207. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part VIII. Interaction and Colour in Systems containing Methyl* 4 : 6 : 4′ : 6′*-Tetranitrodiphenate and Various Hydrocarbons.*

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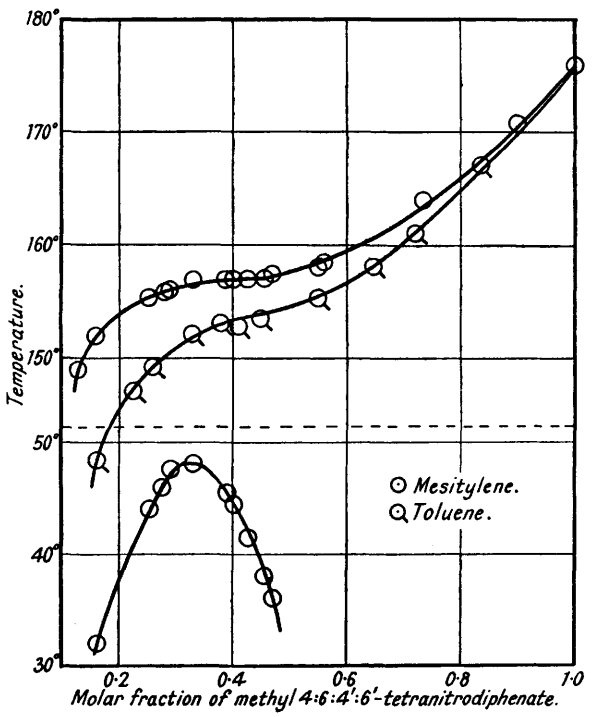
Methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate interacts in the liquid phase with aromatic hydrocarbons always with the production of colour. In many cases solid complexes (of composition 2 mols. of nitro-ester to 1 mol. of hydrocarbon) can be obtained from the coloured liquids. In several cases, however, no solid complexes can be obtained, and in two of them it is shown that the liquid components either tend to separate (toluene) into coloured liquid layers or actually do separate (mesitylene).

Polynitro-compounds interact in the liquid phase with aromatic and unsaturated hydrocarbons, generally with the production of colour. This effect has been taken as indicating



that the interaction giving rise to it is chemical (involving the breaking and making of covalent linkages) as distinct from physical (dipole association) (Werner, *Ber.*, 1909, **42**, 4334; Pfeiffer, *Annalen*, 1924, **440**, 256; Bennett and Willis, J., 1929, 256; Moore, Shepherd, and Goodall, J., 1931, 1447).

In the present communication it is shown that the interaction of methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate with various aromatic hydrocarbons takes place with the production of colour even when it is apparent that the van der Waals forces between like molecules in the systems are less than those between unlike (separation into two liquid layers). The ester is a very pale yellow solid and its solution in carbon tetrachloride is nearly colourless. When, however, any one of numerous aromatic hydrocarbons is added to the solution, a coloration ranging from lemon-yellow to orange according to the hydrocarbon is produced. Determinations of temperatures of solid–liquid equilibria in the two-component systems containing nitro-ester and aromatic hydrocarbon show that, whereas benzene, the xylenes, naphthalene, and acenaphthene can form stable solid complexes with the nitro-compound, toluene, mesitylene, and diphenyl do not, even though the liquid phases are coloured. It was moreover found that the shape of the " melting-point " curve for toluene and the nitro-ester is of the type associated with components which in the liquid phase tend to separate into two liquid layers (Sidgwick, " The Electronic Theory of Valency," p. **144**), and actual separation was observed in the metastable region below the temperatures of solid–liquid equilibrium in systems containing mesitylene (see figure). From these facts we conclude that if the colour in the partially miscible phases is due to chemical interaction as distinct from electrical polarisation, the amount of such interaction must be small.

On p. 974 will be found a list of the solid complexes, with their m. p.'s, which we have obtained either as solid phases in two-component systems or by crystallising methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate from methyl alcohol in the presence of the appropriate hydrocarbon. We have recorded those aromatic hydrocarbons which do not give solid complexes under the same conditions as the others. In all cases, whether solid complexes could be obtained or not, the liquid phases were coloured. It may also be noted (i) that the compositions of the solid complexes are all 2 molecules of nitro-ester to 1 of hydrocarbon, except in the case of acenaphthene where the ratio is 1 : 1; (ii) that the solids are all very pale yellow except the 1 : 1 acenaphthene complex, which is deep yellow.

Experimental.

