Interaction of Polynitro-compounds with Aromatic Hydrocarbons and Bases. Part XII. Complexes of* N-*Alkylated Anilines with* s-*Trinitrobenzene and* s-*Trinitrotoluene.*

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[Reprint Order No. 5264.]

Colour measurements have been used to derive association constants for the interactions of *N*-alkylanilines with *s*-trinitrobenzene and *s*-trinitrotoluene in *cyclo*hexane. The amounts of interaction between a nitro-compound and members of homologous series have been compared for the *N*-mono- and the *NN*-di-*n*-alkylaniline series. For the higher members of both series, increased chain-length results in complexes of greater stability. The wave-length of maximum absorption due to the interaction rises with the first few members of both these series, thereafter remaining sensibly constant. The effect of changing the solvent has also been measured.

The results are discussed mainly in the light of Mulliken's concept of charge-transfer complexes (*J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801).

Interactions between nitro-compounds (Lewis acids) and bases, including Lewis bases such as aromatic hydrocarbons, appear to be of two kinds. There are those which take place slowly, usually with change of colour, and yield new compounds which can be isolated and to which definite structures can be assigned. Such is the compound obtained by Meisenheimer (*Annalen*, 1902, **323**, 219) from the action of the bases OMe^- and OEt^- on *s*-trinitrophenetole and *s*-trinitroanisole respectively. These interactions involve *s*-orbital functions of the carbon atoms and result in the formation of new covalent bonds. Secondly, there are interactions which take place instantaneously and may or may not involve an alteration in the electronic absorption bands. No new localised bonds are apparently formed, the forces involved being those of dispersion, polarisation, multi-pole and hydrogen bonding.

An important interaction within this second class is the charge-transfer type of complex described by Mulliken (*J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801). The components of the complexes are presumably held together by the forces arising from the resonance of a no-bond structure involving dispersion, polarisation, and multi-pole forces, with a structure in which there is donation of an electron from one molecule to another (the dative function). It is expected that this type of interaction will permit an excited state not corresponding to higher electronic levels in either component separately, but characteristic of the complex as a whole. Transitions to this state should give rise to absorption in the visible or near ultra-violet region of the spectrum. There is evidence (Ross, Bassin, Finkelstein, and Leach, *J. Amer. Chem. Soc.*, 1954, **76**, 69; Ross and Kuntz, *ibid.*, p. 74) for two types of interaction between two species of molecules, one involving only dispersion and similar forces, the other being a charge-transfer interaction. Optical

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* Part XI, *J.*, 1953, 3817.

methods will normally give an estimate of the degree of charge-transfer complex formation, whereas some other methods such as partition will give a measure of the sum of all types of interaction.

In the present communication we record a study of the interaction of *N*-alkylanilines with *s*-trinitrobenzene and *s*-trinitrotoluene in solution. Light absorption assumed to be characteristic of this type of interaction has been used in an application of the colorimetric method described by Foster, Hammick, and Wardley (*J.*, 1953, 3817) to determine the degree of association.

In the case of interactions of *N*-alkylanilines with *s*-trinitrobenzene and *s*-trinitrotoluene the colours produced correspond to absorption away from the absorption bands of either component so that the methods involving successive approximations are avoided. Most of the determinations were made in *cyclo*hexane. This solvent was chosen primarily because of the small interaction to be expected between solvent and solutes. It also has very low extinction coefficients in the region 200—600 mμ and, compared with many other paraffins, is relatively easy to purify.

An association constant K is defined as :

$$K = [AB]/[A][B] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where [AB], [A], and [B] are the equilibrium concentrations in mole/l. of the complex and the two components respectively. If a and b are the concentrations of the two components on the assumption that there is no interaction, and $b \gg a$, it has been shown (Foster, Hammick, and Wardley, *loc. cit.*) that then :

$$Ka\varepsilon - KD = D/b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ε is the extinction coefficient of the complex, and D the optical density of the solution assumed to be wholly due to the complex. K and ε may be evaluated by plotting D/b against D for a series of solutions of varying b and constant a.

By this method we have determined K and ε for a series of *N*-alkylaniline–*s*-trinitrobenzene and –*s*-trinitrotoluene interactions in various solvents.

