Additive Compounds of *s*-Trinitrobenzene with Amino Derivatives of Complex Aromatic Hydrocarbons.

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In a series of papers it has been pointed out that *s*-trinitrobenzene forms additive compounds with many aromatic hydrocarbons, amines, phenols and phenolic ethers (J. C. S , *Trans.* 1901, *79*, 522 ; 1903, S3, 1384 ; 1906, *89*, 583 ; 1910, *97*, 773; 1911, *99*, 209, this Journal Vol. I p. 149). As a rule the additive compounds obtained from naphthalene derivatives are more stable than those derived from the corresponding benzene compounds and the object of the work described in this paper has been to ascertain whether the amino derivatives of complex hydrocarbons, such as phenanthrene, anthracene, acenaphthene and fluorene, yield still more stable additive compounds with trinitrobenzene.

The behaviour of trinitrobenzene towards the following compounds has been studied :—α and p -modifications of 9-aminophenanthrene, 4-aminophenanthrene and the isomeric 2-amino compound, 9-aminoanthracene, α and p -anthramines, α and p anthrols, their ethyl ethers and the potassium derivative of α-anthrol, 2-aminofluorene, diaminofluorene, 9-amino-acenaphthene.

The experiments prove that all the amino derivatives examined yield additive compounds with trinitrobenzene. With the exception of amino-fluorene, all the compounds are formed by the union of equimolecular quantities of base and of trinitrobenzene.

The colours of the additive compounds are relatively deep being, as a rule, either black or deep brown.

The additive compounds derived from anthracene are relatively more deeply coloured than those derived from naphthalene as shown in the following table :—

	Colour of additive compound.		Colour of additive compound.
Anthracene	Scarlet	Naphthalene	Pale yellow
α-Anthramine	Black	α-Naphthylamine	Brick red
P- do	,,	β - do	
α-Anthrol	deep redbrown	α-Naphthol	Orange yellow
P- do	,,	p- do	
Ethyl ethers	Scarlet or brick red.	Ethyl ethers	Canary yellow

The compounds are comparatively stable and can be crystallised from most solvents, but determinations of the molecular weights show that in dilute benzene solution nearly complete dissociation into the components takes place.

The compounds, on the whole, resemble the additive compounds from the naphthylamines, but several of them appear to be incapable of yielding acetyl derivatives.

The additive compounds derived from α and β-anthrols and thier ethyl ethers are not so deeply coloured as the corresponding compounds from α and β-anthramine. This is in complete accord with previous results and is to be attributed to the feebler auxochrome effect of the hydroxyl group as compared with the amino group. (Compare this vol. p. 152, also J. C. S. *Trans.* 1911, *99*, 209).

EXPERIMENTAL.

α-9-*Aminophenanthrene.* The *additive compound*, $C_{14}H_9NH_2, C_6H_3(NO_2)_3$, separates when hot alcoholic solutions of its components are mixed, it crystallises from chloroform in dark chocolate coloured needles m. p. 220 - 221.°

0·2863 gave 40·6 c. c. of nitrogen at 27° and 671 mm. N=14·0%
$C_{20}H_{14}O_6N_4$ requires N = 13·8

0·1130 dissolved in 17·42 of pure benzene lowered the freezing point 0·140° M = 218

0·202 in 13·065 of pure benzene raised the boiling point 0·187° M = 221. Molecular weight for the completely dissociated compound is 203.

When warmed with acetic anhydride the additive compound yields an *acetyl* derivative, $C_{14}H_9NH.CO.CH_3, C_6H_3(NO_2)_3$, which crystallises from 90 per cent alcohol in golden yellow needles melting at 190°.

0·0880 gave 11·0 cc. of nitrogen at 23° and 686 mm. N = 12·8
$C_{22}H_{16}O_7N_4$ requires N = 12·5.

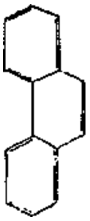
The β-modification of 9-Aminophenanthrene also forms an *additive compound*, $C_{20}H_{14}O_6N_4$, with tf-trinitrobenzene. This crystallises from alcohol in light red, nodular masses, or from chloroform, in which it is readily soluble, in clusters of minute reddish crystals of m. p. 101·5 - 105°.