(1) *Solid–liquid Equilibria.*—The temperatures at which liquid phases of known composition were in equilibrium with solid phases were determined by the " synthetic " method. Weighed quantities of methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate, m. p. 176·1° (corr.) (Ullmann and Engi, *Annalen*, **1909**, **366**, 79, give m. p. 175°), were introduced into glass bulb-tubes with weighed amounts of purified hydrocarbon, and sealed. The tubes were heated, with shaking, in a paraffin-bath until a homogeneous liquid was obtained, and then allowed to cool until crystallisation

Benzene :

N	0·0612	0·192	0·332	0·336	0·455	0·535	0·567	0·685	0·848	1·000
T	127°	141·5°	149·5°	150°	154°	155·5°	156·5°	160·5°	172·5°	176°

Toluene :

N	0·086	0·160	0·226	0·260	0·329	0·377	0·410	0·450	0·550	0·667	0·720	0·835	1·000
T	135°	141°	147°	149°	152°	153°	152·5°	153·5°	155·5°	158°	161°	167°	176°

o-*Xylene :*

N	0·157	0·236	0·332	0·418	0·485	0·574	0·604	0·670	0·710	0·802	1·000
T	150·5°	156°	159°	162·5°	164°	165°	165·5°	170°	172°	174·5°	176°

m-*Xylene :*

N	0·141	0·301	0·403	0·539	0·570	0·622	0·666	0·720	0·855	1·000
T	136°	151°	155·5°	159°	159·5°	160°	160°	162·5°	171·5°	176°

p-*Xylene :*

N	0·164	0·205	0·250	0·359	0·381	0·500	0·595	0·635	0·705	0·825	1·000
T	137·5°	140·5°	144°	153°	154°	159°	162·5°	163·5°	169°	174·5°	176°

Mesitylene :

(i) *Solid–liquid* (top part of figure).

N	0·132	0·167	0·253	0·281	0·290	0·332	0·392	0·402
T	149°	152°	155°	156°	156°	157°	157°	157°
N	0·425	0·455	0·470	0·550	0·556	0·735	0·902	1·000
T	157°	157°	157·5°	158°	158·5°	164°	170·8°	176°

set in. The bath was then slowly heated, and the temperature noted at which the last minute crystal disappeared. The preceding data were obtained and plotted in the figure (N = molar fraction of nitro-ester, $T°$ = equilibrium temperature).

(ii) *Liquid–liquid* (bottom part of figure). (Temperatures of liquid–liquid equilibria were found by allowing homogeneous liquid mixtures of the components in the usual sealed tubes to cool below the temperatures of solid–liquid equilibria without agitation. The temperatures at which opacity, due to the separation of minute drops of a second liquid phase, appeared on cooling and disappeared on heating were averaged and are given below.)

N	0·167	0·253	0·281	0·290	0·332	0·392	0·402	0·425	0·455	0·470
T	32°	44°	46°	47·5°	48°	45·5°	44·5°	41·5°	38°	36°

As the plot of these data in the figure shows, the critical solution temperature is *ca.* 48°, at the composition N = 0·33 of nitro-ester.

Diphenyl:

N	0·327	0·440	0·521	0·585	0·608	0·730	0·771	0·802	0·907	1·000
T	127°	143·5°	153°	158·5°	160·5°	168°	168·5°	170·5°	174°	176°

Naphthalene:

N	0·190	0·290	0·350	0·495	0·600	0·652	0·701	0·785	0·920	1·000
T	148·5°	156°	159°	165°	168·5°	169°	168·5°	169°	0·175°	176°

The temperature–composition curves for the systems containing nitro-ester and (i) toluene, (ii) mesitylene, are plotted in the figure. The data for the other hydrocarbon systems when plotted show either congruent m. p.'s at the composition 2 nitro-ester : 1 hydrocarbon (*m*-xylene, naphthalene), or non-congruent curves clearly tending to maxima at that composition (benzene, *o*- and *p*-xylenes), or no indication of the existence of stable solid complexes at the temperatures of the equilibria (toluene, mesitylene, diphenyl).

A number of solid complexes were obtained by crystallising mixtures of nitro-ester (1 mol.) and hydrocarbon (4 mols.) from pure methyl alcohol. In all cases where solid complexes were obtained, they had the above composition, except that the complex with acenaphthene had the composition 1 : 1. The compositions were determined by analysis either by combustion (marked C in the table below) or by means of standard titanous chloride solution (marked T in the table). Data derived from equilibria data are marked E.

Hydrocarbon.	Composition (ester : hydrocarbon).	M. p. of complex.	Hydrocarbon.	Composition (ester : hydrocarbon).	M. p. of complex.
Benzene	2 : 1 (E)	156° *	*pp'*-Ditolyl	No complex from MeOH	—
Toluene	No complex (E)	—	Diphenylmethane		—
o-Xylene	2 : 1 (E)	165 *	Triphenylmethane		—
m-Xylene	2 : 1 (E)	160	Hexamethylbenzene ...		—
p-Xylene	2 : 1 (E)	164 *	Indene	2 : 1 (C)	159·2°
Mesitylene	No complex (E)	—	Nitrobenzene	2 : 1 (T)	121
Diphenyl	No complex (E)	—	*m*-Dinitrobenzene	2 : 1 (T)	70
Naphthalene	2 : 1 (E)	167·5	*s*-Trinitrobenzene	2 : 1 (T)	142·5
Anthracene	2 : 1 (C)	164	α-Nitronaphthalene.....	2 : 1 (T).....	135
Acenaphthene	1 : 1 (C)	163	*oo'*-Dinitrodiphenyl ...	2 : 1 (T)	115
			pp'-Dinitrodiphenyl ...	No complex from MeOH	—

* Incongruent m. p.

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