EXPERIMENTAL

All solutions were made up by weight in standardised glassware. The optical densities were measured by a Beckman Quartz Spectrophotometer (model DU), 10 mm. cells being used throughout.

Materials.—The *N*-alkylanilines were purified by standard methods. The monoalkylanilines were purified as their hydrochlorides except *N*-*n*-pentylaniline which was purified as its toluene-*p*-sulphonyl derivative. The dialkylanilines were purified by fractionation under reduced pressure. In particular the following hitherto unprepared alkylanilines were obtained by heating the respective alkyl bromides with aniline under the conditions given in Table 1.

TABLE 1. *Preparation of new alkylanilines.*

No.	Product, *N*-subst.	Alkyl bromide (moles)	Aniline (moles)	KOH (moles)	Temp.	Time (hr.)	Yield (%)
1	*N*-*n*-Nonyl	0·12	0·54	—	100°	12	55
2	*N*-*n*-Decyl	0·5	2·7	—	100	10	46
3	*N*-*n*-Undecyl	0·1	0·5	—	100	10	40
4	*NN*-Di-*n*-octyl	0·2	0·1	0·2	130	12	42
5	*NN*-Di-*n*-decyl	0·12	0·06	0·12	130	12	45

	Found (%)					Required (%)			
	C	H	N	Cl	Formula	C	H	N	Cl
1	82·3	11·6	6·0	—	$C_{15}H_{25}N$	82·2	11·4	6·4	—
1, HCl	70·4	10·3	5·5	13·9	$C_{15}H_{25}N,HCl$	70·5	10·2	5·5	13·9
2	82·4	11·6	6·0	—	$C_{16}H_{27}N$	82·4	11·6	6·0	—
2, HCl	71·7	10·4	5·2	—	$C_{16}H_{27}N,HCl$	71·2	10·5	5·2	—
3	83·0	11·7	—	—	$C_{17}H_{29}N$	82·6	11·7	—	—
3, HCl	72·0	10·6	4·9	12·7	$C_{17}H_{29}N,HCl$	71·9	10·7	4·9	12·5
4	82·9	12·5	4·5	—	$C_{22}H_{39}N$	83·3	12·3	4·4	—
4, HCl	—	—	—	9·7	$C_{22}H_{39}N,HCl$	—	—	—	10·0
5	83·5	12·4	3·6	—	$C_{26}H_{47}N$	83·6	12·6	3·7	—
5, HCl	—	—	—	8·5	$C_{26}H_{47}N,HCl$	—	—	—	8·6

Aniline was prepared by the hydrolysis of carefully purified acetanilide.

The b. p.s and refractive indices of the alkylanilines and the m. p.s of some of their hydrochlorides are given in Table 2.

TABLE 2. *Mono- and di-alkylanilines.*

N-Substituent	B. p./mm.	n_{D}^{20}	M. p. of hydrochloride	*N*-Substituent	B. p./mm.	n_{D}^{20}
H	76°/15	1·5863	198°	Di-*n*-propyl	126°/10	1·5272
Methyl	92°/20	1·5704	121	Di-*n*-butyl	96°/2	1·5188
Ethyl	97—97·5°/20	1·5559	176	Di-*n*-pentyl	164°/15	1·5130
n-Propyl ...	100°/10	1·5412	150	Di-*n*-hexyl	188—189°/30	1·5080
n-Butyl	124°/20	1·5331	115	Di-*n*-octyl	197—198°/3 [b]	1·5007
n-Pentyl ...	125°/15	1·5275	93	Di-*n*-decyl	210°/0·7 [c]	1·4966
n-Hexyl	144°/12	1·5230	75—76			
n-Heptyl ...	160°/20 [a]	1·5189	78			
n-Octyl	200°/36	1·5150	82			
n-Nonyl	178°/9	1·5120	84			
n-Decyl	198°/11	1·5094	88			
n-Undecyl ...	205°/10	1·5083	89			
n-Dodecyl ...	M. p. 28°	solid	93			
Dimethyl ...	72—72·5°/10	1·5585	—			
Diethyl	91°/10	1·5421	—			
*iso*Propyl ...	107°/8	1·5392	175·5			
tert.-Butyl ...	92—93°/20	1·5374	—			
*cyclo*Pentyl	144°/19	1·5650	157·5			
*cyclo*Hexyl	167°/24	1·5602	203			
*cyclo*Heptyl	170°/15	1·5605	—			

[a] This agrees with the value given by Hickinbottom (*J.*, 1937, 1119), 160—161°/21 mm., but not with that, 125°/30 mm., quoted by Emerson (*J. Amer. Chem. Soc.*, 1938, **60**, 2023). [b] Hydrochloride, m. p. 99° (not sharp). [c] Hydrochloride, m. p. 101° (not sharp).

