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C. - Additive compounds of trinitrobenzene
J. J. Sudborough

RE-PRINTS

C.—*Additive Compounds of Trinitrobenzene*

By JOHN JOSEPH SUDBOROUGH.

IN continuation of the investigations on the capacity of polynitro-aromatic compounds to form additive derivatives (compare T., 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773; 1911, **99**, 209) the compounds enumerated in tables I—IV have been prepared.

During the progress of this work descriptions of a few additive compounds of aromatic hydrocarbons with polynitro-compounds have appeared. Kremann (*Monatsh.*, 1911, **32**, 609) has described a compound of trinitrobenzene with fluorene in the molecular proportions of 3 to 2, and A. Buguet (*Compt. rend.*, 1909, **149**, 857) has prepared compounds of *s*-trinitrobenzene with phenanthrene and acenaphthene, the compounds consisting of equimolecular quantities of the components.

The compounds characterised by an asterisk could only be obtained by using an excess of the hydrocarbon or base. In all the other cases the products were prepared by using theoretical quantities of trinitrobenzene and of hydrocarbon or base and crystallising from a suitable solvent, usually alcohol, but occasionally benzene. In the case of *p*-aminobenzophenone a mixture of benzene with a little alcohol was used, and with the diethylphenylenediamines, a mixture of benzene and light petroleum.

Conclusions.

(1) One of the most interesting facts established is that aromatic hydrocarbons form additive compounds with trinitrobenzene in much the same manner that they do with picric acid. Many of these compounds are comparatively stable, and can be crystallised from suitable solvents. As a rule the colour of these additive compounds is not so marked as the colours of the corresponding amino- or hydroxy-derivatives. It will be noticed that the colour of the hydrocarbon additive compounds is usually yellow, with the exception of the compound with anthracene, the colour of which is bright red.

In a previous communication (T., 1910, **97**, 780) it was suggested that the formation of additive compounds from aromatic amines, phenols, phenolic ethers, and sulphur compounds could probably be attributed to the latent valencies of the nitrogen, oxygen, or sulphur atoms. The isolation of stable compounds of hydrocarbons with trinitrobenzene raises the question as to whether in all cases the addition may not be of the same type and be due to the unsaturated character of the aromatic nucleus present.

It is hoped that a study of the ultraviolet absorption spectra of some of these compounds may throw some light on this question.

It is well known that quinones form coloured additive compounds with phenols and aromatic amines, and Pfeiffer has shown recently (*Annalen*, 1914, **404**, 1) that phenolic ethers and aromatic hydrocarbons, such as durene and hexamethylbenzene, also form coloured additive compounds with chloranil. From this Pfeiffer concludes that the addition is not due to the presence of the amino-, substituted amino-, or hydroxy-group present in the amine or phenol, but is due to the unsaturated aromatic nucleus, each carbonyl group being able to satisfy the latent valencies of one benzene nucleus, and he represents such additive compounds by the following type of formula:

$$C_6Me_6 \;.\;.\;.\; O{:}C_6H_4{:}O \;.\;.\;.\; C_6Me_6.$$

It would appear probable that the formation of compounds between polynitro-aromatic compounds on the one hand and aromatic hydrocarbons, amines, phenols, phenolic ethers, and sulphur compounds on the other is due to latent valencies of the nitro-groups and of the aromatic residues of the hydrocarbon, phenol, or amine (compare Pfeiffer, *loc. cit.*, p. 13). The hydroxy-, alkyloxy-, amino-, and alkylamino-groups act mainly as auxochromes, but at the same time tend to increase the stability of the additive compounds.

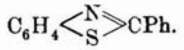
On Pfeiffer's scheme these additive compounds are represented as follows:

$$C_6H_3(NO_2)_3 \; . \; . \; . \; C_{10}H_8.$$
$$C_6H_3(NO_2)_3 \; . \; . \; . \; C_{10}H_7{\cdot}OH.$$
$$C_6H_3(NO_2)_3 \; . \; . \; . \; C_{10}H_7{\cdot}NH_2.$$

(2) The question of the number of molecules of trinitrobenzene with which one molecule of the aromatic compound can combine is of considerable importance. An examination of the various additive compounds prepared by Somerhoff (*Diss.*, Zurich, 1904) and the present author tends to prove that the number of molecules of trinitrobenzene does not vary with the number of amino-, substituted amino-, hydroxy-, or alkyloxy-groups present, but rather with the number of aromatic nuclei. In this connexion a condensed system of several benzene or of benzene and heterocyclic rings has to be regarded as a single nucleus.

