233. *Organic Molecular Compounds. Part II.*

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IN Part I (J., 1929, 256) the view was advocated that the components of many molecular compounds are united by some form of true valency bond, and tentative suggestions were put forward as to how such unions might be formulated. It was pointed out that, in the large class of complex formed between polynitro-compounds on the one hand and bases or aromatic hydrocarbons on the other, the relation between the two components must be that of acceptor and donor molecules respectively.

A study of the stabilities of such complexes in chloroform solution by a partition method, since published by Moore, Shepherd, and Goodall (J., 1931, 1447), led these authors to the conclusion that combination with production of colour was accompanied by a second phenomenon involving association of nitro- or polynitro-compounds with picric acid without any increase of colour. The latter they regard as probably due to dipole association and not usually leading to the isolation of solid compounds. The possibility of isolating a crystalline complex is, however, so much influenced by the solvent chosen and the solubility relationships of the substances concerned that too much stress should not be laid on any failure to obtain solid complexes. Compounds of nitrobenzene with both di- and tri-nitrobenzene have in fact since been demonstrated by thermal analysis (Hammick, Andrew, and Hampson, J., 1932, 171; Hammick and Hanson, J., 1933, 669), and a complex of α-nitronaphthalene with trinitrobenzene is also known (Sudborough, J. 1916, **109**, 1339).

As regards the main combination, however, the influence of various substituents on the degree of combination found by Moore and his colleagues is entirely compatible with the view that the base or hydrocarbon molecule functions as donor.

On the assumption that one nitro-group serves as the point of attachment in such complexes, the function of additional nitro-groups being a polar reinforcement of the first group, we concluded that in this capacity they should be open to replacement by other electron-attracting groups, and this was in part confirmed by the demonstration that 5-nitrobenzene-1 : 3-disulphonyl chloride and methyl 5-nitro*iso*phthalate formed compounds with several hydrocarbons and a base respectively, although this behaviour had not previously been recognised as shown by *mono*nitro-compounds. This point required further investigation, and we now describe a study of the formation of such complexes by several other mononitro-compounds of the type $C_6H_3(NO_2)X_2$. *5-Nitro*iso*phthalyl chloride* (X = COCl), *5-nitro*iso*phthalonitrile* (X = CN), *5-nitro*iso*phthalamide* (X = CO·NH$_2$), *5-nitro-1 : 3-bismethylsulphinylbenzene* and the corresponding *disulphone* (X = SO·CH$_3$ and SO$_2$·CH$_3$) have been prepared and examined from this point of view, and at the same time the related 2 : 4-dinitrobenzonitrile, 3 : 5-dinitrobenzoic *nitrile*, amide, ester, and acid chloride were included. To make the study logically complete, we then prepared and examined two substances of the type $C_6H_3X_3$, in which X was respectively COCl and CN.

In the examination of compound formation we regard the formation of an intense colour when the components are mixed in solution as significant, particularly when associated with the separation of a coloured crystalline molecular compound which is analysed. It has been suggested that colour production in solution is not necessarily evidence of chemical action, but we prefer the view that, in general, the production of intense visible colour when two colourless substances are mixed is to be regarded as indicating some new molecular species.

The nitrile, ester, amide, and acid chloride of 3 : 5-dinitrobenzoic acid all readily yield a number of molecular compounds, usually of the molecular ratio 1 : 1. The dinitronitrile combines in the ratio of 2 : 1 with benzidine, which is readily understood in view of the presence of two basic centres : it also yields 2 : 1 compounds with fluorene, diphenyl, and anthracene—substances having in the molecule two separate benzene nuclei not directly fused together. This also is in accord with a rule formulated by Sudborough (*loc. cit.*) and is consistent with our general view that each separate nucleus may become a donating centre.