*cyclo*Hexane was mechanically stirred with 20% oleum for 12 hr., then washed with dilute potassium permanganate solution and with water, and dried ($CaCl_2$): it had b. p. 81°/762 mm., n_{D}^{20} 1·4267.

n-Hexane was washed six times with 10% oleum, then with water, and dried ($CaCl_2$); the main fraction had b. p. 68·5—69·5°/761 mm., n_{D}^{20} 1·3758.

n-Heptane: A pure sample, washed once with 10% oleum and fractionated, had b. p. 98°/758 mm., n_{D}^{20} 1·3877.

Chloroform, washed six times with water, dried ($CaCl_2$), and distilled, had b. p. 61°/758 mm., n_{D}^{20} 1·4450.

Carbon tetrachloride, purified as described by Smitz-Dumont (*Chem. Ztg.*, 1897, **21**, 511), had b. p. 77°/763 mm., n_{D}^{20} 1·4600.

s-Tetrachloroethane, distilled from potassium carbonate, had b. p. 146°/761 mm., n_{D}^{20} 1·4950.

1 : 4-Dioxan, purified as recommended by Vogel ("A Textbook of Practical Organic Chemistry," Longmans, London, 1948, p. 175), had m. p. 11·0°, n_{D}^{20} 1·4220.

Decalin (*cis-trans* mixture), purified as prescribed by Zelinsky and Turowa-Pollack (*Ber.*, 1932, **65**, 1299), had b. p. 192°/763 mm., n_{D}^{20} 1·4792.

s-Trinitrobenzene, recrystallised four times from alcohol, had m. p. 122°.

s-Trinitrotoluene, recrystallised four times from alcohol, had m. p. 80·5°.

NNN'N'-Tetramethyl-*p*-phenylenediamine was purified as the hydrochloride, the free base being subsequently distilled *in vacuo*. It had m. p. 51°.

TABLE 3. ($a = 3{\cdot}76 \times 10^{-4}$M.)

	Wave-length :	450 mμ		460 mμ		470 mμ		480 mμ		490 mμ		500 mμ	
No.	*b*(M)	*D*	*D*/*b*	*D*	*D*/*b*	*D*	*D*/*b*	*D*	*D*/*b*	*D*	*D*/*b*	*D*	*D*/*b*
1	0·270	0·339	1·25	0·345	1·28	0·351	1·30	0·352	1·30	0·319	1·18	0·296	1·10
2	0·240	0·325	1·35	0·330	1·37	0·338	1·40	0·338	1·40	0·310	1·29	0·285	1·19
3	0·210	0·315	1·50	0·320	1·52	0·325	1·55	0·321	1·53	0·295	1·40	0·273	1·30
4	0·179	0·295	1·65	0·301	1·68	0·307	1·72	0·305	1·70	0·279	1·56	0·260	1·45
5	0·148	0·273	1·84	0·280	1·89	0·286	1·93	0·286	1·93	0·257	1·73	0·242	1·63
6	0·118	0·248	2·10	0·252	2·14	0·256	2·17	0·257	2·18	0·231	1·96	0·217	1·84
7	0·0875	0·212	2·42	0·217	2·48	0·222	2·54	0·222	2·54	0·200	2·29	0·187	2·14

The following are details of a typical determination of an association constant in the case of *NN*-dimethylaniline–*s*-trinitrobenzene in *cyclo*hexane solution; the results given in Tables 4—7 were obtained by the same procedure.

