1·00	0·298	290
20·6	1·00	0·56	280
5·15	2·00	0·121	250
10·3	2·00	0·24	240

Mean 270 ± 10

o-*Chloroaniline.*

10^4b	10^4a	r	K
1290	0·50	0·34	2·6
1310	0·50	0·27	2·1
647	1·00	0·074	1·1
655	1·00	0·107	1·6
1290	1·00	0·176	1·4
1310	1·00	0·145	1·1
2590	1·00	0·369	1·4
647	2·00	0·043	0·7
655	2·00	0·049	0·8
1290	2·00	0·082	0·6

Mean 1·3 ± 0·2

m-*Chloroaniline.*

10^4b	10^4a	r	K
4050	0·50	0·87	2·1
1010	1·00	0·093	0·9
1350	1·00	0·176	0·9
2030	1·00	0·207	1·0
1010	2·00	0·070	0·6
2030	2·00	0·143	0·7

Mean 0·9 ± 0·2

o-*Toluidine.*

10^4b	10^4a	r	K
157	0·50	0·102	6·5
314	0·50	0·24	7·6
157	1·00	0·117	7·5
314	1·00	0·29	9·2
629	1·00	0·86	14
79	2·00	0·072	9·2
157	2·00	0·170	10·9

Mean 9·3 ± 1·6

N-*Methyl*-o-*toluidine.*

10^4b	10^4a	r	K
61·8	0·50	0·26	41
123·6	0·50	0·61	49
30·9	1·00	0·145	47
61·8	1·00	0·35	58
123·6	1·00	0·68	55
30·9	2·00	0·150	49
61·8	2·00	0·301	49

Mean 48 ± 4

NN-*Dimethyl*-o-*toluidine.*

10^4b	10^4a	r	K
1·46	0·50	0·47	3600
2·92	0·50	0·92	3400
0·73	1·00	0·24	4500
0·73	1·00	0·175	4100
1·46	1·00	0·40	3400
0·37	2·00	0·098	5300

Mean 4100 ± 500

N-*Ethyl*-o-*toluidine.*

10^4b	10^4a	r	K
6·60	0·50	0·26	400
13·2	0·50	0·59	450
26·4	0·50	1·41	490
3·30	1·00	0·13	420
6·60	1·00	0·23	350
13·2	1·00	0·51	400
1·65	2·00	0·043	280
3·30	2·00	0·072	230
6·60	2·00	0·15	230

Mean 360 ±70

p-*Toluidine.*

10^4b	10^4a	r	K
38·2	0·50	0·19	50
76·4	0·50	0·38	50
19·1	1·00	0·103	54
38·2	1·00	0·21	56
76·4	1·00	0·47	62
19·1	2·00	0·117	62
38·2	2·00	0·22	60

Mean 56 ± 3

N-*Methyl*-p-*toluidine.*

10^4b	10^4a	r	K
4·94	1·00	0·136	280
9·88	1·00	0·30	310
19·7	1·00	0·68	350
4·94	2·00	0·150	320
9·88	2·00	0·32	340
9·88	2·00	0·30	330
19·7	2·00	0·64	310

Mean 320 ±15

NN-*Diethylaniline.*

10^4b	10^4a	r	K
0·516	0·50	0·77	13000
1·03	0·50	1·76	20000
0·258	1·00	0·24	38000
0·516	1·00	0·51	28000

Mean 25000 ± 3000

p-*Chloroaniline.*

10^4b	10^4a	r	K
2400	0·50	0·140	0·6
600	1·00	0·062	1·0
1200	1·00	0·136	1·1
2400	1·00	0·313	1·3
300	2·00	0·023	0·8
600	2·00	0·057	0·9

Mean 0·9 ± 0·2

NN-*Dimethyl*-p-*toluidine.*

10^4b	10^4a	r	K
0·523	0·50	0·130	2800
1·05	0·50	0·25	2600
0·262	1·00	0·063	3100
0·523	1·00	0·126	3100
1·05	1·00	0·23	2700
0·262	2·00	0·055	3500
0·523	2·00	0·101	3100

Mean 3000 ± 200

N-*Ethyl*-p-*toluidine.*

10^4b	10^4a	r	K
1·42	0·50	0·17	1300
2·84	0·50	0·32	1200
0·71	1·00	0·081	1300
1·42	1·00	0·16	1300
2·84	1·00	0·29	1100
0·71	2·00	0·053	900
1·42	2·00	0·120	1000

Mean 1100 ± 100

Pyridine.

10^4b	10^4a	r	K
0·70	0·50	0·32	5500
1·40	0·50	0·56	4600
0·35	1·00	0·140	6200
0·35	1·00	0·140	6200
0·70	1·00	0·26	5300
0·70	1·00	0·28	5800
1·40	1·00	0·51	4800
1·40	1·00	0·54	5100
0·35	2·00	0·103	6300
0·70	2·00	0·44	5500

Mean 5600 ± 400

Quinoline.