The isomeric 2 : 4-dinitrobenzonitrile gives colours with both bases and hydrocarbons in solution, but no crystalline compound was actually isolated. It is possible that the less symmetrical structure of this substance determines a lower stability of the complexes, but more probably the failure to isolate a compound is a result of the relative solubilities of the substances in the solvents used. An examination was therefore made of the melting-point curve for the system 2 : 4-dinitrobenzonitrile–β-naphthylamine and a remarkably stable 1 : 1 complex was recorded of m. p. 135° (the nitrile has m. p. 99·6° ; the amine 112·1°).

In the more novel class of compounds, as the behaviour of each was examined with a similar representative set of hydrocarbons and amines, an indication is obtained as to the comparative tendencies to the formation of complexes. In this respect the groups X are found to fall into the following relative positions of diminishing tendency to promote compound formation : (*a*) $COCl > CO_2Me > CO{\cdot}NH_2$; (*b*) $SO_2Cl > SO_2Me > SOMe$; and (*c*) $NO_2 > CN > CO_2Me$. These comparisons are clearly consistent with the view that the substituents favour the formation of molecular compounds according to the strength of their polar effects, since the above series follow the order of diminishing (observed or presumable) inductive effects. The outstanding position of the nitro-group, however, as compared, *e.g.*, with the cyano-group suggests that not merely the inductive but also an electromeric effect is concerned.

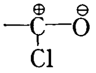
The examination of the two substances of the type $C_6H_3X_3$ provided the interesting result that the *trinitrile* forms compounds with two amines, and the triacid *chloride* coloured complexes with five aromatic hydrocarbons and one amine.

The formulation of this class of complex remains a matter of some difficulty. In Part I the view was adopted that attachment was dative from the hydrocarbon or amine to the nitro-compound, and that it must be actually from a single ethylene bond, suitably polarised, to a nitro-group—also suitably polarised. Further evidence that the ethylene bond can function as a single donating group has been provided recently (Anderson, J., **1934**, 971), but the experiments of Hammick and Sixsmith (J., **1935**, 580) are more nearly related to our work, and they undoubtedly provide the most convincing evidence yet found that in the case of the combination of the hydrocarbon indene with a polynitro-compound, the union is effected reversibly at a measurable speed, and consequently involves some covalency change. At the same time, direct evidence was obtained that the double bond of indene is concerned and becomes inert in the complex. It is probable, although admittedly not certain, that the same is true for such complexes of other hydrocarbons. In our own experiments no indication has been obtained of any time factor in combination or the development of colour.

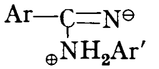
These authors discuss the possibility that the union is between a double bond and a nitro-group, but we find it impossible to accept their representation of this for the following reasons: (*a*) the polarisation of the nitro-group in the way they suggest appears to us to be unsound, being opposite to the familiar kationoid behaviour of this group; (*b*) the formulation does not appear to represent the nitro-compound as acceptor in the complex; (*c*) this formulation could be extended to include the groups COCl and CN only by postulating other polarisations of an equally improbable kind; (*d*) the formulation does not appear to provide any explanation of the intense colour of the complexes.

That combination may occur at the nitro-group seems to be inevitable from the occurrence of a red complex of naphthalene with hexanitroethane (Will, *Ber.*, 1914, **47**, 964), but the complexes formed by trimesic acid trichloride and *s*-tricyanobenzene show that the nitro-group is not essential.

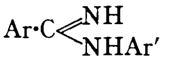
Attachment to the COCl group in the polarised form (I) appears to be a possibility according to the method previously suggested (Part I) for the nitro-group, but when the same conception is applied to the cyano-group the formula (II) is deduced for the complex with a primary amine. Such a substance must tend to pass into the form (III), which is


$-\overset{\oplus}{\underset{Cl}{C}}-\overset{\ominus}{O}$

(I.)


$Ar-\underset{\oplus NH_2Ar'}{C}=N^{\ominus}$

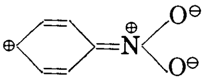
(II.)