The following substances form additive compounds of the type one molecule of trinitrobenzene with one molecule of the substance: The hydrocarbons naphthalene, anthracene, phenanthrene, acenaphthene, chrysene, and retene; aniline, its homologues and substituted derivatives; mono- and di-alkylated anilines; naphthylamines, their alkyl derivatives and substitution products; naphthols and alkylated naphthols; phenylenediamines, tolylenediamines, and naphthylenediamines; triaminotoluene; phenylhydrazones derived from aliphatic ketones; quinoline, *iso*quinoline, their tetrahydro-derivatives, and substituted amino- and hydroxy-derivatives; methylindole, phenylpyrazolones.

The following groups of substances form additive compounds of the type two molecules of trinitrobenzene with one molecule of the substance: Hydrocarbons containing two benzene nuclei, for example, *s*-diphenylethane, stilbene, tolane, dihydroanthracene, **α**-dinaphthylmethane, and their amino-derivatives, for example, diaminostilbene, aminodiphenylmethane, and diaminodiphenylmethane. Aromatic secondary amines, for example, diphenylamine, phenyl-**α**- and -**β**-naphthylamines, **αα**- and **ββ**-dinaphthylamines, various tolylnaphthylamines. Derivatives of aromatic ketones, for example, tetramethyldiaminobenzophenone. Phenylhydrazones derived from aromatic aldehydes or ketones, for example, benzaldehydephenylhydrazone, cinnamaldehydephenylhydrazone, acetophenonephenylhydrazone. Esters containing two or more benzene nuclei, for example, benzyl salicylate, quinol disalicylate. Benzylidene compounds containing two aromatic nuclei, for example, distyryl diketone; benzylidene β-naphthylamine. Phenolic ethers containing two aromatic nuclei, for example, phenylnaphthyl ethers and dinaphthyl ethers. Azo-compounds, for example, dimethylaminoazobenzene, aminoazonaphthalene. Certain sulphur compounds containing two benzene nuclei, dimethylaniline disulphide, *o*-diaminodiphenyl disulphide, 1-phenylbenzothiazole,



$$\mathrm{C_6H_4} < \genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{S}} > \mathrm{CPh}.$$

There are, however, various exceptions to these generalisations:

(*a*) Several compounds form additive compounds of two different types. Thus phenyl-β-naphthylamine, asarone (trimethoxypropenylbenzene), and tetramethyldiaminobenzophenone can give compounds containing equimolecular quantities of the components and also compounds containing two molecules of trinitrobenzene to one of amine. Both series of compounds are stable.

(*b*) Quite a number of substances containing two or more independent aromatic nuclei form compounds with trinitrobenzene in the molecular proportions one to one. Among such substances may be mentioned: 1-benzeneazo-2-naphthylamine, diethylaminobenzylidene-*p*-aminomethylaniline, *o*:*o*-diaminostilbene, tetramethyl-*p*-diaminotriphenylmethane, tetramethyldiaminobenzhydrol, tetramethyldiaminotriphenylmethane, paraleucaniline, aminobenzophenone, phenyl salicylate, phenyl-α-naphthyl ether, benzylidene-α-naphthylamine, *m*-nitrobenzaldehydephenylhydrazone, αα-diphenylpyridine, acridine and its derivatives, triphenylpyrrole.

(*c*) In a few cases one molecule of trinitrobenzene combines with two molecules of the substances, for example, carbostyril, dibenzylaniline, and naphthionic acid. The additive compound of trinitrobenzene and fluorene has the molecular ratio 3:2.

(4) The auxochrome effect of amino- and hydroxy-groups is well observed in the case of quinoline and its derivatives. Quinoline itself gives an additive compound which is almost colourless, whereas the hydroxyquinolines give yellow or brown additive compounds and the aminoquinolines give stable, red, crystalline compounds. The auxochrome effect of an ethylene linking is also observed in the case of stilbene. Thus *s*-diphenylethane gives a very pale yellow-coloured additive compound, and the unsaturated analogue

stilbene a deep canary-coloured compound. Tolane also yields a deep yellow-coloured product.

The difference in colour between the additive compounds of trinitrobenzene with anthracene and dihydroanthracene is also marked.

(5) The results show that most naphthalene derivatives form additive compounds with trinitrobenzene, and that the colour of such compounds is yellow unless an auxochrome such as an amino-, a substanced amino-group, or several hydroxyl groups are present. Substituents such as Br, NO_2, CN, CO_2Et, CHO, Bz do not interfere with the formation of additive compounds. Naphthalene derivatives containing the $SO_2{\cdot}OH$ or SO_2Cl groups, on the other hand, do not appear to form additive compounds with trinitrobenzene.