0·1387 gave 18·3 cc. of nitrogen at 25° and 089 mm. N = 13·5%
It is partially decomposed into its components when recrystallised

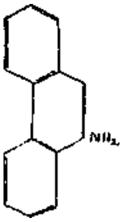
from alcohol and is characterised by its pale colour as compared with the additive compounds of other aromatic amino derivatives. It differs also from practically all the other additive compounds derived from primary amines as it does not appear to be decomposed by hydrogen chloride

A convenient method of estimating the percentage of *s*-trinitrobenzene in many of these additive compounds is to decompose them with dilute hydrochloric acid and weigh the trinitrobenzene left after washing with water. This method works well provided the hydrochloride of the base is fairly readily soluble in water. When the hydrochloride of the base is sparingly soluble in water, or is readily hydrolysed by water, a convenient method is to dissolve the additive compound in benzene, pass in dry hydrogen chloride then remove the precipitated hydrochloride, wash with benzene and after removal of the benzene, weigh the trinitrobenzene. This method gave good results with the additive compounds from α-9-aminophenanthrene and aminofluorene, but the additive compound derived from β -9-aminophenanthrene is not decomposed when hydrogen chloride is passed into its benzene solution.

Schmidt and Heinle (*Ber.* 1911, *44*, 1493) have suggested the following formulae for the α and p modifications of 9-aminophenanthrene :—

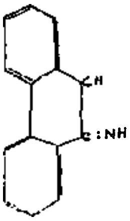


α (Stable)



P (Labile)

The pale colour of the additive compound derived from the p -modification and the fact that the compound does not appear to be decomposed by hydrogen chloride point rather to the absence of an amino group in the original base. It is possible that the base has an imino group and may perhaps be represented by the formula :—



4-Amino-phenanthrene. The additive compound, $C_{14}H_9NH_2,C_6H_3(NO_2)_3$, crystallises from alcohol in chocolate prismatic needles with shining faces m. p.195-196°

0·1601 gave 22·5 cc. of nitrogen at 27° and 673 mm. N = 14·0
$C_{20}H_{14}O_6N_4$ requires 13·8.

It yields a pale yellow *acetyl* derivative.

2-Amino-phenanthrene. The additive compound crystallises from alcohol in slender prismatic needles m. p. 175-176° The amount obtained was too small for analysis.

2-*Aminofluorene.* When molecular quantities of the base and trinitrobenzene are separately dissolved in alcohol and the two solutions mixed, a dark coloured additive compound separates together with a little trinitrobenzene. The additive compound crystallises from alcohol in reddish chocolate coloured needles m. p. 116-117°.

Analysis :—

0·1365 gave 18·2 cc. nitrogen at 22° and 684 mm.

0·3356 „ 0·1622 of trinitrobenzene m. p. 121°.

0·1447 „ 0·0508 H_2O and 0·3190 CO_2.

N=13·7 ; Trinitrobenzene = 48·3 ; C=60·10 and H= 3·90.

These results agree best with the formula 5 $C_{13}H_9NH_2$, 4 $C_6H_3(NO_2)_3$ as shown by the following table :—

	Ratio of mols. of base to trinitrobenzene.			Found
	1:1	3:2	5:4	
	14·8	13·0	13·5	13·7
Trinitro-benzene	54·1	44·0	48·5	48·3
C	57·9	63·2	60·7	60·1
H	3·55	4·02	3·8	3·9

The composition of this compound is more complex than that of any of the additive compounds hitherto studied. Fluorene itself (this vol. 155) yields a compound 3 $C_6H_3(NO_2)_3$,2 $C_{13}H_{10}$, but most hydrocarbons, amines, and phenols yield compounds of the type 1 mol. of trinitrobenzene and 1 mol. of the substance, or 2 mols. of trinitrobenzene and 1 mol. of the substance.

Confirmation of the above composition was obtained by taking the base and trinitrobenzene in different proportions mixing their alcoholic solutions and determining whether pure additive compound or additive compound with excess of trinitrobenzene or base separated. It was found that when the two components were taken in the molecular proportions 5:4 that nothing but additive compound could be isolated. When other proportions were used small amounts of colourless crystals were obtained in some of the latter fractions and these could usually be identified as trinitrobenzene or aminofluorene.

Determination of the molecular weight by the cryoscopic method in benzene solution gave the following results :—

i. 0·1390 in 17·42 of benzene gave a lowering of 0·2103°. M = 190.

ii. 0·1691 in 17·42 of benzene gave a lowering of 0·2686°. M=181.

When the additive compound was prepared from benzene solutions dark chocolate brown needles m. p. 114-115° were obtained. On analysis these proved to have the composition $C_{13}H_9NH_2,C_6H_3(NO_2)_3$.

0·1458 gave 20·6 cc. nitrogen at 29° and 689 mm. nitrogen=14·2

0·1499 ,, 21·25 ,, 29 and 689 ,, =14·25

01032 ,, 0 0550 of trinitrobenzene (m. p. 121°) = 53·3%

$C_{13}H_9NH_2,C_6H_3(NO_2)_3$ requires 14·2% of nitrogen and 54 1% of trinitrobenzene.