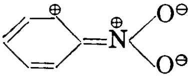

$Ar{\cdot}C{<}^{NH}_{NHAr'}$

(III.)

an amidine. But the complex actually obtained from *s*-tricyanobenzene and α-naphthylamine is coloured, and unstable to aqueous acids in a way which is quite incompatible with its formulation as an amidine. This difficulty is avoided if it be assumed that in all these cases the acceptor molecule accepts at a nuclear carbon atom, activation of the adjacent double bond having been influenced by the presence of polar substituent groups. The bonding will then be from carbon to carbon unless a base is involved, in which case the nitrogen atom may (and with saturated bases clearly must) be directly involved. This view has the advantage that it affords some explanation of the special importance of the nitro-group in promoting complex formation, since this group may assist not only by its general polar influence but by its electromeric polarisation, the polarisation originally postulated being extended into the nucleus in the form (IV) or (V). The cyano-group can presumably assist only by its general polar effect.

(IV.)

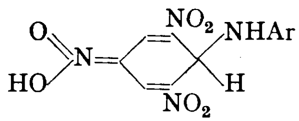


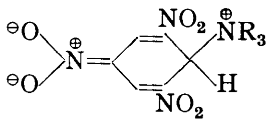


(V.)

The formula thus evolved for the complex of a primary amine with a polynitro-compound is virtually identical with (VI), originally suggested by Sudborough (J., 1901, **79**, 523) but later abandoned by him for the less definite views of Pfeiffer (J., 1916, **109**, 1340). At that time this formula appeared to be inapplicable to the case of a tertiary base, but that difficulty no longer exists, since such a formula as (VII) is conceivable.

(VI.)





(VII.)

A similar view has recently been taken by Buehler, Hisey, and Wood (*J. Amer. Chem. Soc.*, 1930, **52**, 1939). The union of parts by a carbon-to-carbon linkage may be regarded as an unstable and incomplete action, somewhat analogous to the more stable self-addition of anthracene and the diene syntheses.

EXPERIMENTAL.

Preparation of 3 : 5-*Dinitrobenzonitrile.*—3 : 5-Dinitrobenzoic acid was converted into its chloride, b. p. 211—213°/16 mm., which crystallised from carbon tetrachloride in colourless needles, m. p. 66—67°. The action of concentrated aqueous ammonia yielded the amide, m. p. 180—181°. This was dried for 2 hours at 110°, and then heated with phosphoric oxide (1¼ mols.) in an oil-bath at 200—210° for 4 hours. The cooled product was extracted with water and then with boiling ethyl alcohol. 3 : 5-*Dinitrobenzonitrile* was thus obtained in yellow monoclinic prisms, m. p. 127° (yield, 55% from the amide) (Found : C, 43·5; H, 1·6. $C_7H_3O_4N_3$ requires C, 43·5; H, 1·6%).

Derivatives of 5-*Nitro*iso*phthalic Acid.*—5-Nitro*iso*phthalic acid, m. p. 246°, was converted by phosphorus pentachloride into its *chloride*, which, twice crystallised from carbon tetrachloride, had m. p. 66—68° (Found : Cl, 28·3. $C_8H_3O_4NCl_2$ requires Cl, 28·6%). This reacted with concentrated aqueous ammonia to give the diamide, m. p. above 300°.

The diamide (dried at 110° for 2 hours) was heated with phosphoric oxide (2½ mols.) in an oil-bath at 240—245° for 8 hours. The product was washed with water and then boiled out with hot glacial acetic acid, from which it crystallised in yellow needles (yield, 38%). The 5-*nitro*-1 : 3-*dicyanobenzene* obtained was recrystallised from benzonitrile and then from amyl alcohol, forming minute colourless needles with a straight extinction, m. p. 205° (Found : C, 55·5; H, 1·9. $C_8H_3O_2N_3$ requires C, 55·5; H, 1·75%).

