347. *The Problem of Chemical Linkage. Part II. The Absorption Spectra of Some Dipole Association Products.*

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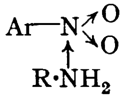
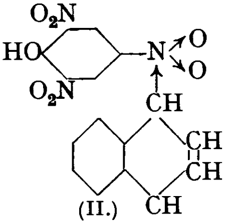
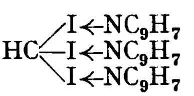
The existence of additive complexes of arylamines with nitrohydrocarbons has been explained on the basis of the formation of a co-ordinate link between the nitrogen atom of the amino-group and that of one of the nitro-groups (I) (Bennett and Willis, J., 1929, 256); further, picrates of polynuclear hydrocarbons are said to be formed by co-ordination of a negatively polarised carbon atom of a benzene nucleus with nitrogen of a nitro-group (II). Similarly, the compound of iodoform and quinoline (Rhoussopoulo, *Ber.*, 1883, **16**, 202) has been formulated with three co-ordinate links between iodine and nitrogen (III).



(I.)



(II.)



(III.)

An alternative explanation of the existence of these additive complexes is that they are associations produced by van der Waals forces, which are now known to be of three

Fig. 1.

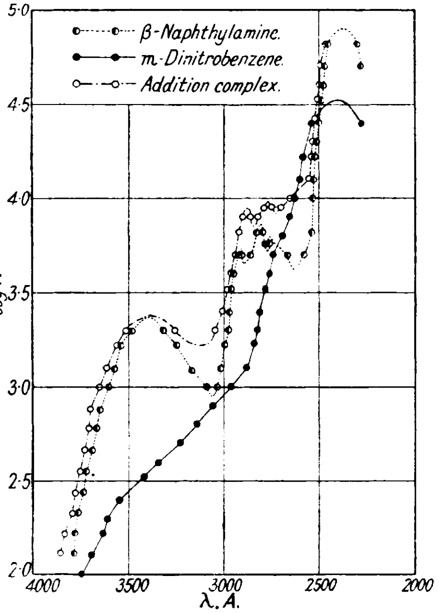
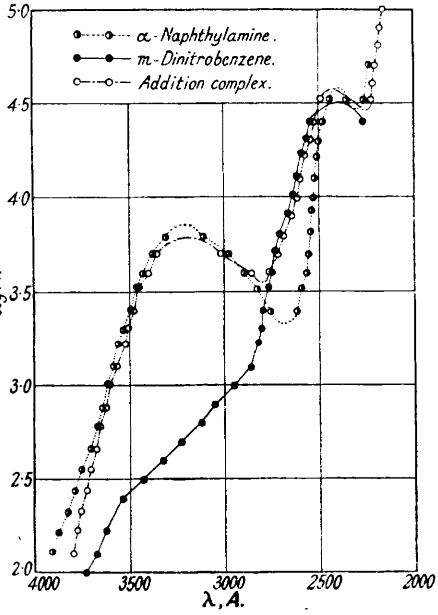


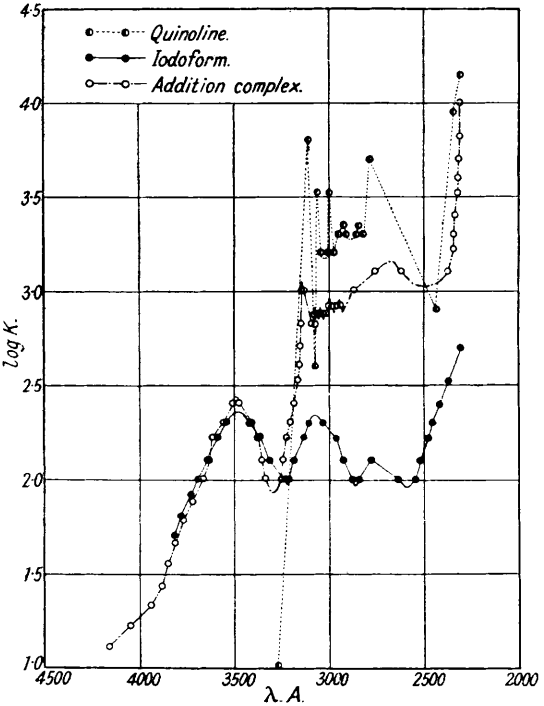
Fig. 2.