(6) Pyrrole, its phenyl, tolyl, and triphenyl derivatives all yield additive compounds with trinitrobenzene. The compound with pyrrole has a yellow colour (van Romburgh, *Rec. trav. chim.*, 1895, **14**, 67), those with phenyl- and tolyl-pyrroles a canary yellow colour, and the compound with triphenylpyrrole a purple colour.

(7) Attention has already been drawn (T., 1910, **97**, 776) to the difference in colour between the additive compounds of benzene with quinoline derivatives on the one hand and with tetrahydro-derivatives of quinoline on the other. Another example is given here, namely, 1-ethyltetrahydroquinoline, which forms a black additive compound with trinitrobenzene.

(8) So far it has not been found possible to isolate additive compounds of trinitrobenzene with the following substances: Diphenylmethane, triphenylcarbinol, diphenylfulvene, xanthone, fluorenone, benzil, cinnamylideneacetic acid, resorcinol dimethyl ether, *p*-dihydroxydiphenylmethane, *pp*-diphenol, naphthalenesulphonic acids and- sulphonyl chlorides, acetyl-*p*-phenylenediamine, benzamidine, piperazine, antipyrine, phenacetin, strychnine, bornylamine.

In conclusion, I have to thank Messrs. S. H. Beard and R. Rungaswamy Naidu for valuable assistance in the analytical portion of the work.

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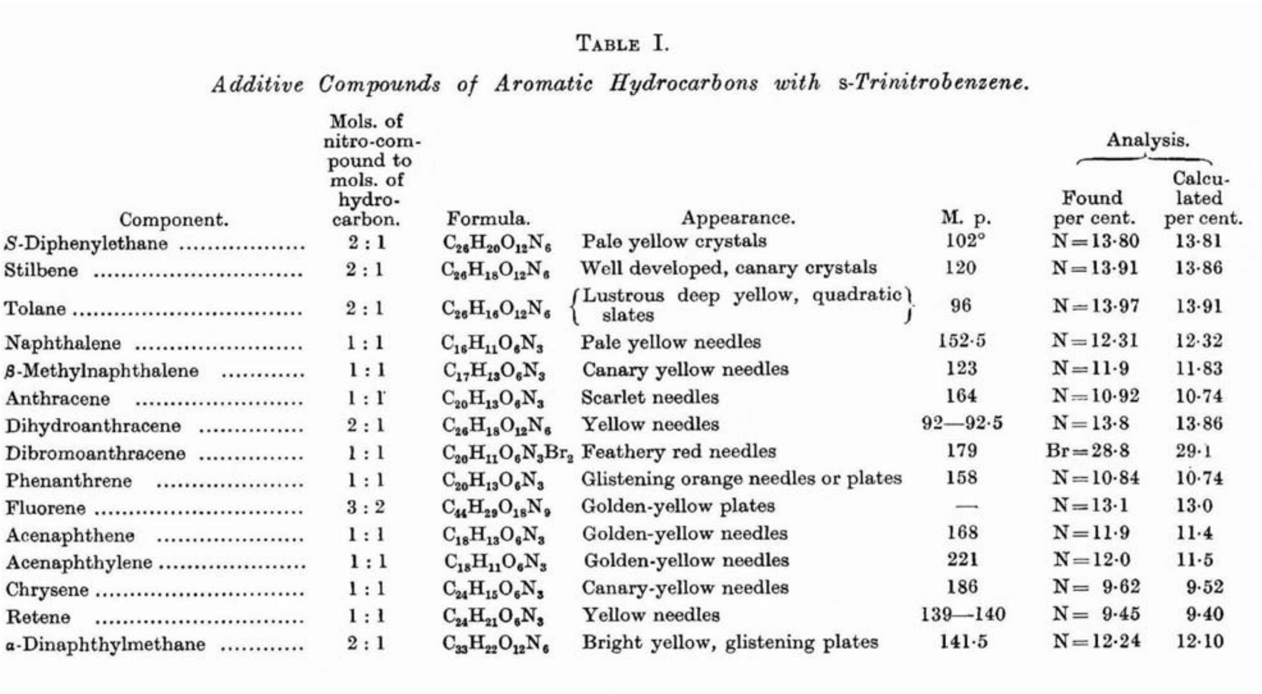

TABLE I.

