Studies on the Organic Molecular Compounds. Part III. On the Molecular Compound-Formation of Aromatic Hydrocarbons with Nitro-Compounds and with Antimony Trihalides.

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It has been shown by a number of investigators that many condensed or non-condensed aromatic ring compounds, such as naphthalene, phenanthrene, anthracene, durene, hexamethylbenzene, diphenyl, dibenzyl, tolane, etc., form addition compounds with nitro compounds and similar substances. The writer has discussed this matter in connexion with compound-formation and halochromism in previous papers.[1]

I. Binary Systems of Condensed Ring Substances. All the aromatic hydrocarbons mentioned here either have been proved or are considered to have the construction, as a whole, of a plane ring molecule, and may be seen to form similar binary phase diagrams with a nitro component. It may therefore be concluded that, in these binary systems, compound-formation is due to the affinity between the unsaturated carbon linkings and the nitro radicals. In the solid crystalline state, however, another condition may be necessary, namely, the formation of a crystal lattice of the addition compound, a condition that is disregarded in the liquid or gaseous state. Consequently, organic molecular compound-formation in the crystalline state is greatly affected by the structure of the component, particularly, the shape of the molecule. All the systems studied showed distinct halochromism when fused, pointing to the presence of molecular compounds in the liquid state, of which, however, only half the number gave crystalline compounds. The result is given in Table 1.

(1) The compound ratio was 1:1, except in the following cases:[2]

3 : 1 phenanthrene—*p*-dinitrobenzene;
2 : 1 naphthalene—styphnic acid, benzene—trinitrobenzene, benzene—picryl chloride;
3 : 2 naphthalene—tetranitrobenzene, acenaphthene–picramide;
2 : 3 pyrene—styphnic acid, fluorene—trinitrobenzene;
1 : 2 fluorene—tetranitrobenzene;
2 : 3 & 1 : 1 phenanthrene—tetranitrobenzene;
1 : 1 & 1 : 2 pyrene—*m*-dinitrobenzene.

(2) The order of compound-formation of nitro compounds with these hydrocarbons was almost the same as that was shown in the previous paper.[1]

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(1) This Bulletin, **15** (1940), 92, 137.
(2) As to the metastable compound, a more detailed report will be published at a not distant date.

Table 1.

A: B(Melting point) / B(Melting point)	[80.0]	[150.0]	[109.5]	[96.0]	[100.5]	[3.5]×	[116.0]	[217]	[251]
Trinitrobenzene [123.0]	1:1 [152.5]×	1:1× [149.5]	1:1 [205.0]	1:1 [168]×	1:1 (158)×	2:1 [71]× or 1:1×	2:3 [105.0]×	1:1 [165]×	1:1 (186)×
Picric acid [122.0]	1:1 [151.5]×	1:1 [218]×	1:1 (183)×	1:1 [160.2]×	1:1 (145)×	1:1 U×	1:1 [84]×	1:1 U×	1:1× U
Tetranitrobenzene [126.0]	3:2 [139.5]	1:1 [163.5]	1:1 [134.0]	1:1 [110.5]	2:3 [139.0] 1:1 U (1:2)	—	1:2 [130.0]	1:1 [171.0]	1:1 U? Decomposed
Picramide [188.5]	1:1 [169]×	1:1 [236.0]	1:1 [191.5]	3:2 [97.0] or 1:1×	1:1× [166.0]	1:1×	1:1 U×	1:1× [163.5]	1:1 U
Trinitrocresol [108.5]	1:1 [126.0]×	1:1 [163.0]	1:1 [144.0]	1:1 [117.9]×	1:1 [113.1]×	—	1:1 [107.2]×	Decomposed×	1:1 U
Styphnic acid [182.0]	2:1 [144.0] or 1:1×	2:3 [173.0] or 1:1	1:1 [178.5] or (2:3)	1:1 [154]×	1:1 [126]×	—	1:1 U×	V or 1:1×	V
Trinitrotoluene [81.5]	1:1 [98]×	1:1 [164.5]	1:1 [133.0]	1:1 [105.7]×	1:1 [84]×	—	1:1 [85]×	V×	V
Picryl chloride [83.0]	1:1 [92]×	1:1 [134.0]	1:1 [120.0]	1:1 [113.2]×	1:1 [88]×	2:1 [39]× or 1:1×	1:1 [64.0]×	1:1 [141.0]×	V
2,4-Dinitrophenol [113.5]	1:1 [92.5]×	1:1 [146.5]	1:1 [92.0]	1:1 [86.0]×	V×	—	V×	V×	V
2,4-Dinitrotoluene [71.0]	1:1 [61]×	1:1 [92.5]	1:1 [73.5]	1:1 [61]× or V×	V×	V×	V×	V×	V
Trinitroanisol [68.0]	V or (1:1 [94.0])	1:1 [104.5]	1:1 [75.0]	V	V	—	V	V	V
p-Dinitrobenzene [173.5]	1:1 [119.0]×	1:1 U	V	V×	3:1 [81]×	V×	V×	V×	V
m-Dinitrobenzene [90.0]	1:1 [50.8] D×	1:1 [92.7] 1:2 [82.5]	1:1 [77.0]	1:1 [72.3]×	V×	V×	V×	V×	V
o-Dinitrobenzene [117.0]	V×	V	V	V×	V×	V×	V×	V×	V
2,6-Dinitrotoluene [65.0]	V×	V	V	V×	V×	V×	V×	V×	V
3,4-Dinitrotoluene [53.0]	V×	V	V	V×	V×	V×	V×	V×	V
p-Nitrophenol [113.0]	V×	V	V	V×	V	—	V	V×	V
m-Nitrophenol [96.5]	V	V	V	V×	V	—	V	V or 1:1×	V
o-Nitrophenol [45.0]	V×	V	V	V×	V	—	V	V×	V

× The data from literature.