Derivatives of Trimesic Acid.—Trimesic acid was prepared as described by Ullmann and Uzbachian (*Ber.*, 1903, **36**, 1799) except that the use of a mechanical stirrer made it possible to reduce the time of oxidation by half (yield, 78%). The dried acid was converted into its *trichloride* by heating with phosphorus pentachloride (3½ mols.) and fractional distillation under reduced pressure. The trichloride had b. p. 213°/13 mm., and crystallised from light petroleum at 0° in colourless needles, m. p. 35—37° (Found : Cl, 40·2. $C_9H_3O_3Cl_3$ requires Cl, 40·1%).

The trichloride was converted by concentrated aqueous ammonia into the triamide, m. p. 365° (corr.; decomp.). This substance was insoluble in all the solvents examined. It was dried at 120° for 2 hours, powdered, and heated with phosphoric oxide (4 mols.) at 300—320° for 15 hours. The cooled product was washed with water and extracted with boiling alcohol (yield, 9%). s-*Tricyanobenzene*, so obtained, crystallised from methyl alcohol in colourless needles with a straight extinction, m. p. 261—263° (corr.) (Found : C, 70·5; H, 2·0. $C_9H_3N_3$ requires C, 70·6; H, 2·0%).

Preparation of Derivatives of 5-*Nitro*-1 : 3-*bismethylthiobenzene.*—Nitrobenzene-3 : 5-disulphonic acid was best prepared by boiling a mixture of benzene-*m*-disulphonyl chloride (60 g.), oleum (120 g. of 20%), and nitric acid (200 g., *d* 1·5) for 12 hours. The mixture was evaporated on the steam-bath, and on cooling, solidified to a mass of crystals of the free acid. This was collected on a sintered-glass filter and dried on porous earthenware. The free acid was converted by warming with phosphorus pentachloride (4 mols.) into the acid chloride, m. p. 93° (yield, 68%).

5-Nitrophenylene-1 : 3-dithiol was produced when the nitrobenzenedisulphonyl chloride (10 g.), dissolved in glacial acetic acid (75 c.c.), was reduced by hydriodic acid (*d* 1·7; 98 c.c. with 50 c.c. of acetic acid). After 1 hour, the mixture was diluted, and sulphur dioxide passed to remove iodine. The product was filtered off, washed with water, and dried. It was a fine brown powder, m. p. 140—150° (decomp.) (yield, 92%).

The dithiol (6 g.) was heated at 58° with 300 c.c. of 50% alcohol, and potassium hydroxide (4 g. in 50 c.c. of water) added slowly with shaking. After 2 hours at 58°, the deep red solution was cooled to 40°, and methyl sulphate (6·5 c.c.) added. After ½ hour the mixture was made strongly alkaline and left over-night. The product was filtered off, washed with water, and recrystallised from alcohol. 5-*Nitro*-1 : 3-*bismethylthiobenzene*, $C_6H_3(NO_2)(SMe)_2$, was thus obtained in pale yellow needles (1·6 g.), m. p. 92° (Found : C, 44·8; H, 4·2. $C_8H_9O_2NS_2$ requires C, 44·6; H, 4·2%). It was oxidised by perhydrol in cold acetic acid to the *disulphoxide*, m. p. 176—185° (presumably a mixture of stereoisomerides, but these were not separated) (Found : C, 38·5; H, 3·4. $C_8H_9O_4NS_2$ requires C, 38·9; H, 3·6%).

An excess of perhydrol in boiling glacial acetic acid gave the *disulphone*, $C_6H_3(NO_2)(SO_2Me)_2$, white microscopic needles from dilute acetic acid, m. p. 214° (Found: C, 34·1; H, 3·0. $C_8H_9O_6NS_2$ requires C, 34·4; H, 3·2%).

Molecular Compounds.—The two components were mixed, usually in approximately equimolecular proportion but sometimes with an excess of one, in a suitable solvent, and the compound which crystallised was filtered off. This was in certain cases recrystallised, but more often analysed forthwith. Particular attention was paid to the colour of the compound and to any coloration in the solution, whether a crystalline compound was isolated or not.