Additive Compounds of Aromatic Hydrocarbons with s-*Trinitrobenzene.*

Component.	Mols. of nitro-compound to mols. of hydro-carbon.	Formula.	Appearance.	M. p.	Analysis.	
					Found per cent.	Calculated per cent.
S-Diphenylethane	2 : 1	$C_{26}H_{20}O_{12}N_6$	Pale yellow crystals	102°	N=13·80	13·81
Stilbene	2 : 1	$C_{26}H_{18}O_{12}N_6$	Well developed, canary crystals	120	N=13·91	13·86
Tolane	2 : 1	$C_{26}H_{16}O_{12}N_6$	Lustrous deep yellow, quadratic slates	96	N=13·97	13·91
Naphthalene	1 : 1	$C_{16}H_{11}O_6N_3$	Pale yellow needles	152·5	N=12·31	12·32
β-Methylnaphthalene	1 : 1	$C_{17}H_{13}O_6N_3$	Canary yellow needles	123	N=11·9	11·83
Anthracene	1 : 1	$C_{20}H_{13}O_6N_3$	Scarlet needles	164	N=10·92	10·74
Dihydroanthracene	2 : 1	$C_{26}H_{18}O_{12}N_6$	Yellow needles	92—92·5	N=13·8	13·86
Dibromoanthracene	1 : 1	$C_{20}H_{11}O_6N_3Br_2$	Feathery red needles	179	Br=28·8	29·1
Phenanthrene	1 : 1	$C_{20}H_{13}O_6N_3$	Glistening orange needles or plates	158	N=10·84	10·74
Fluorene	3 : 2	$C_{44}H_{29}O_{18}N_9$	Golden-yellow plates	—	N=13·1	13·0
Acenaphthene	1 : 1	$C_{18}H_{13}O_6N_3$	Golden-yellow needles	168	N=11·9	11·4
Acenaphthylene	1 : 1	$C_{18}H_{11}O_6N_3$	Golden-yellow needles	221	N=12·0	11·5
Chrysene	1 : 1	$C_{24}H_{15}O_6N_3$	Canary-yellow needles	186	N= 9·62	9·52
Retene	1 : 1	$C_{24}H_{21}O_6N_3$	Yellow needles	139—140	N= 9·45	9·40
α-Dinaphthylmethane	2 : 1	$C_{33}H_{22}O_{12}N_6$	Bright yellow, glistening plates	141·5	N=12·24	12·10

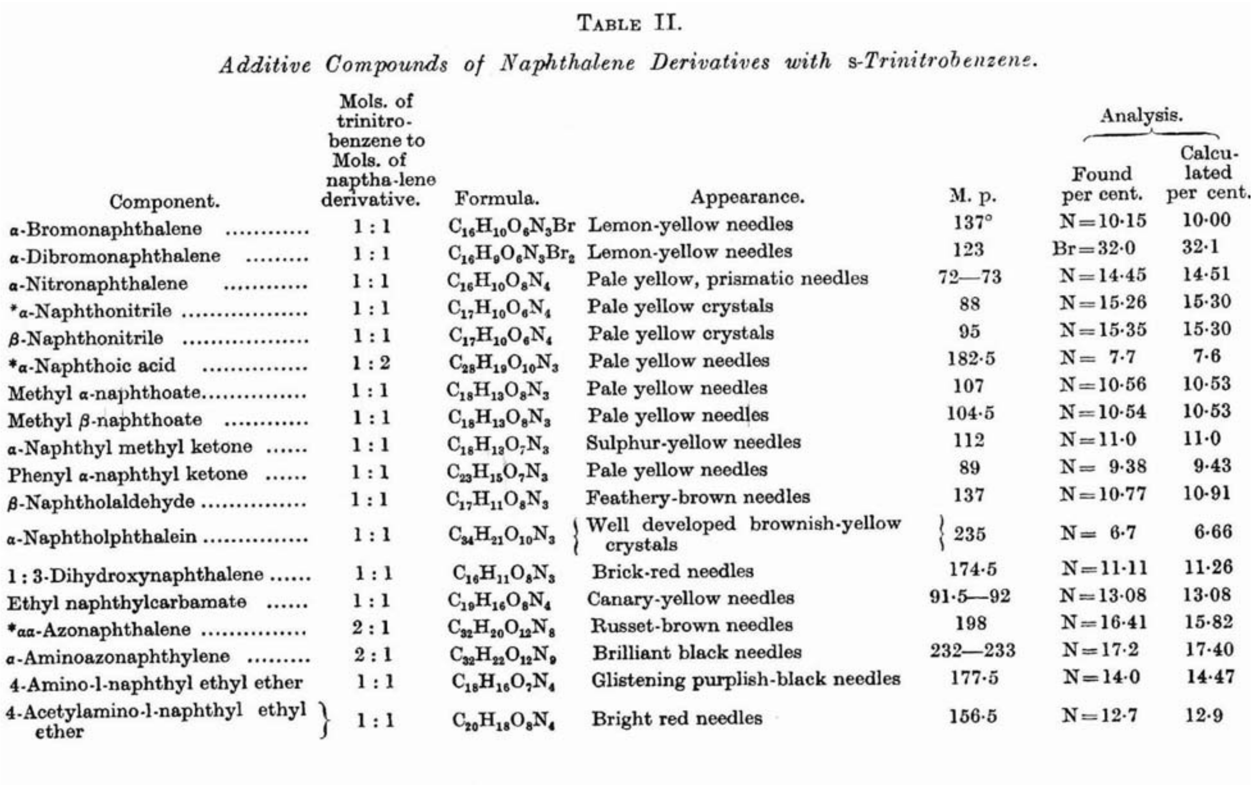

TABLE II.