10^4b	10^4a	r	K
0·427	0·50	0·26	7800
0·853	0·50	0·53	7800
0·213	1·00	0·117	11000
0·427	1·00	0·22	8800
0·853	1·00	0·46	8500
0·213	2·00	0·081	13000
0·427	2·00	0·160	11000

Mean 9700 ± 1000

iso*Quinoline.*

10^4b	10^4a	r	K
0·366	0·50	0·30	12000
0·732	0·50	0·64	12000
0·183	1·00	0·122	17000
0·366	1·00	0·22	12000
0·732	1·00	0·49	12000
0·183	2·00	0·074	17000
0·366	2·00	0·145	13000

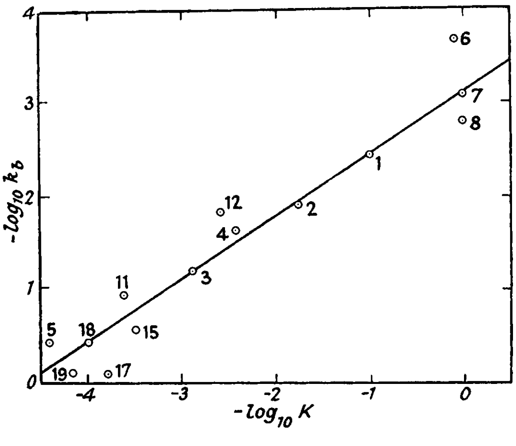
Mean 14000 ± 1500

TABLE 6. *Summary of results with bromophenol-blue in chlorobenzene and anisole.*

pK_b values in water from Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469); k_b = catalytic constant in the decomposition of nitramide (Bell and Trotman-Dickenson, *J.*, 1949, 1288).

		$-\log_{10} K$		pK_b	$-\log_{10}k_b$
	Base	PhCl	Ph·OMe	(H_2O)	(Ph·OMe)
1.	Aniline	−1·0	−1·0	9·42	2·46
2.	*N*-Methylaniline	−1·8	−1·74	9·15	1·92
3.	*NN*-Dimethylaniline	−2·80	−2·87	8·94	1·19
4.	*N*-Ethylaniline	−2·48	−2·43	8·89	1·64
5.	*NN*-Diethylaniline	−4·5	−4·4	7·44	0·44
6.	*o*-Chloroaniline	—	−0·1	11·4	3·70
7.	*m*-Chloroaniline	—	0·0	10·48	3·11
8.	*p*-Chloroaniline	—	0·0	10·00	2·83
9.	*o*-Toluidine	−1·26	−1·0	9·61	—
10.	*N*-Methyl-*o*-toluidine	−1·80	−1·68	9·41	—
11.	*NN*-Dimethyl-*o*-toluidine	−3·51	−3·61	8·14	0·94
12.	*N*-Ethyl-*o*-toluidine	−2·43	−2·6	9·07	1·83
13.	*p*-Toluidine	−1·8	−1·75	8·93	—
14.	*N*-Methyl-*p*-toluidine	−2·66	−2·51	8·67	—
15.	*NN*-Dimethyl-*p*-toluidine	−3·53	−3·48	8·50	0·58
16.	*N*-Ethyl-*p*-toluidine	−2·43	−2·6	9·07	1·83
17.	Pyridine	−3·52	−3·75	8·63	0·09
18.	Quinoline	−4·0	−3·99	9·00	0·44
19.	*iso*Quinoline	−4·2	−4·15	8·76	−0·11

FIG. 4.



DISCUSSION

The indicator constants obtained are not of high accuracy, but are adequate for a semi-quantitative discussion of the effect of substitution. Table 6 shows that the values of K in chlorobenzene and anisole lie very close together in spite of considerable differences in chemical nature and dielectric constant of the solvents. This is good evidence that neither solvent is playing any specific part in determining the position of equilibrium, and the data are therefore more suitable than basic strengths in aqueous solution for judging the effects of substituents. This appears most clearly in the results for the three butylamines in chlorobenzene (Table 3). The three indicator constants are 1600, 17 000, and 69 000 for the primary, secondary, and tertiary amine, respectively, showing the expected progressive effect of introducing the butyl groups. In aqueous solution, on the other hand, the values of pK_b are 3·39, 2·69, and 4·07 : the unexpected rise from the secondary to the tertiary amine occurs also with other aliphatic amines in water, and is no doubt due to hydrogen-bonding between the water and the amine cations (cf. Trotman-Dickenson, *loc. cit.*).

The indicator constants for the aromatic amines (Table 6) follow the expected trends, which do not differ qualitatively from those found in aqueous solution. Successive substitution of methyl groups in the amino-group increases the basic strength, the second one producing a larger change than the first. The effect of ethyl is considerably greater than that of methyl. A methyl group in the ring *o*- or *p*- to the amino-group also increases the basic strength, though the effect is smaller than that of *N*-substitution. Here again some of the results in water are anomalous, since *o*-toluidine appears to be a weaker base than aniline, and *p*-toluidine stronger than *N*-methylaniline.

It is of interest to compare the indicator constants of the aromatic and heterocyclic amines in anisole with their catalytic constants in the decomposition of nitramide in the same solvent, measured by Bell and Trotman-Dickenson (*J.*, 1949, 1288). The latter are recorded as $-\log_{10}k_b$ in Table 6, and Fig. 4 shows a plot of $\log_{10} k_b$ against $\log_{10} K$. There is an approximately linear relation over more than four powers of ten in K, and there are no signs of the systematic deviations found if dissociation constants in water are used as a measure of basic strength, when separate linear relationships are found for the classes of primary, secondary, tertiary, and heterocyclic amines. Similar behaviour has been observed in the base-catalysed decomposition of nitramide in *iso*amyl alcohol (Brönsted, Delbanco, and Tovborg-Jensen, *Z. physikal. Chem.*, 1934, **169**, *A*, 361), where the observed catalytic constants are related simply to basic strengths measured in the same solvent, but not to basic strengths in water. It is likely that the same situation will arise whenever the range of acid–base systems used as catalysts involves substitution on the atom bearing the proton, since under these conditions the effect of substituents upon acid–base strength in polar solvents will often be complicated by solvation effects.

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