types: (*a*) the mutual attraction of two dipoles, (*b*) the attraction of a dipole to a neutral molecule arising from the induced moment produced by the polarisability of the latter, and (*c*) the attraction arising from mutual perturbation of fast-moving dispersion electrons (London, *Z. Physik*, 1930, **63**, 245; *Z. physikal. Chem.*, 1931, *B*, **11**, 222; Slater and Kirkwood, *Physical Rev.*, 1931, **37**, 682). It therefore appeared of interest to compare the absorption spectra of such complexes with those of their components. Earlier work of a similar character has been carried out by von Halban, Briegleb, and their collaborators

(*Z. physikal. Chem.*, 1925, **117**, 461; 1934, *B*, **19**, 255; **27**, 161), but is concerned with the energy of dissociation of more complicated associations which exhibit colour changes on account of the influence of solvent.

Fig. 3.



The absorption spectra of the following substances were examined by the quantitative method described by one of us (Samuel, *Z. Physik*, 1931, **70**, 41), simplified by the introduction of a stable and continuous source of light (a discharge tube with stagnant hydrogen, giving rise to the continuous hydrogen spectrum).

I (*a*) Naphthalene picrate
(*b*) Naphthalene
(*c*) Picric acid

II (*a*) *m*-Dinitrobenzene
(*b*) α-Naphthylamine
(*c*) 1 : 1-Complex of (*a*) and (*b*)

III (*a*) *m*-Dinitrobenzene
(*b*) β-Naphthylamine
(*c*) 1 : 1-Complex of (*a*) and (*b*)

IV (*a*) Iodoform
(*b*) Quinoline
(*c*) 1 : 3-Complex of (*a*) and (*b*).

In all four cases the absorption curve (Figs. 1—4) of the addition complex is a mere superposition of the curve of the first component on the second. Table I, in which the wave-lengths of the observed maxima are given together with the log *K* values, shows that the maxima of the component molecules sometimes overlap, with the result that the addition complex betrays only a single and more or less broadened maximum in place of these two; *e.g.*, the weak maximum of *m*-dinitrobenzene at 2810 A. and the maxima of β-naphthylamine at 2805 and 2740 A. form one broadened maximum at 2765 A. in the curve of the addition complex. Small displacements occur, but they are of the same order as that observed for change of solvent by other investigators; *e.g.*, for iodoform in hexane, alcohol, and carbon tetrachloride, Scheibe (*Ber.*, 1925, **58**, 586) has recorded the following figures :

Hexane, 3480, 3070 A. Alcohol, 3410, 3010 A. Carbon tetrachloride, 3485, 3070 A.

whereas our own measurements for hexane and hexane containing 0·5 mol. of quinoline are as follows :

Hexane, 3490, 3075 A. Hexane + quinoline, 3490, 3065 A.

The absorption coefficient K is defined by the equation $I = I' \times 10^{-Kcd}$, in which I and I' represent the intensity of light before and after absorption, and c and d the con-

FIG. 4.