First component.	Second component.	Solvent.	Colour of solution.	Compound.	Colour of solid.	M. p.	Analysis.*
Methyl 3 : 5-dinitrobenzoate	α-Naphthylamine	MeOH	Deep red	1 : 1	Deep red needles	120°	(cf. Reichstein, *Helv. Chim. Acta*, 1926, **9**, 799)
	β-Naphthylamine	,,	Orange-red	1 : 1	Orange needles	88—90	N, 11·4 (11·4)
	Benzidine	,,	Deep red-brown	1 : 1	Jet-black plates	99—102	C, 58·1 (58·5) H, 4·4 (4·4)
	p-Toluidine	,,	Deep orange-red	1 : 1	Deep red prisms	72	N, 12·8 (12·6)
	Naphthalene	,,	Yellow	1 : 1	Lemon-yellow needles	77—80	N, 8·2 (7·9)
	Acenaphthene	,,	Deep yellow	1 : 1	Bright yellow needles	85—87	N, 7·4 (6·9)
	Phenanthrene	,,	Yellow	1 : 1	Lemon-yellow needles	117—119	N, 7·1 (6·9)
	s-Trimethoxybenzene	,,	Deep yellow	1 : 1	Bright yellow needles	71—73	N, 7·4 (7·1)
3 : 5-Dinitrobenzonitrile	α-Naphthylamine	EtOH	Deep red	1 : 1	Dark red needles	166—169	N, 16·9 (16·7)
	β-Naphthylamine	,,	Orange-red	1 : 1	Deep red needles	109—113·5	N, 16·9 (16·7)
	Benzidine	,,	Dark brown	2 : 1 of base	Black needles	161—163	N, 19·8 † (19·6)
	Dimethylaniline	,,	Purple-red	1 : 1	Deep purple plates	71—73	N, 17·6 (17·4)
	Aniline	,,	Deep red	1 : 1	Orange-red needles	87	N, 19·7 (19·6)
	p-Toluidine	,,	Deep red	1 : 1	Purple-red needles	96—98	N, 18·1 (18·7)
	Naphthalene	,,	Yellow	1 : 1	Pale yellow needles	123	N, 13·2 (13·1)
	Acenaphthene	,,	Deep yellow	1 : 1	Bright yellow needles	148—150	C, 65·5 (65·7) H, 3·9 (3·8) N, 13·1 (13·3)
	Phenanthrene	,,	Yellow	1 : 1	Bright yellow needles	107—108	N, 11·5 (11·3)
	Fluorene	,,	Yellow	2 : 1 of fluorene	Yellow plates	128—130	N, 15·5 ‡ (15·2)
	Diphenyl	,,	Yellow	2 : 1 of diphenyl	Yellow needles	96—99	N, 15·7 § (15·6)
	Anthracene	CCl_4	Orange	2 : 1 of anthracene	Orange plates	151—153	N, 15·1 || (14·9)
	s-Trimethoxybenzene	MeOH	Bright yellow	1 : 1	Lemon-yellow needles	81—82	N, 11·5 (11·6)
	Toluene	C_6H_5Me	Yellow	1 : 1	Yellow crystals	41—94	C_6H_5Me, 32·5 (32·3)
	Mesitylene	$C_6H_3Me_3$	Yellow	1 : 1	Lemon-yellow crystals	92—97	$C_6H_3Me_3$, 38·8 (38·3)
3 : 5-Dinitrobenzoyl chloride	Naphthalene	CCl_4	Yellow	1 : 1	Pale yellow needles	127°	Cl, 9·9 (9·9)
	Anthracene	,,	Orange	1 : 1	Orange-red needles	130—151	Cl, 8·6 (8·7)
	Acenaphthene	,,	Yellow	1 : 1	Bright yellow needles	149—151	Cl, 9·1 (9·2)
	Dimethylaniline	CCl_4 with excess base	Bright red	Red crystals too unstable for analysis			
3 : 5-Dinitrobenzamide	α-Naphthylamine	EtOH	Deep red	1 : 1	Scarlet needles	149	N, 16·0 (15·8)
	Acenaphthene	,,	Yellow	1 : 1	Yellow needles	148—150	N, 11·2 (11·5)
2 : 4-Dinitrobenzonitrile	α-Naphthylamine	EtOH + MeOH	Deep red	No crystalline compounds isolated (but see p. 1114)			
	β-Naphthylamine	,,	Orange-red				
	Benzidine	,,	Dark brown				
	Aniline	,,	Bright orange-red				
	Acenaphthene Anthracene	,,	Canary-yellow				
	Phenanthrene Naphthalene Fluorene Diphenyl	,,	Pale yellow				

