Studies on the Organic Molecular Compounds. Part II. The Influence of Nitro Radicals and Second Substitution Radicals on the Formation of the Aromatic—Nitroaromatic Molecular Compounds. II.

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Molecular Compound Formations in the Equally Nitrated Isomers. In the previous paper[1], molecular compound formation was discussed in connexion with the number of nitro radicals, the number and variety of second substitution radicals in the nitro components, as also with the effects of the presence and the position of hydroxyl group in naphthalene α-, and β-naphthol. In this paper, a comparison is made of the nitro-components. Table 1 gives the essence of the binary systems of α-, β-naphthylamine, α-, β-naphthol, and naphthalene with various nitrobenzenes and their derivatives.

(1) Compound ratio principally 1:1[2], except the following systems:

2 : 1 naphthalene—*vic*-trinitrobenzene, β-naphthylamine—*asym*-trinitrobenzene?, α-naphthylamine—2,4-dinitroanisol;

3 : 2 naphthylamine—2,3-dinitrophenol, naphthalene—2,5-dinitrophenol, β-naphthylamine—3,4-dinitrophenol;

2 : 3 β-naphthol—2,4-dinitroaniline;

1 : 3 naphthalene—2,4-dinitroaniline.

1 : 2 β-naphthol—2,4-dinitrobenzoic acid, β-naphthylamine—3,5-dinitrobenzoic acid;

(2) As mentioned in the previous paper, in the case of naphthylamine and naphthol, the compound formations of the α-isomers are superior to those of the β-isomers.

(3) The effect of second substitution radical in the nitrated benzene nucleus was the same as that described in Part I.

(4) The main part of this paper is taken up with comparisons of compound formations of various isomers of nitrated components. The sequences are[3],

Trinitrobenzenes:—*sym*-compound > *asym*- or *vic*-compound,

Dinitrobenzenes:—*p*- or *m*-compound > *o*-compound,

Trinitrotoluenes:—2,4,6-compound > 2,3,4- or 2,4,5-compound,

Dinitro-phenols or toluenes:—2,4-; 2,5- or 3,5-compound > 2,6-compound > 2,3- or 3,4-compound.

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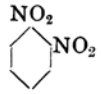
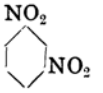
(1) This Bulletin, Vol. 15, No. 3.

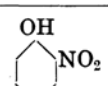
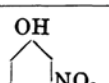
(2) Stable nitro compounds usually combined in the ratio of 1 : 1. The order of stability of nitro compounds, calculated from their heat of combustion, are

p- > *m*- > *o*-dinitrobenzene; *sym*- > *asym*-trinitrobenzene; *p*- > *m*- > *o*-nitrotoluene; 2,4-, 3,5- > 2,6- > 2,5 > 2,3- > 3,4-dinitrotoluene; 2,4,6- > 2,4,5- > 2,3,4-trinitrotoluene.

(3) Some of the molecular compounds of trinitroxylenes that were examined were found to agree with this order.

Table 1. Mol ratio A : B, (τ), and Colour.***

A \ B [Melting point]	Nitrobenzene	Dinitrobenzenes		
				
	[5.7]	[117.0]	[90.0]	[173.5]
α-Naphthylamine	—	∨*	1:1 (−6.2)* Red	1:1 U* Brown
β- ,,	—	∨*	1:1 (−46.8)* Red	1:1 U* Brown
α-Naphthol	—	∨	1:1 (7.0) Orange yellow	1:1 U Ruby red
β- ,,	—	∨	1:1 U* Orange yellow	1:1 (−11.8) or (3:2) Orange red
Naphthalene	∨*	∨*	1:1 (−34.2) D* Light yellow	1:1 (−7.5)* Yellow

A [Melting point] \ B [Melting point]	Mononitrophenols		
			
	[45.0]	[96.5]	[113.0]
α-Naphthylamine [50.0]	∨	1:1 (−17.5)* Yellow	1:1 (−13.1)* Yellow
β- ,, [110.0]	∨	1:1 (−39.7)* Yellow	1:1 (−30.8)* Orange yellow
α-Naphthol [96.0]	∨	∨	∨
β- ,, [122.0]	∨	∨	∨
Naphthalene [80.0]	∨*	∨	∨

