144. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons. Part IV. The Interaction of Trinitromesitylene and Trichlorotrinitrobenzene with Hexamethylbenzene and with Naphthalene.*

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Trichlorotrinitrobenzene forms solid complexes and coloured liquid phases with hexamethylbenzene and with naphthalene; trinitromesitylene does not. The sizes of the methyl group and of the chlorine atom being nearly the same and their mesomeric effects being in the same sense, it is concluded that the inhibiting effect of the methyl group is connected with its positive (electron-repelling) inductive effect, which is opposite to that of the electron-attracting chlorine atom. The bearing of these conclusions on the question of the structure of the complexes is discussed.

The solid compounds of trinitrotoluene with aromatic hydrocarbons are less stable than those of trinitrobenzene. The effect of methyl groups on the stability of these complexes is still more marked when a second such group is introduced. For instance, Efremov and Tikhomirova (*Ann. Inst. Anal. Phys. Chim. Leningrad*, 1928, **4**, 92) were unable to obtain solid compounds of trinitro-*m*-xylene with any of a large number of aromatic hydrocarbons.

In order to obtain further insight into the mechanism of this inhibiting effect of the methyl group, we have looked for evidence of intermolecular-compound formation in the two-component systems containing (*a*) trinitromesitylene and (*b*) trichlorotrinitrobenzene with, in each case, hexamethylbenzene or naphthalene. The nitro-compounds were chosen so as (*a*) to eliminate any effect on compound formation due to the presence in the molecules of nuclear hydrogen, and (*b*) to keep the steric effect of the substituent groups as nearly as possible the same, the screening effects of the chlorine atom and the methyl group being very nearly equal.* The mesomeric effect they exert on the benzene nucleus is in each case in the same sense (+ *M*); but the methyl group by its inductive effect (+ *I*) repels electrons, whereas the chlorine atom (— *I*) attracts them. We therefore expected to be able to compare the effect on the stability of the intermolecular complexes of the reversal of the sign of the inductive effect exerted on the nitro-groups by the other nuclear substituents.

Hexamethylbenzene was chosen as one of the aromatic hydrocarbons in order to have under examination nitro-compound–hydrocarbon systems containing no nuclear hydrogen at all.

Our experimental procedure has been to study solid–liquid equilibria in the various two-component systems. Our results, given in detail below, show that no solid complexes are stable in the trinitromesitylene systems, but that each of the hydrocarbons studied forms a solid complex with trichlorotrinitrobenzene. Moreover, the liquid phases in the trinitromesitylene and trichlorotrinitrobenzene systems are colourless and yellow respectively.

EXPERIMENTAL.

Temperatures of solid–liquid equilibrium in the various systems were determined by the synthetic method. Weighed amounts of the two components were sealed up in weighed bulb-tubes, which were shaken in a variable thermostat until a (mean) temperature T° was found at which a small crystal of solid phase remained unchanged. Data are given below and plotted in the figure.

Trinitromesitylene (T.N.M.)–*Hexamethylbenzene* (H.M.B.).

Mol.-fractn. H.M.B.	0·00	0·09	0·18	0·27	0·40	0·50	0·60	0·67
T	232·0°	231·0°	226·2°	220·2°	211·7°	205·0°	196·1°	187·5°
Solid phase	T.N.M.							

Mol.-fractn. H.M.B.	0·70	0·74	0·80	0·86	0·90	1·00
T	185·0°	180·0°	169·3°	158·4°	159·0°	165·0°
Solid phase	T.N.M.				H.M.B.	

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* The radius of the chlorine atom being taken as 0·99 A. and the radius of revolution of the C–H link in the methyl group as 1·09 A., a scale diagram (for which we are indebted to Mr. M. W. Lister) shows that the surface of the chlorine atom would be 0·07 A. nearer than the sphere of revolution of the methyl group to an atom or group on the benzene nucleus between them.

Trinitromesitylene (T.N.M.)–*Naphthalene* (N.).

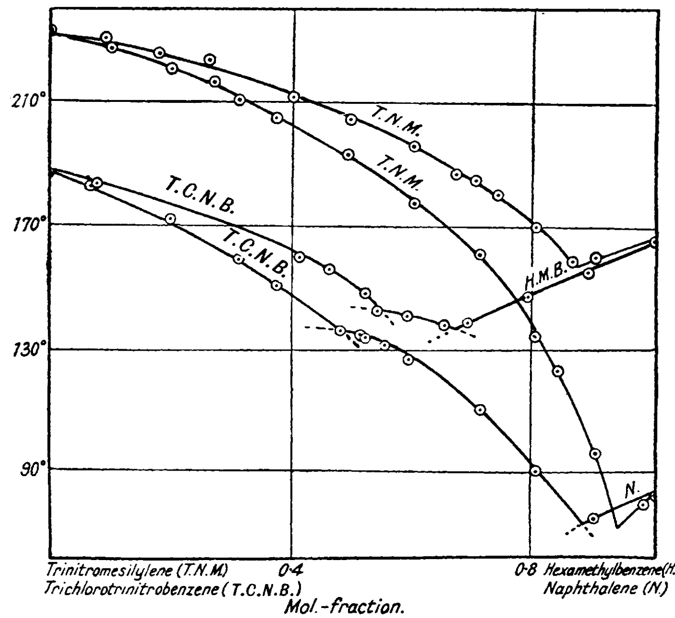
Mol.-fractn. N.	0·0	0·10	0·20	0·27	0·37	0·49	0·60	0·71	0·80	0·84	0·90	0·98	1·00
T	232·0°	229·0°	220·7°	216·5°	205·2°	192·5°	177·0°	160·0°	135·5°	122·0°	95·3°	78·5°	80·0°
Solid phase	T.N.M.											N.	