A : B (Melting point) shows the value of the crystal from solution.

(3) The hydrocarbon sequence was usually naphthalene, pyrene, fluoranthene > acenaphthene > phenanthrene, benzene > fluorene > anthracene, chrycene.

Certain irregularity was found in the molecular compounds of tetranitrobenzene and styphnic acid.

(4) Halochromic phenomenon was seen in the following order, pyrene, acenaphthene, anthracene > phenanthrene, fluorene > chrycene > fluoranthene > naphthalene > benzene.

(5) It is interesting to note that the molecular compound of dissociation type and incongruent type in this Table, lay between the simple eutectic system and the lowest "melting point elevation" system of the congruent type.

II. Binary Systems of Non-Condensed Ring Substances. The tendency to form molecular compounds of methyderivatives of benzene seemed to become very marked according as the increase of the number of substituents, while their compounds ratios were not simple, showing sometimes a phase diagram of "partially miscible type." In the case of certain compounds having two aromatic rings separated, as each of the separated ring can unite with one molecule of the nitro component, one molecule combine with two molecules of the nitro components.[3] Since in these cases, the shape of the component molecules greately affects the compound-formation, it is not possible to discuss the matter merely on the basis of the plane formula commonly used in the organic chemistry.

Table 2.

	Mesitylene	Prehnitene	Durene	Pentamethyl-benzene	Hexamethyl-benzene
Trinitro-benzene	—	—	2 : 1 [101.0°] PM 1 : 1 (U)*	3 : 2 [121.0°] PM (1 : 1)	1 : 1 (175°)*
Picric acid	m : n*	1 : 1 (U)*	∨ [E : 64.5°]	3 : 2 [124.0°] PM or 1 : 1 (131°)*	1 : 1 (170°)*

	Diphenyl	p, p′-Ditoluyl	Dibenzyl	Stilbene	Tolane
Trinitro-benzene	1 : 1 [U]*	1 : 1 [D : 91.0°]	1 : 2 (102°)*	1 : 2* [121.5°]	1 : 2 (96°)*
Picric acid	∨*	∨ [E : 93.0°]	∨*	1 : 1 [U : 93.0°]	1 : 2 (111°)*

	Diphenyl-methane	Triphenyl-methane	Diphenylamine	Azobenzene	p-Aminoazo-benzene
Trinitro-benzene	—	PM	1 : 2 (100.0°)	1 : 2 (132°)*	1 : 2 [158°]
Picric acid	∨*	PM*	1 : 2 [U : 70.0°] or 1 : 1 [U]*	∨*	Decomposed

* Data from literature.
D: Dissociation type.
U: Incongruent type.
PM: Partially miscible type, the molecular compound of which separates two non-miscible liquids at melting point.
V: Simple eutectic type whose eutectic point is E.
( ) Melting points in parentheses represent those of crystals obtained from solution.

III. Molecular Compounds of Antimony Trihalides. The relationships just described were found to hold true of the organic-inorganic molecular compounds of Menshutkin,[4] some of which, with the writer's

(3) J. J. Sudborough, *J. Chem., Soc.*, **109** (1916), 1339.
(4) B. Menshutkin, *Chem. Zentr.* **1910**, II, 378; **1911**. II. 751; **1912**, I, 408; II, 1436; **1913**, I, 804.

Table 3.

A : B (τ) / A \ B	$SbCl_3$	$SbBr_3$
$C_6H_3(CH_3)_3$ 1, 3, 5	1 : 2 (45.0) 1 : 1 U	1 : 2 (25.0) 1 : 1 U
C_6H_6*	1 : 2 (28.5)	1 : (28.0)
$C_6H_3(CH_3)_3$ 1, 2, 4	1 : 2 26.5) 1 : 1 U or [1 : 1 (−15.6)]	1 : 2 U 1 : 1 U [1 : 2 (−17.5)]
$C_6H_5CH_3$	1 : 2 (25.5) 1 : 1 U	1 : 2 U 1 : 1 U
$C_6H_4(CH_3)_2$ 1, 4	1 : 2 (16.9) or 1 : 1 U	1 : 2 (0.4)
$C_6H_5C_2H_5$	1 : 2 (19.3) 1 : 1 (49)	1 : 1 U
$C_6H_4(CH_3)_2$ 1, 3	1 : 2 (8.3) 1 : 1 U or [1 : 1 (0)]	1 : 1 U
$C_6H_4(CH_3)_2$ 1, 2	1 : 2 (−5.2) 1 : 1 (−3.2)	1 : 1 (−8.5)
$CH_3 \cdot C_6H_4 \cdot CH(CH)_3$ 1, 4	1 : 2 U 1 : 1 U	1 : 1 U or [1 : 1 (0.5)]
$C_6H_5(CH_2)_2CH_3$	1 : 2 U or 1 : 1 (−13.3)	1 : 1 U