* The values in parentheses are the theoretical percentages. † The 1 : 1 compound requires N, 18·6%. ‡ The 1 : 1 compound requires N, 11·7%. § The 1 : 1 compound requires N, 12·1%. || The 1 : 1 compound requires N, 11·3%.

First component.	Second component.	Solvent.	Colour of solution.	Compound.	Colour of solid.	M. p.	Analysis.*
1·Nitro-3 : 5-dicyanobenzene	α-Naphthylamine	$COMe_2 + H_2O$	Deep red	1 : 1	Deep red needles	147—149	N, 17·4 (17·7)
	β-Naphthylamine	n-C_5H_{11}·OH	Orange-red	1 : 1	Dark red needles	105—107·5	N, 17·5 (17·7)
	Benzidine	,,	Brown	2 : 1 of benzidine	Chocolate-brown plates	173	N, 21·0 † (21·1)
	p-Toluidine	,,	Deep red	1 : 1	Deep red needles, decomp. on keeping	62	N, 19·8 (20·0)
	Aniline	NH_2Ph	Deep red	1 : 1	Bright red prisms	95—170	N, 20·7 (21·0)
	Acenaphthene	$COMe_2 + H_2O$ or n-C_5H_{11}·OH	Yellow	1 : 1	Yellow prisms	156—160	N, 12·8 (12·8)
	Anthracene	,, or HOAc	Yellow	No crystalline compounds isolated			
	Phenanthrene						
	Fluorene						
	Naphthalene		Pale yellow				
	Diphenyl						
5 Nitro*iso*phthalyl chloride	Acenaphthene	CCl_4	Yellow	1 : 1	Greenish-yellow needles	139—143	Cl, 17·8 (17·7)
	Phenanthrene	,,	Bright yellow	1 : 1	Pale yellow feathery crystals	134—137	Cl, 16·4 (16·7)
	Anthracene	,,	Deep yellow	1 : 1	Golden-yellow needles	122—154	Cl, 17·1 (16·7)
5-Nitro*iso*phthalamide	α- and β-Naphthylamines	Glycol	Brown-yellow	No compounds isolated			
	p-Toluidine	,,	,,				
	Aniline	,,	,,				
	Acenaphthene	,,	Pale yellow				
	Anthracene						
	Phenanthrene						
5-Nitro-1 : 3-bismethylsulphonylbenzene	α-Naphthylamine	$Bu^{\alpha}OH$	Deep red	1 : 1	Red-brown plates	139—172 (indef.)	N, 6·6 (6·6)
	Aniline	,,	Deep red	1 : 1	Dark red prisms	126	$PhNH_2$, 24·5 24·65 (25·0%)
	β-Naphthylamine	,,	Red	No compounds isolated			
	Acenaphthene	,, or HOAc	Lemon-yellow				
	Phenanthrene	,,	Very pale yellow				
	Anthracene						
	Mesitylene	$C_6H_3Me_3$	Pale yellow				
	Naphthalene	$Bu^{\alpha}OH$ or HOAc	No visible coloration				
	Diphenyl						
	Fluorene						
5-Nitro-1 : 3-bismethylsulphinylbenzene	α-Naphthylamine	n-C_5H_{11}·OH	Deep orange-red				
	β-Naphthylamine	,,	Orange-red				
	Benzidine	,,	Reddish-brown				
	Aniline	,,	Orange-red				
	Anthracene	,,	Yellow				
	Phenanthrene	,,	Very pale yellow				
	Acenaphthene	,,					
	Naphthalene	,,	No visible coloration				
	Fluorene	,,					
	Diphenyl	,,					
s-Tricyanobenzene	α-Naphthylamine	EtOH	Bright yellow	1 : 1	Dark yellow needles	165—167	C, 76·7 (77·0) H, 4·2 (4·1)
	Benzidine	,,	Brown	1 : 1	Yellow-brown plates	168 (decomp.)	N, 23·1 ‡ (22·9)
	Aniline	,,	Bright yellow	No compounds isolated			
	Dimethylaniline	,,					
	β-Naphthylamine	,,					
	p-Toluidine	,,					
	No visible colour with hydrocarbons.						
Trimesic acid trichloride	Naphthalene	Low b. p. paraffin dried over Na	Pale yellow	1 : 1	Almost colourless crystals	97—101	Cl, 26·7 (27·1)
	Acenaphthene	,,	Yellow	1 : 1	Lemon-yellow needles	134—137	Cl, 25·6 (25·4)
	Phenanthrene	,,	Yellow	1 : 1	Yellow needles	129—131	Cl, 23·8 (24·0)
	Anthracene	,,	Yellow	1 : 1	Orange-yellow needles	120—152	Cl, 24·1 (24·0)
	Fluorene	,,	Yellow	1 : 1	Yellow needles	75—77	Cl, 24·9 (24·7)
	Dimethylaniline	,,	Deep red	1 : 1	Scarlet needles	34—82	Cl, 27·4 (27·5)
	Mesitylene	$C_6H_3Me_3$	Purple	None isolated			