Additive Compounds of Naphthalene Derivatives with s-*Trinitrobenzene.*

Component.	Mols. of trinitro-benzene to Mols. of naptha-lene derivative.	Formula.	Appearance.	M. p.	Analysis.	
					Found per cent.	Calculated per cent.
α-Bromonaphthalene	1 : 1	$C_{16}H_{10}O_6N_3Br$	Lemon-yellow needles	137°	N=10·15	10·00
α-Dibromonaphthalene	1 : 1	$C_{16}H_9O_6N_3Br_2$	Lemon-yellow needles	123	Br=32·0	32·1
α-Nitronaphthalene	1 : 1	$C_{16}H_{10}O_8N_4$	Pale yellow, prismatic needles	72—73	N=14·45	14·51
*α-Naphthonitrile	1 : 1	$C_{17}H_{10}O_6N_4$	Pale yellow crystals	88	N=15·26	15·30
β-Naphthonitrile	1 : 1	$C_{17}H_{10}O_6N_4$	Pale yellow crystals	95	N=15·35	15·30
*α-Naphthoic acid	1 : 2	$C_{28}H_{19}O_{10}N_3$	Pale yellow needles	182·5	N= 7·7	7·6
Methyl α-naphthoate	1 : 1	$C_{18}H_{13}O_8N_3$	Pale yellow needles	107	N=10·56	10·53
Methyl β-naphthoate	1 : 1	$C_{18}H_{13}O_8N_3$	Pale yellow needles	104·5	N=10·54	10·53
α-Naphthyl methyl ketone	1 : 1	$C_{18}H_{13}O_7N_3$	Sulphur-yellow needles	112	N=11·0	11·0
Phenyl α-naphthyl ketone	1 : 1	$C_{23}H_{15}O_7N_3$	Pale yellow needles	89	N= 9·38	9·43
β-Naphtholaldehyde	1 : 1	$C_{17}H_{11}O_8N_3$	Feathery-brown needles	137	N=10·77	10·91
α-Naphtholphthalein	1 : 1	$C_{34}H_{21}O_{10}N_3$	Well developed brownish-yellow crystals	235	N= 6·7	6·66
1 : 3-Dihydroxynaphthalene	1 : 1	$C_{16}H_{11}O_8N_3$	Brick-red needles	174·5	N=11·11	11·26
Ethyl naphthylcarbamate	1 : 1	$C_{19}H_{16}O_8N_4$	Canary-yellow needles	91·5—92	N=13·08	13·08
*αα-Azonaphthalene	2 : 1	$C_{32}H_{20}O_{12}N_8$	Russet-brown needles	198	N=16·41	15·82
α-Aminoazonaphthylene	2 : 1	$C_{32}H_{22}O_{12}N_9$	Brilliant black needles	232—233	N=17·2	17·40
4-Amino-1-naphthyl ethyl ether	1 : 1	$C_{18}H_{16}O_7N_4$	Glistening purplish-black needles	177·5	N=14·0	14·47
4-Acetylamino-1-naphthyl ethyl ether	1 : 1	$C_{20}H_{18}O_8N_4$	Bright red needles	156·5	N=12·7	12·9