A : B (τ) / A \ B	$SbCl_3$	$SbBr_3$
$C_6H_5CH_2CH_2C_6H_5$	1 : 4 (8.7) 1 : 2 U	1 : 4 (1.9)
$C_6H_5NNC_6H_5$	1 : 4 (8.7)	1 : 4 U
$(C_6H_5)_2CH_2$	1 : 2 (42.3)	1 : 2 (18.3)
$C_6H_5CHCHC_6H_5$	1 : 2 (7.3)	1 : 2 Viscous
$C_6H_5C_6H_5$	1 : 2 (−1.2)	1 : 2 U
$(C_6H_5)_3CH$	1 : 1 U	∨

A : B (τ) / A \ B	$SbCl_3$	$SbBr_3$
C_6H_5OH	1 : 2 (−25.3)	1 : 2 U
$C_6H_5OCH_3$	1 : 2 (4.4) 1 : 1 U	1 : 1 (0.5)
$C_6H_5OC_2H_5$	1 : 1 (19.9)	1 : 1 (16.0)
C_6H_5COH	1 : 1 (14.0)	1 : 1 (1.5)
$C_6H_5COCH_3$	1 : 1 (1 .0) or ∨	1 : 1 (−19.5)
$C_6H_4 \cdot CH_3 \cdot NO_2$ 1, 2	1 : 1 (2.5)	1 : 1 U
C_6H_5CN	[1 : 1 (−8.5)]	[1 : 1 (−2.5)]
$C_6H_4 \cdot CH_3 \cdot Cl$ 1, 2	1 : 1 (−15.4)	∨
$C_6H_4 \cdot CH_3 \cdot NO_2$ 1, 2	Viscous, glassy	∨
$C_6H_5NO_2$	[1:1 (−45.5)D] or ∨	∨
$C_6H_4 \cdot CH_3 \cdot NO_2$ 1, 4	[1 : 1 (−55.0)]	∨
$C_6H_4(NO_2)_2$ 1, 3	∨ or [1 : 1 U]	∨
C_6H_5F, C_6H_5Cl, C_6H_5Br	1 : 1 U	∨
C_6H_5I	[1 : 1 U] or ∨	∨
$C_6H_4 \cdot CH_3 \cdot Cl$ 1, 3	[1 : 1 U]	∨
$C_6H_4 \cdot CH_3 \cdot Cl$ 1,4, $C_6H_4Cl_2$ 1, 4, $C_6H_4Br_2$ 1, 4, $C_6H_5CO_2H$, C_6H_5COCl, $C_6H_3SO_3H$	∨	∨

* In the writer's experiment pentamethylbenzene and durene gave superior compound-formation, their τ are almost 85 and 31 in type 1 : 2. Methylation of the benzene nucleus seems to increase compound-formation, while that of the side chain reverses the result.

additional data, are given in Table 3. Like a nitro compound, antimony trichloride or tribromide gives a combination of a type similar to an aromatic ring. By an arrangement of the antimony trihalide molecular compounds in the order of "melting point elevation", compound-formation was clearly shown to be closely related to the configuration of the aromatic compound. These systems were proved from the diagram to have usually two sets of compounds. Of these two compounds the less stable one (ratio 1:2) was obtained only when the aromatic component exhibited a superior compound-formation. It was moreover found that antimony chloride was more strongly additive than the bromide, and that compound-formation of the benzene derivatives decreased when atoms of halogen or of negative groups having properties similar to the halogens were introduced into the benzene nucleus. Certain regularity was also found in Table 3, between compound-formation and the substitution of benzene nucleus.

Experimental.

I. *Binary Systems of Pyrene and of Fluoranthene.* Pyrene and fluoranthene exhibited compound-formations that closely resemble each other, the former slightly more marked than the latter. See Figs. 1, 2 for diagrams.

(1) Pyrene—2,4,6-trinitrobenzene.

Pyrene: 9.0 mg.

Mol% pyrene	100.0	84.0	55.3	48.6	37.3	26.0	17.2
Melting point	150.0	193.5	244.0	245.5	241.5	227.0	204.0
Thawing point	149.0	141.2	210.0	244.5	165.0	106.0	105.0

Pyrene: 20.0 mg.

Mol% pyrene	95.5	87.5	77.8	67.9
Melting point	148.0	166.0	209.3	235.5
Thawing point	142.0	141.6	142.0	146.0

Trinitrobenzene: 20.0 mg.

Mol% trinitrobenzene	95.0	82.6
Melting point	147.0	205.0
Thawing point	116.0	116.0

Eutectic point: 141.5°, 116.0° (metastable: 105.5°); 90.0 mol%, 2.0 mol% pyrene.

Compound (1:1): reddish orange prisms, melting at 245.5°. Sublimable by heating.

(2) Fluoranthene—2,4,6-trinitrobenzene.

Trinitrobenzene: 9.8 mg.

Mol% trinitrobenzene	73.8	58.1	46.9	30.1	16.1
Melting point	188.5	203.0	204.0	—	124.5
Thawing point	103.0	117.0	149.0	98.0	97.0

Fluoranthene 4.3 mg.