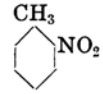
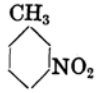
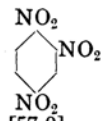
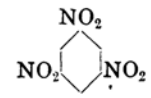
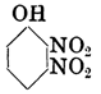
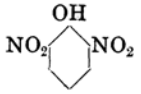
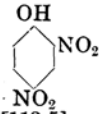
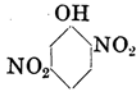
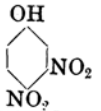
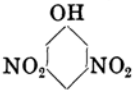
A [Melting point] \ B [Melting point]	Mononitrotoluenes		
			
	—	[15.5]	[52.7]
α-Naphthylamine [50.0]	—	—	∨
β- ,, [110.0]	—	—	∨
α-Naphthol [96.0]	—	—	∨
β- ,, [122.0]	—	—	∨
Naphthalene [80.0]	—	∨*	∨*

Table 1.—(*Continued*)

Trinitrobenzenes		
 [121]	 [57.0]	 [123 0]
Viscous, decomposed Decomposed 1:1 (−6.5) Bright red 1:1 (−28.5) Brown 2:1 (14.5) Yellow	1:1 Ca. 7.5) Black 2:1 (−12) ?, decomposable Dark brown 1:1 (−9.5) Brown red 1:1 (−26.0) or (1:2) (−5.7) Orange red Brown red 1:1 (−16.0) Yellow	1:1 (127.5)** Dark red 1:1 (45 0)* Red 1:1 (84.0) Orange 1:1 (36.0) Orange yellow 1:1 (51.0)* Light yellow

Dinitrophenols					
 [145.0]	 [63.3]	 [113.5]	 [106.0]	 [134.5]	 [123.0]
3:2 (17.0) Black 3:2 (−19.5) Black ∨ ∨ ∨	1:1 (40.3) Deep yellow 1:1 (18.3)** Deep yellow 1:1 (0.8) Bright red 1:1 (−16.7) Bright red 1:1 (−13.8) Brgiht yellow	1:1 (23.6)* Reddish brown 1:1 (−39.4)* Brown red 1:1 (14.7) Orange red 1:1 (−8.3) Orange red 1:1 (−4.0)* Yellow	1:1 (23.0) Black 1:1 (−11.5) Black 1:1 (17.4) Ruby red 1:1 (3 4) Ruby red 3:2 (10.1) or (1:1) Orange	1:1 (3.7) Yellowish brown 3:2 (−36.8) ? Yellowish brown ∨ ∨ ∨	1:1 (24.0) Brown yellow 1:1 (−19.5) Deep yellow 1:1 (−2.5) Yellowi h orange 1:1 (−29.5) Orange yellow 1:1 U Light yellow

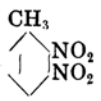
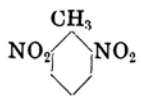
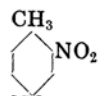
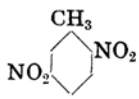
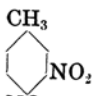
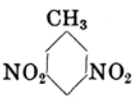
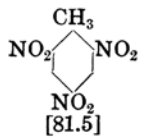
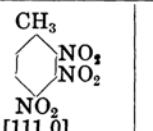
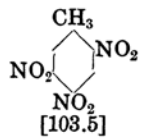
Dinitrotoluenes****					
 —	 [65.0]	 [71.0]	 [50.2]	 [59.0]	 [82.3]
∨ ∨ ∨ ∨ ∨	∨* ∨* 1:1 U Brown yellow ∨ ∨*	1:1 (1.5,* Bright red ∨ 1:1 (15.0) Orange yellow 1:1 (−19.5) Lemon yellow 1:1 (−14.5)* Light yellow	1:1 (0.0) Reddish purple ∨ 1:1 (11.9) Bright red 1:1 (−8.5) Orange red 1:1 (−19.6) Yellow	∨* ∨* ∨ ∨ ∨*	1:1 (41.7)* 1:1 (−43.2) D* — — 1:1 (−18.7)*

Table 1.—

A [Melting point]	B [Melting point]	Trinitrotoluenes		
		 [81.5]	 [111.0]	 [103.5]
α-Naphthylamine	[50.0]	1:1 (76.5)** Reddish brown	—	—
β- ,,	[110.0]	1:1 (16.2)* Red	—	Viscous, decomposed
α-Naphthol	[96.0]	1:1 (37.8) Orange	1:1 (−15.5) Brown red	1:1 (−17.8) Orange red
β- ,,	[122.0]	1:1 (8.3)* Orange yellow	1:1 (−35.0) Brown red	1:1 (−2.8) Red
Naphthalene	[80.0]	1:1 (17.3)* Light yellow	1:1 (4.5) Yellow	1:1 (−2.8) Yellow

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., **122**.