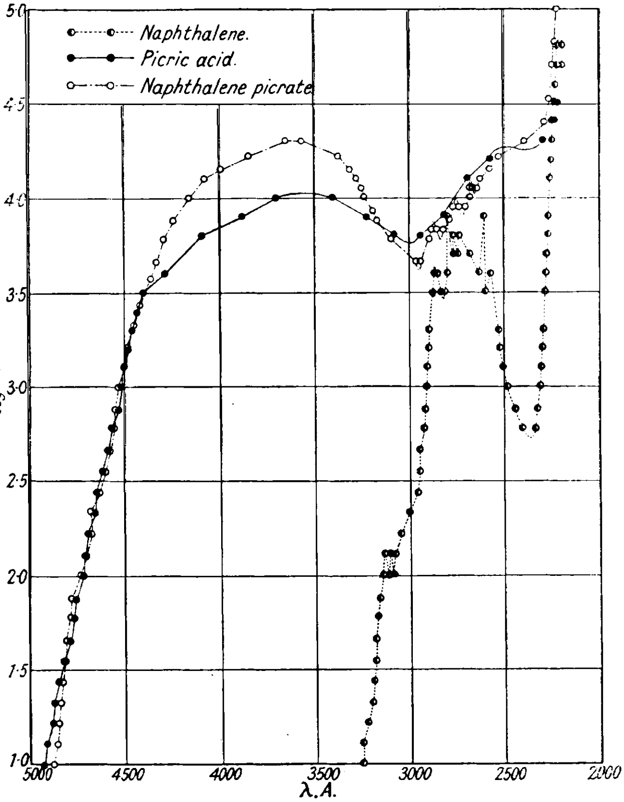


TABLE I.

Comparison of Maxima.

a-Naphthylamine	λ	3205	2400							
	log K	3·84	4·62							
m-Dinitrobenzene	λ	3610	2810	2400						
	log K	2·3	3·4	4·47						
Addn. complex	λ	3620	3200	2420						
	log K	3·0	3·79	4·6						
β-Naphthylamine	λ	3400	2915	2805	2740	2380				
	log K	3·35	3·73	3·84	3·79	4·9				
m-Dinitrobenzene	λ	3610	2810	2400						
	log K	2·3	3·4	4·47						
Addn. complex	λ	3700	3380	2885	2765	2370				
	log K	2·88	3·39	3·93	3·97	4·91				
Quinoline	λ	3115	3060	3005	2920	2840	2770			
	log K	3·8	3·53	3·52	3·35	3·35	3·7			
Iodoform	λ	3490	3075	2735						
	log K	2·37	2·36	2·14						
Addn. complex	λ	3490	3140	3065	3050	3000	2950	2870	2690	
	log K ...	2·41	3·0	2·95	2·95	2·93	2·93	3·0	3·16	
Picric acid	λ	4100	3555							
	log K ...	3·8	4·03							
Naphthalene	λ	3125	3105	3085	2860	2795	2770	2735	2605	2570
	log K ...	2·12	2·12	2·12	3·62	3·90	3·80	3·80	3·90	3·60
Naphthalene picrate	λ	4000	3605	(Curve		2865	2755	2670		
	log K ...	4·15	3·8	broadened)		3·87	3·98	4·5		

centration and thickness respectively of the solution. From this, the equation $\log I'/\log I = K_0c_0d_0 = K_1c_1d_1 + K_2c_2d_2$ may be deduced, in which the subscript 0 denotes the mixture, and 1 and 2 denote the constituent molecules. If d is constant, then $c_1 = c_2 = \frac{1}{2}c_0$, and the formula $K_0 = \frac{1}{2}(K_1 + K_2)$ is obtained, which is valid if there is no mutual interaction whatever between the components; deviations from this will therefore indicate the degree of mutual interaction. In Table II, the values of $\log \frac{1}{2}(K_1 + K_2)$ have been calculated from the absorption curves of the components concerned, and compared with the measured log K values for the addition complex. Wave-lengths close to the maxima have been taken, since in the exact region of the maxima themselves, particularly for broadened maxima, the determinations are sometimes a little inaccurate. The deviation from the law of additivity is very small indeed, and is usually of the order of 0·2 as in the cases of the deviations produced by change of solvent, due to the different polarisation of the absorbing molecules (cf. Scheibe, *loc. cit.*). The deviation is always positive in complexes of the type AB, indicating a slight displacement of the curve as a whole, but is negative in the iodoform–quinoline complex, which is of the type AB_3 and to which our simple formula is inapplicable. Furthermore, where two curves do not overlap, *i.e.*, where K_1 or K_2 is zero, the increase of the log K value of the non-overlapped band is larger. For instance, at 3600 A., where quinoline does not betray any absorption, the log K value

TABLE II.