Mol% fluoranthene	100.0	95.1	71.7	62.4	51.1	28.6	17.2	10.7
Melting point	109.5	106.0	183.0	200.0	204.5	188.3	164.5	139.8
Thawing point	108.5	98.0	99.0	99.0	202.0	103.0	103.0	103.0

Eutectic point: 98.5°, 103.0°; 86.8 mol%, 4.0 mol% fluoranthene.

Compound (1:1): bright yellow prisms or needles, melting at 205.0°. Difficultly sublimable. Light voluminous crystals were obtained from the alcoholic solution.

Pyrene and fluoranthene gave the most stable compounds with trinitrobenbene. When fused they scarcely dissociated; by further heating, the molecular compounds sublimed without decomposing.

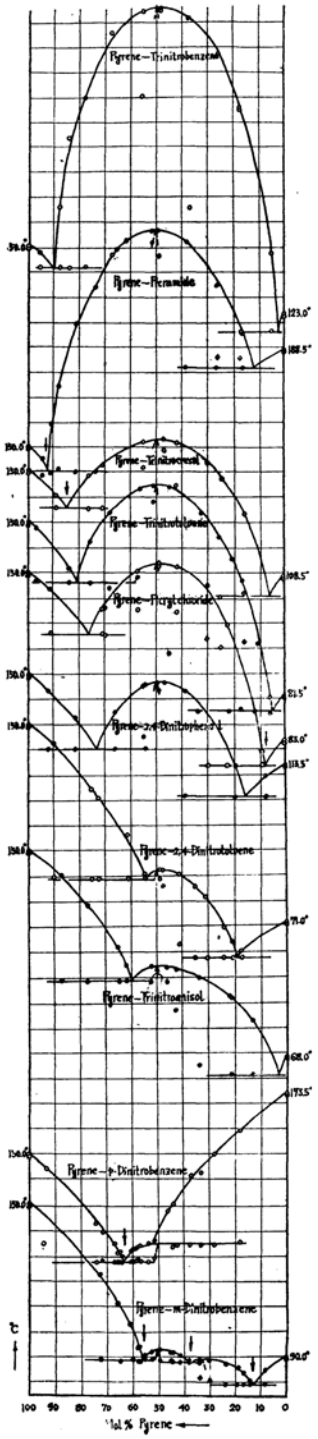

Fig. 1.

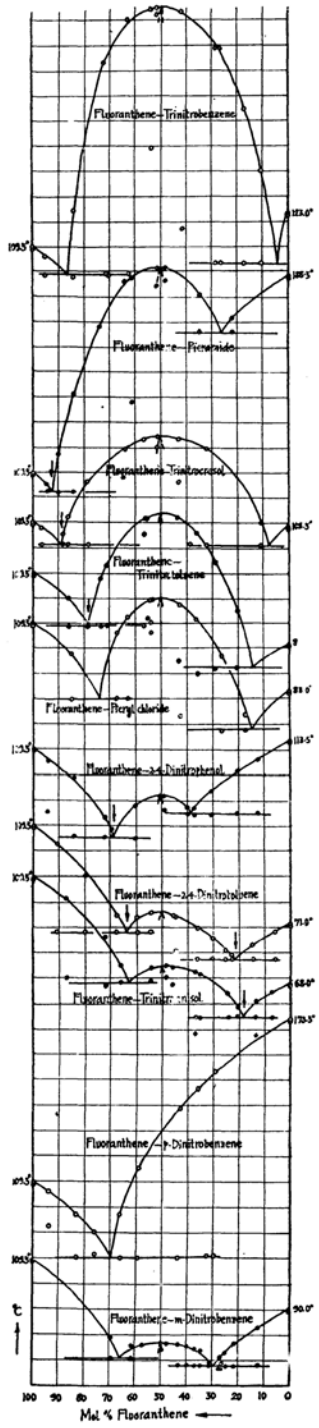

Fig. 2.

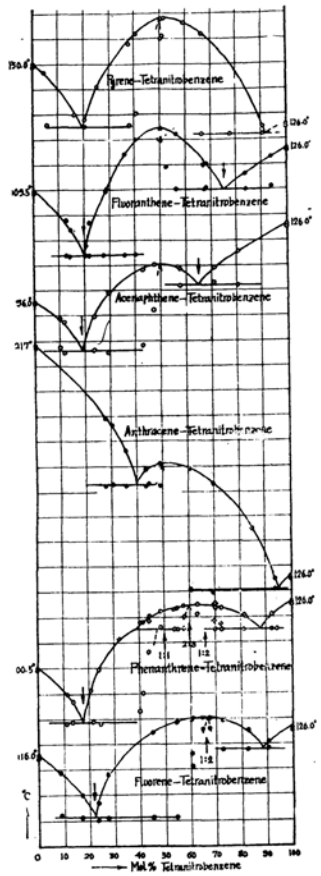

Fig. 3.

(3) Pyrene—picramide.

Pyrene: 9.4 mg.

Mol% pyrene	94.7	88.2	65.4	52.0	50.3	38.6	26.9	16.6
Melting point	145.0	174.0	228.5	235.5	236.0	231.0	213.5	195.5
Thawing point	138.0	141.0	139.5	231.0	225.0	181.0	180.5	180.5

Pyrene: 17.0 mg.