Association Constant for the Interaction between NN-*Dimethylaniline and* s-*Trinitrobenzene in* cyclo*Hexane Solution.*—Beer's law was shown to be obeyed by *NN*-dimethylaniline solutions in

TABLE 4. *Complexes with* s-*trinitrobenzene in* cyclo*hexane solution.*

N-Substituent in aniline	*K* (l./mole)	λ (mμ)	ε$_\lambda$ (l. mole^{-1} cm.$^{-1}$)	Temp.
H	3·0	390	1700	20·0°
	3·3	430[1]	—	20·0
Methyl	7·7	435	1180	20·0
	7·8	435	1190	18·0
Ethyl	8·4	445	1150	19·8
	8·4	445	1100	19·0
n-Propyl	7·3	445	1230	18·5
	7·2	445	1190	18·5
n-Butyl	8·2	445	1180	19·0
	8·6	445	1220	24·5
	8·2	445	1200	19·0
	8·2	445	1190	19·0
n-Pentyl	8·0	445	1120	20·0
	8·0	445	1180	19·0
n-Hexyl	9·1	445	1160	20·0
	8·8	445	1200	19·0
n-Heptyl	9·8	445	1140	18·3
	9·4	445	1180	18·3
n-Octyl	9·0	445	1220	20·0
	9·2	445	1260	18·0
n-Nonyl	10·7	445	1190	18·0
	10·5	445	1250	18·0
n-Decyl	11·3	445	1190	18·0
	11·1	470[1]	1120	18·0
	11·2	445	1140	20·0
n-Undecyl	11·3	445	1080	18·0
	11·1	445	1160	18·0
n-Dodecyl	11·6	445	1070	18·0
	11·6	445	—	18·0
Dimethyl	9·3	450[1]	1260	20·0
	9·5	460[1]	1280	20·0
	9·5	470[1]	1300	20·0
	9·5	480[1]	1300	20·0
	9·5	490[1]	1180	20·0
	9·6	475	1300	20·0
Diethyl	6·5	501	1120	20·0°
	6·6	501	1050	19·5
Di-*n*-propyl	6·5	504	1150	20·0
	6·4	504	—	20·0
Di-*n*-butyl	7·4	505	1120	18·0
	7·4	505	1100	18·0
Di-*n*-pentyl	9·0	510	990	19·0
	9·0	510	1000	19·0
Di-*n*-hexyl	9·8	510	980	19·0
	9·6	510	980	18·7
Di-*n*-octyl	10·0	510	980	18·5
	10·0	510	970	19·0
Di-*n*-decylaniline	9·9	511	960	18·4
	10·2	511	960	20·0
*iso*Propylaniline	6·7	445	1180	20·0
	6·7	445	1240	19·5
tert.-Butylaniline	5·5	440[1]	620	20·0
*cyclo*Pentylaniline	8·5	450	1180	20·0
*cyclo*Hexylaniline	9·3	448[1]	1150	18·0
	9·0	450	1060	20·0
*cyclo*Heptylaniline	9·2	450	1140	18·5
	9·2	445[1]	1200	19·0
Tetramethyl-*p*-phenylenediamine	20·4	600	—	19·0

[1] Wave-lengths other than λ$_{\text{max.}}$.

TABLE 5. *Complexes with* s-*trinitrotoluene in* cyclo*hexane solution.*

N-Substituents in aniline	*K* (l./mole)	λ (mμ)	Temp.	*N*-Substituents in aniline	*K* (l./mole)	λ (mμ)	Temp.
Methyl	3·1	420[a]	21·0°	Di-*n*-butyl	2·5	464	18·0°
Ethyl	3·8	420	20·0	Di-*n*-pentyl	3·0	465[b]	18·5
Dimethyl	5·8	430	19·0	Di-*n*-hexyl	3·5	467[c]	18·0
Diethyl	2·4	440	20·0	*iso*Propyl	2·7	440[a]	20·0
Di-*n*-propyl	2·3	464	20·0	*tert.*-Butyl	2·2	440[a]	20·0

[a] Wave-lengths other than λ$_{\text{max.}}$. [b] ε$_{\text{max.}}$ = 640 l. mole^{-1} cm.$^{-1}$. [c] ε$_{\text{max.}}$ = 600 l. mole cm.$^{-1}$.