β-Naphthylamine + m-Dinitrobenzene.

	β-Naphthylamine.		Dinitrobenzene.		Addn. complex, calculated.		Addn. complex, observed	
λ.	K.	log K.	K.	log K.	$\frac{1}{2}(K_1+K_2)$.	$\log \frac{1}{2}(K_1+K_2)$.	log K.	Diff.
3485	2,000	3·30	230	2·47	1,130	3·05	3·34	0·29
3320	2,000	3·30	400	2·61	1,200	3·08	3·47	0·39
3025	1,000	3·00	850	2·93	925	2·97	3·10	0·13
2945	4,000	3·60	1,050	3·02	2,500	3·40	3·66	0·26
2580	5,000	3·70	16,600	4·22	10,800	4·03	4·06	0·03
2500	25,200	4·40	26,300	4·42	25,700	4·41	4·43	0·02

α-Naphthylamine + m-Dinitrobenzene.

	α-Naphthylamine.		Dinitrobenzene.					
3485	2,700	3·43	230	2·47	1,500	3·18	3·38	0·20
3320	6,000	3·78	400	2·61	3,200	3·51	3·75	0·24
3025	4,300	3·63	850	2·93	2,600	3·42	3·60	0·18
2945	4,600	3·66	1,050	3·02	2,800	3·45	3·65	0·20
2580	4,000	3·60	16,600	4·22	10,300	4·01	4·30	0·29
2500	20,500	4·31	26,300	4·42	23,400	4·37	4·50	0·13

Iodoform + Quinoline.

	Iodoform.		Quinoline.					
3600	162	2·21	—	—	81	1·91	2·25	0·34
3300	120	2·08	2·5	0·4	122	2·08	1·95	−0·13
2900	110	2·04	2,000	3·3	1,105	3·04	2·96	−0·08
2600	89	1·95	2,700	3·43	1,400	3·15	3·08	−0·07
2400	290	2·46	7,950	3·9	4,100	3·61	3·11	−0·50

Naphthalene + Picric Acid.

	Naphthalene.		Picric acid.		Picrate, calculated.		Picrate, observed	
λ.	K.	log K.	K.	log K.	$\frac{1}{2}(K_1+K_2)$.	$\log \frac{1}{2}(K_1+K_2)$.	log K.	Diff.
4000	—	—	6,900	3·84	3,450	3·54	4·14	0·60
4500	—	—	830	2·92	415	2·62	3·13	0·51
3200	20	1·33	7,580	3·88	3,800	3·58	3·94	0·36
3050	160	2·21	6,160	3·79	3,200	3·51	3·75	0·24
2900	1,600	3·21	6,760	3·83	4,200	3·62	3·76	0·14
2550	2,500	3·40	13,400	4·13	8,450	3·93	4·19	0·25
2300	1,800	3·25	63,000	4·8	32,400	4·51	4·39	−0·12

of the first iodoform band in the complex is larger than in iodoform itself. This is essentially the same phenomenon as observed by Briegleb (*loc. cit.*) for the complex of anthracene with trinitrobenzene, in which colour is produced by deformation which throws absorption into the visible region.

It is therefore clear that neither the position of the maxima nor the log *K* values indicate that anything more than a small interaction of some kind occurs between the component molecules in these complexes. The character of the curves shows that the chemical individuality of the component molecules is preserved in such associations.

EXPERIMENTAL.

Materials.—The addition complexes of *m*-dinitrobenzene with the naphthylamines were prepared in Prof. S. Bhatnagar's laboratory at Lahore in connexion with another investigation and had the properties described in the literature (Buehler and Heap, *J. Amer. Chem. Soc.*, **1926**, **48**. 3168). Naphthalene picrate was purified by recrystallisation and had m. p. 149°. The iodoform–quinoline complex was prepared as described by Rhoussopoulo (*loc. cit.*), and separated from ether in needles which had m. p. 65° after drying in a vacuum. The ethyl alcohol and hexane used as solvents were purified in the usual way, and their transparency was checked spectroscopically before the solutions were prepared.

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