Mol% pyrene	91.5	81.4	73.8	62.3
Melting point	169.0	199.0	213.0	232.3
Thawing point	139.0	139.5	139.0	—

Eutectic point: 139.5°, 180.5°; 92.0 mol%, 12.2 mol% picramide.
Compound (1:1): brown prisms or plates, melting at 236.0°. Stable, difficultly sublimable.

(4) Fluoranthene—picramide.

Picramide: 8.2 mg.

Mol% picramide	77.7	51.5	38.4	26.2	15.8
Melting point	171.5	191.0	187.5	168.0	141.0
Thawing point	166.0	186.0	138.0	—	102.0

Total fluoranthene: 12.6 mg.

Mol% fluoranthene	90.1	94.7	64.8	51.8	35.2
Melting point	117.5	105.0	186.0	191.0	180.5
Thawing point	101.0	102.0	107.0	184.0	166.0

Eutectic point: 102.0°, 166.0°; 92.8 mol%, 26.7 mol% fluoranthene.
Compound (1:1): fine brownish yellow needles or powder, melting at 191.5°. Stable, difficultly sublimable.

(5) Pyrene—trinitrocresol.

Trinitrocresol: 5.6 mg.

Mol% trinitrocresol	69.9	57.8	44.9	29.0
Melting point	153.5	161.0	161.0	152.0
Thawing point	83.0	144.0	151.0	135.0

Pyrene: 7.3 mg.

Mol% pyrene	89.1	76.5	47.1	24.6	15.3
Melting point	140.0	148.0	163.0	147.0	132.5
Thawing point	135.0	134.5	158.0	100.0	102.0
				(80.0)	(82.0)

Eutectic point: 135.0°, 101.0°; 84.8 mol%, 7.5 mol% pyrene.
Compound (1:1): reddish brown powder, melting at 163.0.

(6) Fluoranthene—trinitrocresol.

Trinitrocresol 11.8 mg.

Mol% trinitrocresol	89.0	67.7	48.3	36.4
Melting point	110.0	139.0	144.0	139.0
Thawing point	101.0	101.0	140.0	—

Fluoranthene: 19.6 mg.

Mol% fluoranthene	96.2	88.3	86.2	78.6	56.8	43.1	38.9
Melting point	107.8	105.0	112.0	126.5	143.0	143.0	—
Thawing point	100.8	101.0	101.0	101.0	105.0	126.0	1018

Eutectic point: 110.0°, 110.0°; 89.0 mol%, 8.2 mol% fluoranthene.
Compound (1:1) yellow needles, melting at 144.0°.

Trinitrocresol gave the widest existence range (*w*).

(7) Pyrene—2,4,6-trinitrotoluene.

Pyrene: 9.1 mg.

Mol% pyrene	97.1	84.4	76.1	68.5	56.9	51.8	45.0	33.0	21.0
Melting point	148.0	132.0	142.5	154.0	163.5	164.5	163.0	153.5	135.5
Thawing point	127.0	126.0	126.0	126.0	128.0	158.0	98.0	75.0	75.0

Trinitrotoluene: 30.0 mg.

Mol% trinitrotoluene	94.4	89.0	83.5	74.1
Melting point	81.0	102.0	127.0	144.0
Thawing point	74.0	75.0	76.0	—

Eutectic point: 126.0°, 75.0°; 81.2 mol%, 4.8 mol% trinitrotoluene.
Compound (1:1): orange plates or prisms, melting at 164.5°.

(8) Fluoranthene—2,4,6-trinitrotoluene.

Trinitrotoluene 5.7 mg.

Mol% trinitrotoluene	63.9	44.3	28.5
Melting point	126.0	131.5	113.0
Thawing point	70.0	92.0	89.0

Fluoranthene: 11.5 mg.

Mol% fluoranthene	86.2	78.8	73.7	56.4	43.3	29.2	20.8
Melting point	100.2	90.0	107.0	132.0	132.0	114.0	95.0
Thawing point	88.5	89.0	88.6	89.0	75.5	72.0	72.8

Eutectic point: 89.0°, 72.5°; 78.8 mol%, 15.0 mol% fluoranthene.
Compound (1:1): fine yellow needles or powder, melting at 133.0°.

(9) Pyrene—picryl chloride.

Picryl chloride: 9.1 mg.

Mol picryl chloride	70.0	57.0	42.6	30.1
Melting point	145.0	152.0	150.0	136.0
Thawing point	73.0	134.0	135.0	125.0

Pyrene: 4.9 mg.

Mol% pyrene	91.0	71.2	49.1	22.4	8.7
Melting point	143.8	134.5	153.5	128.5	79.0
Thawing point	126.0	125.5	152.5	73.0	74.0

Eutectic point: 125.0°, 73.5°; 77.0 mol%, 8.0 mol% pyrene.
Compound (1:1): brownish red prisms or powder, melting at 154.0°.

(10) Fluoranthene—picryl chloride.

Picryl chloride: 9.1 mg.

Mol% picryl chlroide	82.7	63.6	46.0	33.0
Melting point	73.5	111.0	119.0	106.0
Thawing point	67.0	—	110.0	80.0

Fluoranthene: 8.1 mg.