TABLE 6. *The complex* NN-*dimethylaniline*–s-*trinitrobenzene in solvents other than* cyclo*hexane.*

Solvent	*K* (l./mole)	λ$_{\text{max.}}$ (mμ)	ε$_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)	Temp.
n-Hexane	8·2	465	1120	19·0°
n-Heptane	8·2	466	1180	19·4
Decalin	7·2	472	1300	19·4
Carbon tetrachloride	3·4	484	1340	19·0
Chloroform	1·3	486	1140	21·0
s-Tetrachloroethane	0·2	492	—	20·0
1 : 4-Dioxan	0·15	469	—	18·5

TABLE 7. *Complexes with* s-*trinitrobenzene in* n-*heptane.*

Base	*K* (l./mole)	λ$_{\text{max.}}$ (mμ)	ε$_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)	Temp.
N-*n*-Butylaniline	6·2	450	1200	25·0°
N-*n*-Decylaniline	7·2	450	1180	25·0

*cyclo*hexane. Owing to the low solubility, Beer's law for *s*-trinitrobenzene in *cyclo*hexane could not be verified. However the law has been shown to hold for chloroform solutions of *s*-trinitrobenzene.

A series of solutions were made up by weight containing a constant amount of *s*-trinitrobenzene (A), namely, $3{\cdot}76 \times 10^{-4}$M, the concentration of *NN*-dimethylaniline (B) varying as indicated in Table 3. The absorption spectra of solution (1) and a solution of *NN*-dimethylaniline alone in *cyclo*hexane at the same concentration as in (1) were measured in the wavelength region 330—550 mμ to determine the position of the charge-transfer spectrum (Fig. 1). The optical densities of solutions 1—7 were measured at wave-length intervals of 10 mμ from 450 to 500 mμ. The resulting optical densities together with the respective D/b ratios are given in Table 3 from which the respective K and C values in Table 4 are obtained.

The mean temperature of the cell compartment is recorded for each determination in Tables 4—7. In the small range of temperatures involved, the effect of any temperature coefficient appears to be small.

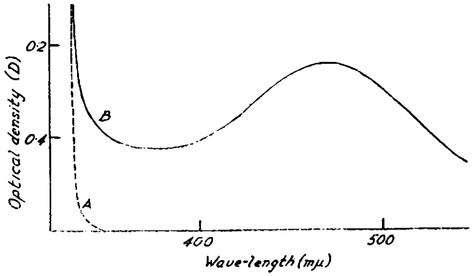


Fig. 1.
A, *Spectrum of* NN-*dimethylaniline* (0·27M) *in* cyclo*hexane.*
B, *Spectrum of a mixture of* NN-*dimethylaniline* (0·27M) *and* s-*trinitrobenzene* ($3{\cdot}76 \times 10^{-4}$M).

Fig. 2. *Association constant* (K) v. *alkyl chain-length of* N-*mono*-n-*alkylaniline*–s-*trinitrobenzene complexes in* cyclo*hexane.*

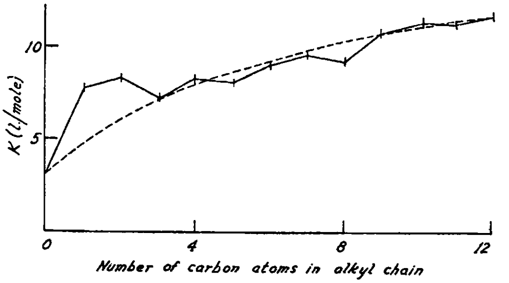
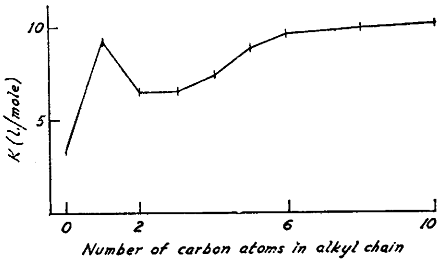


Fig. 3. *Association constant* (K) v. *alkyl chain-length of* NN-*di*-n-*alkylaniline*–s-*trinitrobenzene complexes in* cyclo*hexane.*



In the *N*-mono- and *NN*-di-*n*-alkylaniline series of complexes with *s*-trinitrobenzene, the determinations have all been repeated at least once in the temperature range 18—20°, with samples of alkylaniline prepared by at least two separate syntheses from different samples of the alcohol, with the exception of *N*-*n*-nonyl- and *N*-*n*-undecyl-aniline. Agreement in the final values of K are within ±2·1% of the mean values, with the exception of aniline for which two values within ±5% were obtained. The limits of the differences of the experimental values of K are in every case ±0·2 l./mole. These limits are represented by vertical lines in Figs. 2 and 3. In the case of *NN*-dimethylaniline–*s*-trinitrobenzene in *cyclo*hexane it has been shown that the association constant derived from optical-density measurements over a wave-length range of 50 mμ is constant within this experimental error of 0·2 l./mole.