The compound obtained from benzene solution when acetylated with acetic anhydride gave an *acetyl* derivative. It crystallises from benzene in orange coloured needles m. p. 180-181°.

0·0738 gave 9·8 cc. of nitrogen at 26° and 687 mm. N=13·5. A compound with the molecular ratio 5:4 requires N=13·5%

Diaminofluorene. A small amount of an *additive compound* was obtained from alcoholic solution in the form of black coloured needles m. p. 210".

9-Aminoacenaphthene. This base combines with trinitrobenzene and the product crystallises from alcohol or chloroform in dark prune coloured needles m. p. 213-214°.

0·1326 gave 19·3 cc. of nitrogen at 27° and 688 mm. N=14·7%

0·1012 gave 0·0551 of trinitrobenzene=54·7%
$C_{18}H_{14}O_6N_4$ requires N=14·7% and trinitrobenzene=55·7%.

A determination of its molecular weight in benzene solution proved that considerable dissociation into its components had occured.

0·0515 in 17·42 of benzene produced a depression of 0·069°.
M=214. The theoretical value for $C_{18}H_{14}O_6N_4$ is 382.

When acetylated the additive compound yields an *acetyl* derivative which crystallises from alcohol in yellow needles melting at 157-158°.

9-*Aminoanthracene.* The *additive compound*, $C_{14}H_{9}$ $NH_2,C_6H_3(NO_2)_3$, prepared by mixing together hot alcoholic solutions of the components, crystallises from chloroform in minute purple black needles m. p. 215.5°.

0·1558 gave 20·45 cc. of nitrogen at 18° and 689 mm. N=13·8%
0·0928 gave 0·0488 of trinitrobenzene (m. p. 121°)=52.6%
$C_{20}H_{14}O_6N_4$ requires N=13·8 and trinitrobenzene=52·4%.

9-Acetylaminoanthrasene does not appear to yield an additive compound with trinitrobenzene.

α-*Anthramine.* The *additive compound*, $C_{20}H_{14}O_6N_4$, crystallises from alcohol in raven black slender needles melting at 206-207°.

0·1415 gave 19·0 cc. of nitrogen at 21° and 690 mm. N=14·0%
$C_{20}H_{14}O_6N_4$ requires 13·8%.

α-Acetylanthramine does not form an additive compound with trinitrobenzene.

β-*Anthramine.* β-Anthramine prepared from β-anthrol (Annalen, *212*, 57), yields an *additive compound*, $C_{14}H_9$ $NH_2,C_6H_3(NO_2)_3$, which crystallises from alcohol in glistening black needles m. p. 168·5—169°.

0·0938 gave 12·8 cc. of nitrogen at 22° and 693 mm. N=14·2%

An additive compound could not be obtained from α-Acetylanthramine and trinitrobenzene.

α-*Anthrol.* α-Anthrol yields an *additive compound*, $C_{14}H_9.OH$, $C_6H_3(NO_2)_3$, which crystallises from benzene in minute dark reddish brown plates melting and decomposing at about 101°.

0·1024 gave 10.7 cc. of nitrogen at 22° and 686 mm. N= $C_{20}H_{13}O_7N_3$ requires 10·3%.

rol ethyl ether. The *additive compound*, $C_{14}H_9.OC_2H_5$, $C_6H_3(NO_2)_3$, crystallises from alcohol or acetone in scarlet needles m. p. 149 5—150·5°.

0·1173 gave 11·4 cc. of nitrogen at 24° and 688 mm. N=9·9% $C_{22}H_{17}O_7N_3$ requires 9·7%.

α-Anthrol. The *additive compound*, $C_{14}H_9OK$, $2C_6H_3(NO_2)_3$ crystallises from alcohol in black needles which are not molten at 275°.

0·1328 tfavo 0·0079 gram. of potassium =5·9% $C_{26}H_{15}O_{13}N_6K$, required 5·9%.

β-Anthrol, forms an *additive compound*, also containing equimolecular proportions of nitro compound and phenol. It crystallises from alcohol in deep reddish brown needles melting at 106°.

0·1057 gave 10·8 cc. of nitrogen at 21° and 690 mm. N=10·65% $C_{20}H_{13}O_7N_3$ requires 10·3%

[illegible] *

The ethyl ether also forms an *additive compound*, $C_{14}H_9OEt,C_6H_3(NO_2)_3$ which crystallises from benzene in minute brick red prisms m. p. 147°.

0·1742 gave 15·8 cc. of nitrogen at 21° and 690 mm. N= $C_{22}H_{17}O_7N_3$ requires 9·7%.

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