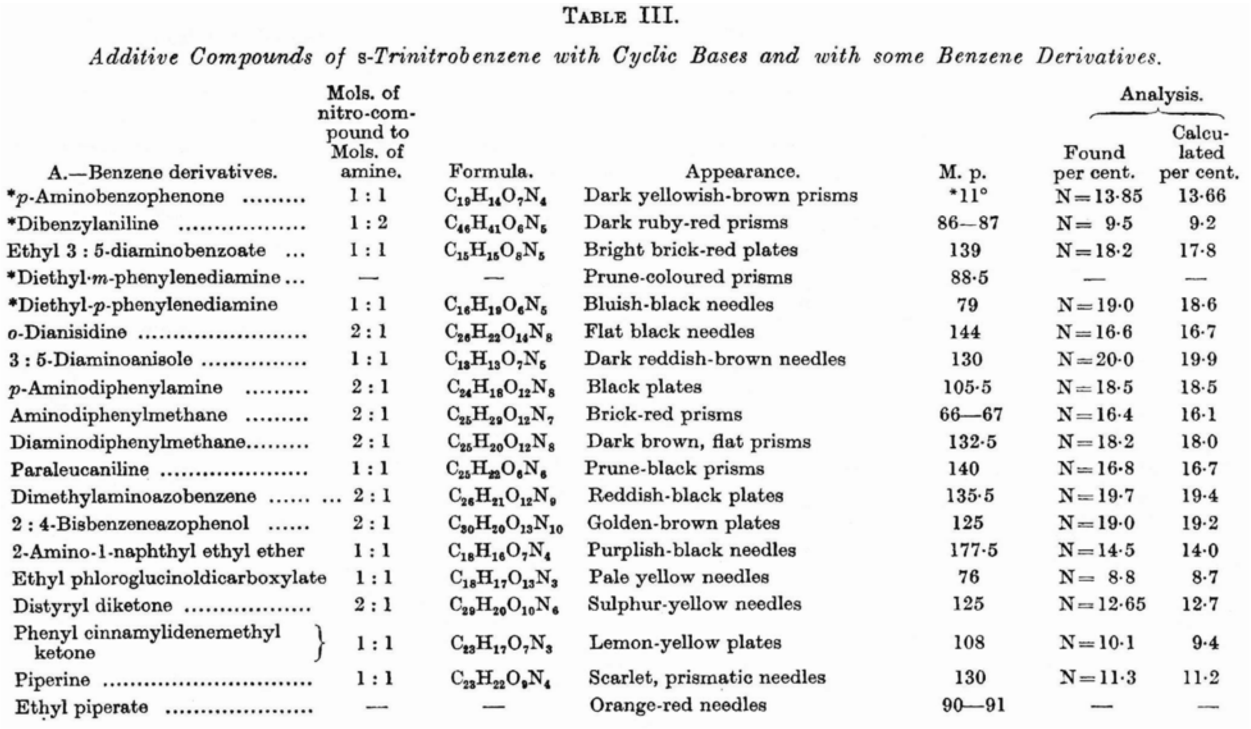

TABLE III.

Additive Compounds of s-*Trinitrobenzene with Cyclic Bases and with some Benzene Derivatives.*

A.—Benzene derivatives.	Mols. of nitro-compound to Mols. of amine.	Formula.	Appearance.	M. p.	Analysis.	
					Found per cent.	Calculated per cent.
**p*-Aminobenzophenone	1 : 1	$C_{19}H_{14}O_7N_4$	Dark yellowish-brown prisms	*11°	N=13·85	13·66
*Dibenzylaniline	1 : 2	$C_{46}H_{41}O_6N_5$	Dark ruby-red prisms	86—87	N= 9·5	9·2
Ethyl 3 : 5-diaminobenzoate ...	1 : 1	$C_{15}H_{15}O_8N_5$	Bright brick-red plates	139	N=18·2	17·8
*Diethyl-*m*-phenylenediamine ...	—	—	Prune-coloured prisms	88·5	—	—
*Diethyl-*p*-phenylenediamine	1 : 1	$C_{16}H_{19}O_6N_5$	Bluish-black needles	79	N=19·0	18·6
o-Dianisidine	2 : 1	$C_{26}H_{22}O_{14}N_8$	Flat black needles	144	N=16·6	16·7
3 : 5-Diaminoanisole	1 : 1	$C_{13}H_{13}O_7N_5$	Dark reddish-brown needles	130	N=20·0	19·9
p-Aminodiphenylamine	2 : 1	$C_{24}H_{18}O_{12}N_8$	Black plates	105·5	N=18·5	18·5
Aminodiphenylmethane	2 : 1	$C_{25}H_{29}O_{12}N_7$	Brick-red prisms	66—67	N=16·4	16·1
Diaminodiphenylmethane.........	2 : 1	$C_{25}H_{20}O_{12}N_8$	Dark brown, flat prisms	132·5	N=18·2	18·0
Paraleucaniline	1 : 1	$C_{25}H_{22}O_6N_6$	Prune-black prisms	140	N=16·8	16·7
Dimethylaminoazobenzene	2 : 1	$C_{26}H_{21}O_{12}N_9$	Reddish-black plates	135·5	N=19·7	19·4
2 : 4-Bisbenzeneazophenol	2 : 1	$C_{30}H_{20}O_{13}N_{10}$	Golden-brown plates	125	N=19·0	19·2
2-Amino-1-naphthyl ethyl ether	1 : 1	$C_{18}H_{16}O_7N_4$	Purplish-black needles	177·5	N=14·5	14·0
Ethyl phloroglucinoldicarboxylate	1 : 1	$C_{18}H_{17}O_{13}N_3$	Pale yellow needles	76	N= 8·8	8·7
Distyryl diketone	2 : 1	$C_{29}H_{20}O_{10}N_6$	Sulphur-yellow needles	125	N=12·65	12·7
Phenyl cinnamylidenemethyl ketone	1 : 1	$C_{23}H_{17}O_7N_3$	Lemon-yellow plates	108	N=10·1	9·4
Piperine	1 : 1	$C_{23}H_{22}O_9N_4$	Scarlet, prismatic needles	130	N=11·3	11·2
Ethyl piperate	—	—	Orange-red needles	90—91	—	—