DISCUSSION

In this discussion it is assumed, in agreement with McConnell and Landauer (*J. Amer. Chem. Soc.*, 1952, **74**, 1221), and Mulliken (*J. Phys. Chem.*, 1952, **56**, 801), that the alkylaniline–*s*-trinitrobenzene and –*s*-trinitrotoluene complexes studied are charge-transfer complexes. At the concentrations and wave-lengths used no evidence for interactions involving a ratio of component molecules other than 1 : 1 has been found. McConnell and Landauer (*loc. cit.*) suggest the presence of 2 : 1 as well as 1 : 1 complexes in an investigation of the interaction of aniline with *s*-trinitrobenzene in chloroform solution. However, these solutions were several times more concentrated than any used in the present work.

Complexes in cyclo*Hexane.*—The association constants (*K*) for the *N*-alkylaniline–*s*-trinitrobenzene complexes range from 3·0 to 11·6 l./mole, and from 2·2 to 5·8 l./mole for the *s*-trinitrotoluene complexes. These results indicate that *s*-trinitrotoluene is a weaker Lewis acid than *s*-trinitrobenzene.

In the monoalkylaniline series, the values of *K* for the respective complexes with *s*-trinitrobenzene tend to increase with increasing alkyl chain-length (Fig. 2), the largest increment in *K* being from aniline to *N*-methylaniline. If a smooth curve is drawn as a correlation of *K* with alkyl chain-length, there appear to be deviations greater than the estimated error of ±0·2 l./mole in *K*. In particular, values of *K* for *N*-methyl- and *N*-ethyl-aniline are large. This may be due to hyperconjugation increasing the electron density in the extended π-orbital system of the alkylanilines, thus increasing their Lewis basicities.

It is difficult to find an explanation for the low value of the association constant of *N*-*n*-octylaniline–*s*-trinitrobenzene. This aniline was synthesised twice from different samples of *n*-octyl alcohol for each of the two determinations of *K*. The infra-red spectrum and the refractive index of the pure base appear to be normal by comparison with other members of this homologous series. Other deviations in Fig. 2 are close to the estimated experimental error, though the comparative smoothness in the variation of *K* in the corresponding *NN*-di-*n*-alkylaniline series of complexes suggests that these deviations may be real. Lack of smoothness might be expected as doubtless many factors, some implicitly steric, are involved in complex formation. Packing effects of the alkyl chain may account for some of the deviations (Anderson and Hammick, *J.*, 1950, 1089).

In the *NN*-di-*n*-alkylaniline complexes with *s*-trinitrobenzene (Fig. 3) there is a large increase in association constant from aniline to *NN*-dimethylaniline, followed by a fall to *NN*-diethylaniline and *NN*-di-*n*-propylaniline, after which there is an increase which appears to be reaching a maximum at about *NN*-di-*n*-decylaniline. A similar effect is observed in the corresponding *s*-trinitrotoluene complexes. The large value of *K* for *NN*-dimethylaniline may again be due to hyperconjugation; this effect may also influence *K* in the *NN*-diethylaniline complex to some extent.

When all the deviations have been considered there remain the trends in the two plots of *K* against alkyl chain-length in which *K* increases with increasing chain-length, the increase becoming less with longer chains. In the dialkyl series the curve appears to reach a maximum at a chain-length of about ten carbon atoms; in the monoalkyl series *K* is still increasing when there are twelve atoms in the alkyl chain. No increase would be expected after *n*-propyl or *n*-butyl, and with longer chains a slight diminution might be expected owing to steric interference. Thus Jones (*J.*, 1935, 1831), when he compared the rates of chlorination of ethers p-X·C_6H_4·OR (X = Cl, Br, CO_2H), found that the effect of the group OR increased in the series R = Me, Et, Pr^n, becoming constant at Bu^n, thereafter falling slightly to R = octadecyl. In contrast to this, Robinson and Smith (*J.*, 1931, 251) have shown that in the nitration of ethers p-MeO·C_6H_4·OR the effect of R = octadecyl is greater than of R = Bu^n or Pr^n. These results of Robinson and Smith correspond with those obtained in the present work, and it seems unlikely that they can be explained by a simple inductive effect. In the case of the polynitrobenzene–alkylaniline complexes however, a dipole induced-dipole structure may be of significance in the no-bond structure in the ground state. The polarisability of the alkylanilines increases with increasing chain-length, and it may be a combination of this increased polarisability with the inductive effect of the alkyl groups in these alkylanilines which results in the observed general relationship between *K* and alkyl chain-length.