Mol% flouoranthene	84.6	62.5	53.6	42.6	26.1
Melting point	98.0	112.0	119.0	117.0	97.0
Thawing ponit	80.0	80.0	106.0	73.0	67.0

Eutectic point: 80.0°, 67.0°; 73.8 mol%, 15.6 mol% fluoranthene.
Compound (1:1): orange yellow prisms or plates, melting ot 120.0°.

(11) Pyrene—2,4-dinitrophenol.

Total dinitrophenol: 11.1 mg.

Mol% dinitrophenol	80.5	92.4	61.0	50.6	44.8	33.5
Melting point	113.0	109.0	143.0	146.5	145.0	134.5
Thawing point	101.0	101.0	101.5	143.0	125.0	120.0

Pyrene: 8.0 mg.

Mol% pyrene	92.3	82.0	54.4	47.0
Melting point	143.0	132.5	146.0	146.0
Thawing point	120.0	120.0	120.0	—

Eutectic point: 120.0°, 101.0°; 73.6 mol%, 15.6 mol% pyrene.
Compound (1:1): reddish orange prisms or plates, melting at 146.3°.

(12) Fluoranthene—2,4-dinitrophenol.

Fluoranthene: 16.6 mg.

Mol% fluoranthene	94.7	72.5	60.5	49.5	37.8
Melting point	105.0	83.0	88.0	91.0	87.0
Thawing point	85.5	75.0	74.5	86.0	84.0

Dinitrophenol: 8.4 mg.

Mol% dinitrophenol	87.4	79.0	69.5	60.0	49.1	30.3	27.6	15.5
Melting point	106.0	101.8	94.0	87.5	92.0	78.2	83.0	99.0
Thawing point	850.	84.5	84.0	84.5	90.5	75.0	75.0	75.5

Eutectic point: 75.0°, 85.0°; 68.8 mol%, 38.8 mol% fluoranthene.
Compound (1:1): yellow prisms, melting at 92.0°.

(13) Pyrene—2,4-dinitrotoluene.

Pyrene: 5.2 mg.

Mol% pyrene	90.2	75.8	61.8	49.4	31.1	21.2
Melting point	142.5	124.5	106.5	92.5	82.0	64.0
Thawing point	90.0	89.0	89.0	89.0	57.5	57.5

Dinitrotoluene: 7.2 mg.

Mol% dinitrotoluene	73.0	55.1	48.1	41.7	35.9	24.2	17.7
Melting point	121.0	90.8	92.0	90.3	85.5	69.0	60.5
Thawing point	89.0	89.0	86.0	63.0	57.5	57.5	57.5

Eutectic point: 89.0°, 57.5°; 54.4 mol%, 19.7 mol% pyrene.
Compound (1:1): yellow prisms, melting at 92.5°.

(14) Fluoranthene—2,4-dinitrotoluene.

Fluoranthene: 14.8 mg.

Mol% fluoranthene	91.0	80.2	59.8	54.8	44.8	36.4	25.3
Melting point	102.5	90.0	74.0	75.5	73.5	69.5	61.0
Thawing point	68.0	68.0	67.8	68.0	60.0	57.0	57.0

Dinitrotoluene: 15.5 mg.

Mol% dinitrotoluene	94.1	85.3	77.0	69.5	54.3	22.1	
Melting point	68.0	63.0	59.0	65.5	74.5	74.5	
Thawing point	57.0	57.0	57.0	57.0	61.0	68.0	

Eutectic point: 68.0°, 57.0°; 64.0 mol%, 22.4 mol% fluoranthene.
Compound (1:1): light yellow powder, melting at 75.5°.

(15) Pyrene—2,4,6-trinitroanisol.

Trinitroanisol: 7.0 mg.

Mol% trinitroanisol	79.6	66.0	53.2	34.6	22.2	
Melting point	92.0	100.0	104.0	112.0	128.0	
Thawing point	61.0	65.0	98.0	98.0	98.0	

Pyrene: 5:8 mg.

Mol% pyrene	87.5	62.4	52.9	43.1	21.8	13.3
Melting point	140.5	104.5	104.5	103.0	92.5	83.0
Thawing point	99.0	98.5	980.	87.0	—	60.5

Eutectic point: 98.5, 60.5; 60.5 mol%, 3.0 mol% pyrene.
Compound (1:1): yellowish orange prisms or plates, melting at 104.5.°

(16) Fluoranthene—2,4,6-trinitroanisol.

Total fluoranthene: 11.0 mg.

Mol% fluoranthene	87.3	72.0	46.3	66.2	54.6	35.3	24.5
Melting point	101.5	86.5	74.0	75.0	74.0	71.5	64.5
Thawing point	70.0	67.0	67.5	68.0	69.0	54.5	54.5

Trinitroanisol: 26.3 mg.

Mol% trinitroanisol	92.8	86.5	79.2	62.7	51.2	
Melting point	65.0	61.5 (47.5)	59.0	72.8	75.0	
Thawing point	55.0	55.0	55.5	55.0 (48.0)	70.0	

Eutectic point: 68.5°, 55.0°; 63.0 mol%, 18.5 mol% fluoranthene.
Compound (1:1): light yellow leafy or powdery crystals, melting at 75.0°.
Trinitroanisol was crystallised with difficulty from the fused liquid without seeding.