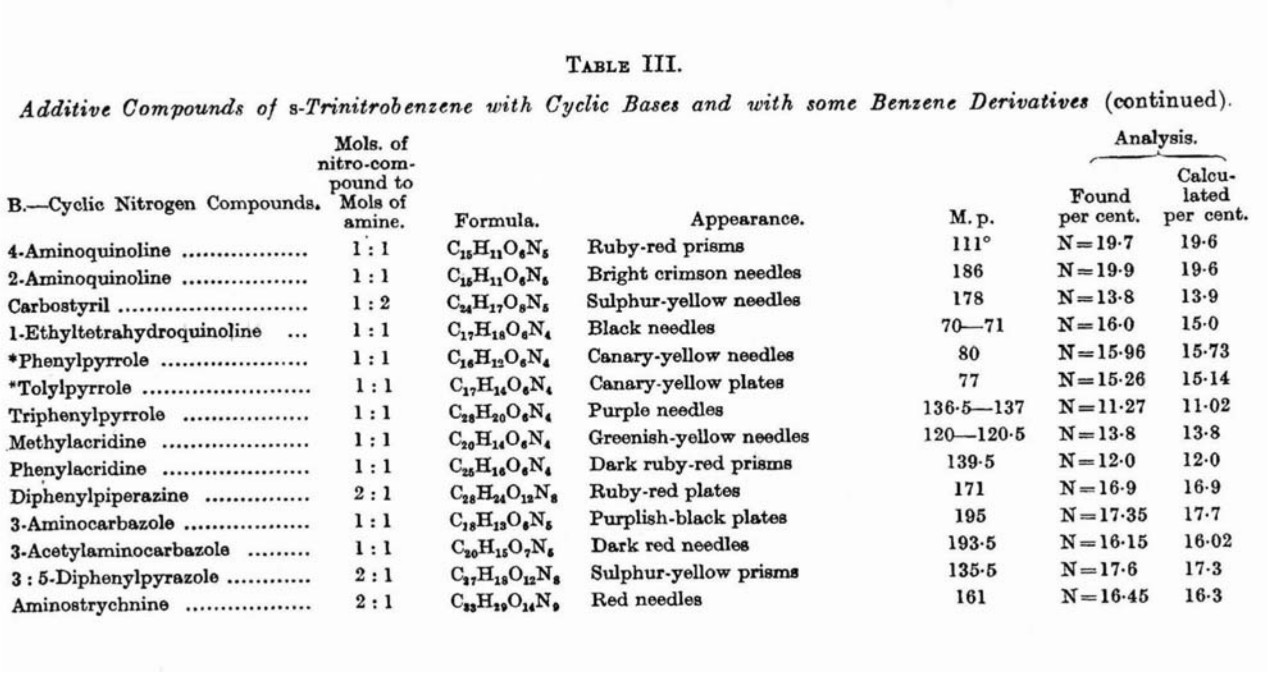

TABLE III.

Additive Compounds of s-*Trinitrobenzene with Cyclic Bases and with some Benzene Derivatives* (continued).