Trichlorotrinitrobenzene (T.C.N.B.)–*Hexamethylbenzene* (H.M.B.).

Mol.-fractn. H.M.B.	0·00	0·08	0·19	0·41	0·46	0·52	0·54	0·59	0·65	0·69	0·79	0·89	1·00
T	187·0°	183·2°	175·0°	159·5°	155·0°	146·9°	141·5°	140·0°	137·5°	138·1°	146·5°	154·5°	165·0°
Solid phase	T.C.N.B.						2 : 1 Compound			H.M.B.			

Trichlorotrinitrobenzene (T.C.N.B.)–*Naphthalene* (N.).

Mol.-fractn. N.	0·00	0·07	0·20	0·31	0·37	0·48	0·51	0·52	0·55	0·59	0·71	0·80	0·90	1·0
T	187·0°	183·0°	171·2°	158·3°	149·8°	135·0°	134·2°	129·8°	130·0°	127·2°	108·9°	89·0°	74·3°	80·0°
Solid phase	T.C.N.B.						2 : 1 Compound						N.	

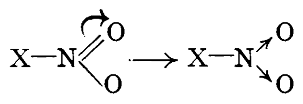


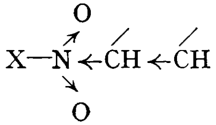
Discussion of Results.

The temperature–composition curves in the figure indicate clearly the existence in the systems containing trichlorotrinitrobenzene of solid complexes with (probably) two molecules of nitro-compound to one of hydrocarbon. On the other hand, no indication is given of the stable existence of solid intermolecular compounds in the corresponding systems containing trinitromesitylene.

Whether or not a solid complex AB will separate from a liquid mixture containing A and B depends not only on the amount of AB present in the liquid phase but also on its solubility (Dimroth and Bamberger, *Annalen*, 1924, **438**, 67). Hence we cannot be quite sure that, because no solid compounds of trinitromesitylene with hexamethylbenzene and naphthalene exist, no chemical interaction takes place between the components in the liquid phases. However, it may be noted that, of the two nitro-compounds, trichlorotrinitrobenzene has the lower melting point (187°) and is more soluble in organic solvents than trinitromesitylene (m. p. 232°). It would therefore not be unreasonable to expect that the hydrocarbon compounds of trinitromesitylene would be less soluble than those of trichlorotrinitrobenzene. The fact therefore that no solid compounds of trinitromesitylene were found points rather strongly to the conclusion that, even if there are any compound molecules present in the liquid phases, they must be relatively much less abundant than in the melts of trichlorotrinitrobenzene and the two hydrocarbons studied. Very strong support for this view comes from the observation that, whereas the trinitromesitylene–hydrocarbon melts are quite colourless, those containing trichlorotrinitrobenzene are bright yellow. (Molten trichlorotrinitrobenzene itself is almost colourless.)

As has been explained above, the steric effects of the substituents methyl and chlorine are very nearly the same, that of the latter being if anything the greater. The mesomeric effects of the methyl group and the chlorine atom being in the same sense, we therefore feel justified in concluding that the difference between the reactivities of the two nitro-compounds is connected with the fact that the inductive effect (+ *I*) of the methyl group makes it electron-repelling whereas the chlorine atom (— *I*) is electron-attracting.


(I.)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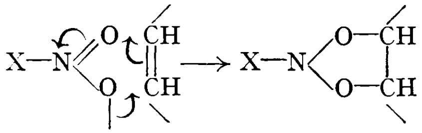
(III.)

According to Bennett and Willis (J., 1929, 256), the interaction of a nitro-group with an aromatic (ethylenic) substance involves the electromeric process (I) either before or during attack by or on an ethylenic bond in the polarised form —CH=CH— to give (II). The primary electromerism in the nitro-group should be facilitated by inductive effects in X tending to repel electrons from the nitrogen to the oxygen atoms. As pointed out above, methyl groups in the aromatic nucleus of X would be expected to do this, the influence of the chlorine atoms acting in the opposite direction. But we have found that the introduction of methyl groups into the trinitrobenzene molecule, far from increasing its readiness to interact with aromatic hydrocarbons, actually stops it altogether.

It has been suggested (J., 1935, 580) that the reactivity of the nitro-group may depend on the electromeric process (III). Such a process would be opposed by the presence of electron-repelling (+ *I*) substituents in X, but should be facilitated, as is found to be the case, by electron-attracting (— *I*) substituents such as the chlorine atom. It will be noticed that on this view the effect of the chlorine atoms on the nitro-groups is the same as that of other electron-attracting substituents (NO_2, SO_2Cl, CN, etc.), without which a single nitro-group is ineffective (Bennett and Willis, *loc. cit.*; Bennett, *Ann. Reports*, 1931, **28**, 138; Bennett and Wain, J., 1936, 1108).

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[*Received, March* 23*rd*, 1938.]