(17) Pyrene—*p*-dinitrobenzene.

Total pyrene: 18.4 mg.

Mol% pyrene	93.4	74.0	66.0	59.8	54.0	46.4	56.5	58.7	60.5	64.0	65.1	66.8
Melting point	144.0	122.3	111.0	113.0	115.0	127.5	114.0	113.0	112.0	109.5	111.3	115.0
Thaw'g point	115.0	107.5	107.5	107.5	107.5	—	107.8	108.0	107.5	107.5	107.5	107.5

Dinitrobenzene: 4.0 mg

Mol% dinitrobenbene	81.8	71.5	66.6	57.5
Melting point	159.0	149.5	142.0	—
Thawing point	115.5	114.5	114.0	114.0

Dinitrobenzene: 3.0 mg.

Mol% dinitrobenzene	62.2	55.4	48.4	41.9	28.4
Melting point	141.0	130.0	116.0	113.5	129.0
Thawing point	114.0	113.0	109.0	108.0	108.5

Eutectic point: 107.5°, 63.7 mol% pyrene.
Pertectic point: 114.5°, 52.0 mol% pyrene.
Compound (1:1): bright red needles with an incongruent melting point.

(18) Fluoranthene—p-dinitrobenzene.

Fluoranthene: 9.6 mg.

Mol% fluoranthene	94.4	83.4	59.4	43.2
Melting point	106.0	97.0	115.0	138.0
Thawing point	92.3	80.0	80.0	80.0

Total fluoranthene: 12.5 mg.

Mol% fluoranthene	66.7	76.9	32.6	29.4
Melting point	97.0	90.0	—	153.0
Thawing point	80.0	81.5	80.5	80.5

Eutectic point: 80.0°, 70.1 mol% fluoranthene.
The solubility of *p*-dinitrobenzene in fluoranthene was rather small.

(19) Pyrene—*m*-dinitrobenzene.

Total dinitrobenzene: 13.9 mg.

Mol% dinitrobenzene	85.4	91.3	83.1	76.2	66.5	62.1	58.6	56.3	55.4	49.9
Melting point	81.0	85.0	84.0	87.0	89.3	89.0	90.5	91.5	91.8	92.5
Thawing point	79.0	79.0	79.0	79.0	88.0	88.0	88.0	88.0	90.0	91.0
					(82.0)					
						47.6	44.9	43.0	39.1	27.7
						92.0	91.0	94.0	103.0	122.5
						89.0	89.0	88.0	89.0	89.0

Pyrene: 7.7 mg.

Mol% pyrene	65.9	57.1	50.4	29.8	21.0
Melting point	111.0	94.0	92.8	89.0	86.5
Thawing point	88.0	88.0	88.5	81.0	79.0

Eutectic point: 89.0°, 88.0°, 79.0°; 56.5 mol%, 36.6 mol%, 13.0 mol% pyrene.
Compound (1:1): orange yellow needles, melting at 92.7°.
Compound (1:2): bright yellow powder, melting at 89.3°.

(20) Fluoranthene—*m*-dinitrobenzene.

Fluoranthene: 8.4 mg.

Mol% fluoranthene	57.0	47.8	39.9	34.5	26.0
Melting point	76.0	76.5	76.0	74.0	69.0
Thawing point	68.5	—	68.0	68.0	67.0

Total dinitrobenzene: 22.6 mg.

Mol% dinitrobenzene	87.9	78.4	63.3	75.2	73.0	69.0	56.8	50.2	38.5	30.7
Melting point	83.0	77.0	74.8	73.0	71.5	69.0	76.5	77.0	76.0	79.5
Thawing point	68.0	67.8	67.5	67.5	66.8	67.5	68.0	74.0	71.0	71.0

Eutectic point: 71.0°, 68.0; 56.0 mol%, 29.0 mol% fluoranthene.
Compound (1:1); light yellow powder, melting at 77.0°.

II. *Binary System of 1,2,4,6-Tetranitrobenzene.* 1,2,4,6-Tetranitrobenzene showed somewhat irregular compound-formation with the hydrocarbons.

Systems of compound ratio 1:1 :—
pyrene, fluoranthene, acenaphthene, anthracene (and chrycene).

Systems of compound ratio other than 1:1 :—
naphthalene, phenanthrene, and fluorene.

The molecular compounds of the latter type seem to dissociate considerably on melting, giving a flat liquidus near the dystectic point in the diagram, Fig. 3.

(21) Pyrene—1,2,4,6-tetranitrobenzene.

Tetranitrobenezene: 9.7 mg.

Mol% tetranitrobenzene	90.4	66.1	50.3	40.6	25.1	16.2
Melting point	125.0	162.0	168.0	162.0	141.0	130.0
Thawing point	122.0	122.0	160.0	130.0	—	—

Pyrene: 7.9 mg.

Mol% pyrene	95.8	79.5	62.0	49.0	40.6	22.3
Melting point	147.0	127.0	158.0	168.0	166.5	—
Thawing point	126.0	125.5	125.5	161.0	—	122.0

Eutectic point: 125.0°, 122.0°; 81.0 mol%, 8.5 mol% pyrene.
Compound (1:1): dark red powder, melting at 168.5.° Stable.