* The values in parentheses are the theoretical percentages. † The 1 : 1 compound requires N, 19·6%.
‡ The 2 : 1 compound requires N, 20·8%.

Thermal Examination of the System 1 : 3 : 5-*Tricyanobenzene–Anthracene*.—The observations were made by the m. p. method of Rheinboldt and Kircheisen (*J. pr. Chem.*, 1926, **113**, 348): the temperatures are corrected, T_1 being the point at which liquid is first detected and T_2 that at which the last solid disappears.

Anthracene, mols. %	0	14·5	26·4	35·2	41·9	50·0
T_1	261·0°	186·5°	185·4°	186·5°	186·0°	185·3°
T_2	262·2	249·5	236·9	225·7	217·1	207·2
Anthracene, mols. %	52·9	60·3	64·7	68·2	83·2	100
T_1	187·5°	186·3°	186·8°	186·5°	188·6°	219·0°
T_2	203·9	191·9	189·8	196·7	213·1	220·6

There is no evidence of compound formation, the eutectic point being at 186·7°, 63 mols. % of anthracene.

The System 2 : 4-*Dinitrobenzonitrile*–β-*Naphthylamine*.—

Nitrile, mols. %	0	8·6	18·1	27·7	37·8	46·2
T_1	111·2°	89·2°	91·3°	90·5°	89·7°	91·1°
T_2	112·1	106·8	97·1	104·3	122·4	132·6
Nitrile, mols. %	51·9	58·0	73·9	81·3	91·2	100
T_1	76·2°	74·3°	75·0°	74·6°	73·8°	98·9°
T_2	134·9	128·9	100·5	83·4	90·9	99·6

The curve reveals a stable compound of composition 1 : 1 and of congruent m. p. 135°, with eutectic points at 90·3°, 23 mols. % of nitrile; and 74·4°, 84 mols. % of nitrile.

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[*Received, May* 14*th*, 1936.]