In the series of complexes of *s*-trinitrobenzene and *s*-trinitrotoluene with *N*-methyl-, *N*-ethyl-, *N*-*iso*propyl-, and *N*-*tert.*-butyl-aniline the association constants in *cyclo*hexane increase from *N*-methyl- to *N*-ethyl-aniline, thereafter decreasing. Alternative explanations, *e.g.*, loss of hyperconjugation (Cardwell and Kilner, *J.*, 1951, 2435) or steric hindrance, might account for the decrease in the respective association constants after *N*-ethylaniline.

There appears to be little correlation between pK_a values of the alkylanilines and their respective association constants with s-trinitrobenzene (Table 8). This is hardly surprising as the pK_a value is a measure of the Brønsted basicity, while the association constant is presumably a measure of the Lewis basicity of the alkylanilines.

The wave-lengths of maximum absorption of the complexes ($\lambda_{max.}$) have been determined from plots of the spectra of the mixtures. As the components in general do not absorb appreciably in the region of absorption by the complex, it is possible by drawing tie-lines over the upper portion of the absorption curve to obtain an estimate of $\lambda_{max.}$. It is, of course, recognised that this value is only an approximate estimation. $\lambda_{max.}$ increases from 390 to 430 mμ in going from aniline–*s*-trinitrobenzene to *N*-methylaniline–*s*-trinitrobenzene, followed by the smaller increase to 445 mμ for the *N*-ethylaniline complex. Thereafter up to the *N*-*n*-dodecylaniline complex, $\lambda_{max.}$ remains constant in the monoalkyl series of aniline complexes with *s*-trinitrobenzene. There is a similar regularity in the *NN*-dialkylaniline series of complexes. With *s*-trinitrotoluene the corresponding wave-lengths are shorter.

TABLE 8.

Base	K[1] (l./mole)	pK_a (H_2O; 25°)	pK_a (75% alcohol)
Aniline	3·1	4·60[2]	4·14[2]
N-Methylaniline	7·7	4·85[3]	—
N-Ethylaniline	8·4	5·11[3]	4·25[2]
N-*n*-Propylaniline ...	7·2	5·02[3]	—
N-*n*-Butylaniline ...	8·2	—	4·02[2]
N-*n*-Hexylaniline ...	8·9	—	4·02[2]
N-*n*-Octylaniline ...	9·1	—	4·02[2]
NN-Dimethylaniline ...	9·5	5·12[2]	3·90[2]
NN-Diethylaniline	6·5	6·56	5·41[2]
NN-Di-*n*-propylaniline	6·4	5·59[3]	—
NN-Di-*n*-butylaniline...	7·4	—	4·51[2]
NN-Di-*n*-hexylaniline...	9·7	—	4·39[2]
NN-Di-*n*-octylaniline ...	10·0	—	4·37[2]

[1] Association constant of the interaction with *s*-trinitrobenzene in *cyclo*hexane. [2] Wepster, personal communication. [3] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

Compared with the correlation of *K* with chain-length, that of $\lambda_{max.}$ is comparatively simple and may possibly be related to the fact that the inductive effect of the alkyl groups becomes constant after the first few members. Assuming that the excited state is mainly the dative structure A^-B^+ (A representing the nitro-compound, and B the alkylaniline) and that $\lambda_{max.}$ is a function of the energy of excitation from the ground state to this level, then it is clear that the inductive effect of the alkyl groups will have a large effect on this dative structure compared with the effect on the no-bond structure which largely determines the ground state. $\lambda_{max.}$ may therefore be expected to become constant as the inductive effect of the alkyl group becomes constant. On the other hand, *K* takes account of a ground-state no-bond structure in which the dative structure participates only to a small extent (Mulliken, *loc. cit.*).