(22) Fluoranthene—1,2,4,6-tetranitrobenzene.

Tetranitrobenezene: 11.0 mg.

Mol% tetranitrobenzene	83.6	68.0	52.2	36.0	20.2	12.7
Melting point	116.0	120.0	132.0	124.0	88.0	98.0
Thawing point	110.0	110.0	119.0	84.0	84.0	84.0

Tetranitrobenzene: 6.4 mg.

Mol% tetranitrobenzene	93.9	67.2	56.1	50.1	40.2	28.4	21.7	14.2
Melting point	123.0	120.0	132.0	134.0	130.0	110.0	97.0	94.0
Thawing point	111.0	110.0	110.0	129.0	84.0	84.0	84.0	83.7

Eutectic point: 84.0°, 110.0°; 80.1 mol%, 25.3 mol% fluoranthene.
Compound (1:1): brown powder, melting at 134.0°.

(23) Acenaphthene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 10.0 mg.

Mol% tetranitrobenzene	80.2	70.6	57.2	42.9	29.0	11.8	0.0
Melting point	115.0	109.0	108.5	108.0	99.0	75.0	96.0
Thawing point	102.0	103.0	101.8	78.0	75.0	87.0	95.0

Tetranitrobenzene: 3.4 mg.

Mol% tetranitrobenzene	47.0	23.5	9.9
Melting point	110.0	89.5	88.5
Thawing point	92.0	76.0	77.0

Eutectic point: 76.0°, 102.0°; 81.0 mol%, 35.8 mol% acenaphthene.
Compound (1:1): reddish brown prisms, melting at 110.5°.

(24) Anthracene—1,2,4,6-Tetranitrobenzene.

Tetranitrobenzene: 8.5 mg.

Mol% tetranitrobenzene	93.5	84.2	69.3	48.7	43.0	35.4	27.1
Melting point	125.0	145.0	163.0	171.0	168.5	176.0	189.0
Thawing point	121.0	—	119.0	162.0	162.0	162.0	162.0

Tetranitrobenzene: 5.5 mg.

Mol% tetranitrobenzene	60.4	44.7	30.1
Melting point	169.0	—	186.0
Thawing point	120.5	163.0	163.0

Eutectic point: 163.0°, 120.5; 60.5 mol%, 5.8 mol% anthracene.
Compound (1:1): deep red prisms or needles, melting at 171.0..

(25) Phenanthrene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 7.4 mg.

Mol% tetranitrobenzene	94.0	81.0	62.3	53.7	40.2	23.8	13.6	0.0
Melting point	—	121.0	125.0	123.0	118.0	99.0	87.0	100.5
Thawing point	115.0	115.0	121.0	115.0	83.0	78.0	79.0	100.0

Tetranitrobenzene: 5.1 mg.

Mol% tetranitrobenzene	92.1	81.5	72.0	54.9	41.3	32.0	20.7	11.4
Melting point	121.0	121.0	123.3	123.5	118.0	111.5	91.0	90.0
Thawing point	115.0	—	115.0 (117.0)	115.0	90.0	78.0	79.0	78.0

Tetranitrobenzene: 5.3 mg.

Mol% tetranitrobenzene	69.6	57.5	48.5	43.8
Melting point	123.5 (125.5)	124.5	122.5	120.5 (118.5)
Thawing point	115.0 (118.0)	120.0 (115.0)	116.0	106.0

Eutectic point: 79.0°, 115.0°; 82.2 mol%, 12.0 mol%, phenanthrene.
Pertectic point: 115.0°, 61.5 mol% phenanthrene.
Compound (2:3): orange red needles, melting at 125.0°.
Compound (1:1): reddish orange needles with an incongruent melting point.

Under certain conditions of heating, the thawing and melting points were not uniform, another metastable combination (1:2) can thus be expected.

(26) Fluorene—1,2,4,6-tetranitrobenzene.

Total fluorene: 9.1 mg.

Mol% fluorene	100.0	76.9	55.0	39.4	35.1	27.5	45.7
Melting point	116.0	97.0	124.5	129.0	130.0	129.0	128.3
Thawing point	115.0	90.0	91.0	111.0	125.5	117.5	91.0

Tetranitrobenzene 8.7 mg.

Mol% tetranitrobenzeene	90.3	82.4	67.4	60.2	27.2	17.0	8.6
Melting point	120.5	125.0	130.0	129.5	108.0	100.2	190.0
Thawing point	118.0	117.5	126.0	116.0	91.0	91.0	92.0

Eutectic point: 91.0°, 117.5°; 78.0 mol%, 12.0 mol% fluorene.
Compound (1:2): orange red prisms or needles, melting at 130.0°.

Summary.

As in the case of the nitro components discussed in Parts I and II, on the formation of crystalline molecular compounds, regularity was found also in the aromatic hydrocarbon components of condensed or non-condensed ring structure. The predominant tendency to compound-formation seems to be affected by the structure of both components, although it differs considerably from that in solutions. All the observed systems were almost halochromic when fused, about half the number of which gave crystalline compounds, some of which are shown in the phase diagrams. The effect of substituents of benzene ring in the binary systems containing antimony trihalides was also studied.

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