B.—Cyclic Nitrogen Compounds.	Mols. of nitro-compound to Mols of amine.	Formula.	Appearance.	M. p.	Analysis.	
					Found per cent.	Calculated per cent.
4-Aminoquinoline	1 : 1	$C_{15}H_{11}O_6N_5$	Ruby-red prisms	111°	N=19·7	19·6
2-Aminoquinoline	1 : 1	$C_{15}H_{11}O_6N_5$	Bright crimson needles	186	N=19·9	19·6
Carbostyril	1 : 2	$C_{24}H_{17}O_8N_5$	Sulphur-yellow needles	178	N=13·8	13·9
1-Ethyltetrahydroquinoline ...	1 : 1	$C_{17}H_{18}O_6N_4$	Black needles	70—71	N=16·0	15·0
*Phenylpyrrole	1 : 1	$C_{16}H_{12}O_6N_4$	Canary-yellow needles	80	N=15·96	15·73
*Tolylpyrrole	1 : 1	$C_{17}H_{14}O_6N_4$	Canary-yellow plates	77	N=15·26	15·14
Triphenylpyrrole	1 : 1	$C_{28}H_{20}O_6N_4$	Purple needles	136·5—137	N=11·27	11·02
Methylacridine	1 : 1	$C_{20}H_{14}O_6N_4$	Greenish-yellow needles	120—120·5	N=13·8	13·8
Phenylacridine	1 : 1	$C_{25}H_{16}O_6N_4$	Dark ruby-red prisms	139·5	N=12·0	12·0
Diphenylpiperazine	2 : 1	$C_{28}H_{24}O_{12}N_8$	Ruby-red plates	171	N=16·9	16·9
3-Aminocarbazole	1 : 1	$C_{18}H_{13}O_6N_5$	Purplish-black plates	195	N=17·35	17·7
3-Acetylaminocarbazole	1 : 1	$C_{20}H_{15}O_7N_5$	Dark red needles	193·5	N=16·15	16·02
3 : 5-Diphenylpyrazole	2 : 1	$C_{27}H_{18}O_{12}N_8$	Sulphur-yellow prisms	135·5	N=17·6	17·3
Aminostrychnine	2 : 1	$C_{33}H_{29}O_{14}N_9$	Red needles	161	N=16·45	16·3

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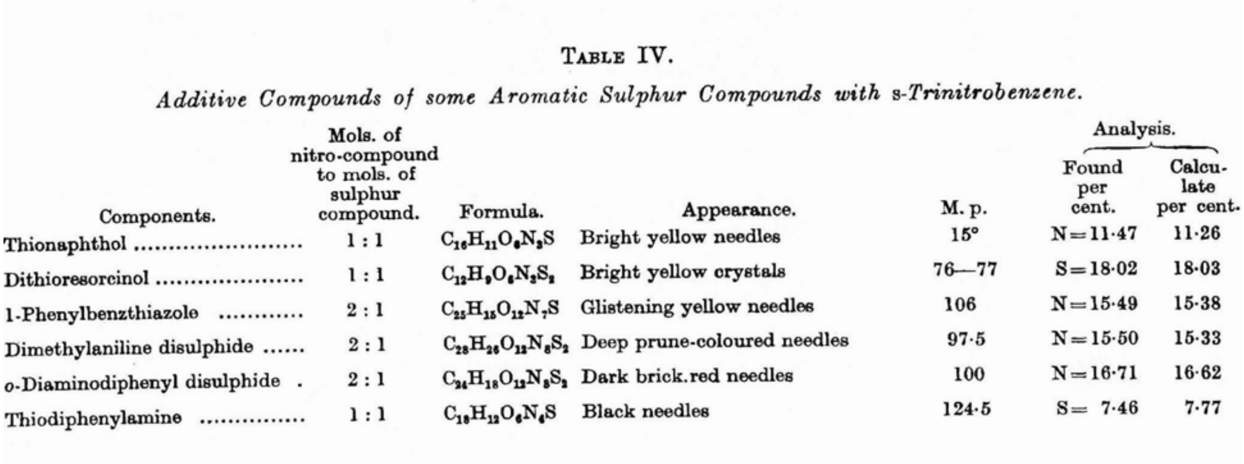

TABLE IV.

Additive Compounds of some Aromatic Sulphur Compounds with s-*Trinitrobenzene.*

Components.	Mols. of nitro-compound to mols. of sulphur compound.	Formula.	Appearance.	M. p.	Analysis.	
					Found per cent.	Calcu-late per cent.
Thionaphthol	1 : 1	$C_{16}H_{11}O_6N_3S$	Bright yellow needles	15°	N=11·47	11·26
Dithioresorcinol	1 : 1	$C_{12}H_9O_6N_3S_2$	Bright yellow crystals	76—77	S=18·02	18·03
1-Phenylbenzthiazole	2 : 1	$C_{25}H_{15}O_{12}N_7S$	Glistening yellow needles	106	N=15·49	15·38
Dimethylaniline disulphide	2 : 1	$C_{28}H_{26}O_{12}N_8S_2$	Deep prune-coloured needles	97·5	N=15·50	15·33
o-Diaminodiphenyl disulphide .	2 : 1	$C_{24}H_{18}O_{12}N_8S_2$	Dark brick.red needles	100	N=16·71	16·62
Thiodiphenylamine	1 : 1	$C_{18}H_{12}O_6N_4S$	Black needles	124·5	S= 7·46	7·77