The values of molar extinction coefficient at the wave-length of maximum absorption ($\varepsilon_{max.}$) for the *N*-monoalkylaniline–*s*-trinitrobenzene complexes are all within the range 1010—1260 l. mole^{-1} cm.$^{-1}$. $\varepsilon_{max.}$ for aniline is considerably higher (1700 l. mole^{-1} cm.$^{-1}$). For the *NN*-dialkylaniline–*s*-trinitrobenzene complexes $\varepsilon_{max.}$ gradually falls from 1270 to 960 l. mole^{-1} cm.$^{-1}$. *N*-*tert.*-Butylaniline–*s*-trinitrobenzene is exceptional in exhibiting no maximum in the wave-length range 360—800 mμ; also $\varepsilon_{445\ m\mu}$ is low (660 l. mole^{-1} cm.$^{-1}$) compared with the extinction coefficient of the corresponding *N*-*n*-butylaniline complex. The two values of $\varepsilon_{max.}$ determined for *s*-trinitrotoluene complexes are considerably lower than the values of the corresponding *s*-trinitrobenzene complexes.

The observation that the intensities of the charge-transfer transitions of the interactions of *N*-alkylanilines with *s*-trinitrobenzene show no strong correlation with the association constants of the interactions or with the wave-lengths of the transitions agrees with the conclusions made after a study of the interaction of iodine with various Lewis bases by McConnell, Ham, and Platt (*J. Chem. Phys.*, 1953, **21**, 66). There does, however, appear to be a correlation between the wave-length of maximum absorption of the charge-transfer spectrum of the complex and the wave-length of the longest ultra-violet absorption maximum of the component alkylaniline for all the *s*-trinitrobenzene interactions studied in the present work (Table 9).

TABLE 9.

Base	$\lambda_{max.}$ (base alone in CXA) (mμ)	$\lambda_{max.}$ (complex with *s*-trinitrobenzene in CXA) (mμ)
Aniline	285	390
N-Methylaniline	296	435
N-Ethylaniline	296	445
N-*n*-Doedcylaniline	296	445
NN-Dimethylaniline	298	475
NN-Diethylaniline	304	501
NN-Di-*n*-propylaniline	305	504
NN-Di-*n*-pentylaniline	305	510
NN-Di-*n*-decylaniline	305	510
NNN'N'-Tetramethyl-*p*-phenylenediamine	328	600

CXA = *cyclo*hexane.

Variation of the Solvent.—For the complex *NN*-dimethylaniline–*s*-trinitrobenzene, the effect of changing the solvent from *cyclo*hexane to *n*-hexane is to reduce the association constant from 9·5 to 8·2 l./mole. There is a small alteration in the wave-length maximum of the charge-transfer spectrum, but the intensity of the absorption remains constant within the limits of experimental error. The association constant is the same in *n*-heptane as in *n*-hexane, and decreases in the series of solvents *n*-hexane > decalin > carbon tetrachloride > chloroform > *s*-tetrachloroethane > 1 : 4-dioxan. The association constant of *NN*-dimethylaniline–*s*-trinitrobenzene in chloroform ($K = 1{\cdot}3$ l./mole) agrees well with that obtained by Ley and Grau (*Ber.*, 1925, **58**, 1765), namely, $K = 1{\cdot}5$ l./mole, though in the present determination particularly dilute solutions had to be used to obtain a linear plot of D/b against D (see above).

Probably the most important cause of variation of association constant with solvent is the competition by the solvent for complex formation. *cyclo*Hexane, which is reported to form a complex with iodine (Hastings, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2900), may also interact with *s*-trinitrobenzene and, though the association constant will undoubtedly be small, the effect may be significant owing to the large concentration of solvent. There appears to be a difference in the order of effect of a series of solvents on the degree of association of *NN*-dimethylaniline–*s*-trinitrobenzene complexes compared with the effect of the same solvents on the stability of certain iodine complexes (Kortum and Walz, *Z. Electrochem.*, 1953, **57**, 73).

The authors are grateful to Dr. K. T. Hanson for the gift of pure *n*-heptane. One of them (R. F.) acknowledges a grant given by the Department of Scientific and Industrial Research. Some analyses are by Mr. F. C. Hall.

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