** The data of the crystal from the solution (Pfeiffer, "Organische Molekülverbindungen," 2 Aufl., 366, 356, Stuttgart (1927); Hertel and Mischnat, *Ann.*, **451** (1927), 197; Hepp, *Ann.*, **215** (1882), 378).

*** The colour of the melt (mixed in the compound ratio), not of the crystal obtained from the solution. Some of the colours of the latter are shown in bracket [ ].

In these aromatic—nitroaromatic binary systems, the ortho substitution radicals somewhat hinder molecular compound formation. Notwithstanding its excellent combination energy in solution or gas[5], *o*-dinitrobenzene formed no crystalline molecular compound with aromatic ring[4]. Analogous results were noted in the *o*-dinitro-phenols and toluenes; the *o*-trinitro compounds (*vic*-, *asym*-trinitrobenzene, 2,3,4- or 2,4,5-trinitrotoluene, etc.) exerts only weak compound formation.

The influence of the ortho substituted second radical is not simple, but in 2,6-dinitro-phenol or toluene, the presence of a hydroxyl or methyl radical hindered compound formation[6], while in the dinitrophenol—naphthylamine system, the tendency to form another type of molecular combination was increased, the *o*-dinitro, and even the mononitro compound, was a distinct molecular compound; "complex isomerism"[7] was found espcially in the cases of the 2,6- and 3,5-dinitrophenols.

(5) Although all the systems listed in Table 1 showed distinct halochromism when fused, in the case of a simple eutectic system, the phenomenon vanished on solidification.

Halochromism of these molecular compounds was greatly affected by the substituent (auxochrome) of their component. The sequence of the effects was

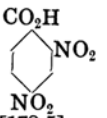
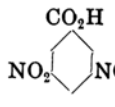
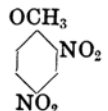
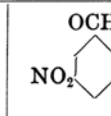
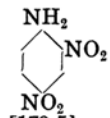
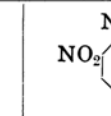
(4) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur", 114, Stuttgart (1937).

(5) Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., **122**.

(6) R. Kremann, and O. Rodinis, *Monatsh.*, **27** (1906), 130.

(7) E. Hertel, *Ann.*, **451** (1927), 197.

(*Concluded*)

Dinitrobenzoic acids		Dinitroanisols		Dinitroanilines	
 [178.5]	 [205.0]	 [87.0]	 [105.5]	 [179.5]	 [137.0]
—	1:1, decomp. [Brown red]	2:1 (−4.3) Red	1:1 (−3.3) Ruby red	1:1 U Dark red	1:1 U Dark brown
—	1:2 U [Deep red]	∨	∨	∨	1:1 (−34.0) Dark brown
1:1 U Reddish orange	1:1 (41.5) Brown	1:1 (2.0) Brown yellow	1:1 (−7.3) Orange yellow	1:1 (2.3) or U Orange yellow	1:1 U Brown red
1:2 U or ∨ Red	1:1 (22.0) Brown yellow	1:1 (−22.0) Yellow	∨	2:3 U Brown yellow	1:1 (12.0) Brown red
1:1 U Orange	1:1 (39.5) Lemon yellow	1:1 (−33.5) Yellowish white	1:1 U Yellowish white	1:3 U Chrom yellow	1:1 U Light brown

**** The present writer devised an effective separation by adding α-naphthylamine or naphthol to the nitrated mixture of Sirks (*Rec. trav. chim.*, **27** (1908), 211.) in order to form a molecular compound only with the 2,5-dinitro isomer. The molecular compound, which easily crystallised, was filtered, and decomposed with acid or with ammonia according as whether napnthol or naphthylamine was used.

(a) Variety of substituent: $NH_2 > OH > (H)$, OCH_3, CH_3,
(b) Position of substituent: α-position > β-position (in naphthalene derivatives), *o*- or *p*-position > *m*-position (in benzene derivatives).

In the nitro component with three substituents, this rule still seemed to hold, for example, *sym*-trinitrobenzene was less halochromic than the *vic*- or *asym*-isomer, presumably because of the meta position of the three nitro radicals in the former. Of the six isomers of dinitrophenol, the 2,3- or 2,5-compound having two nitro radicals in ortho or para position, and the nitro and hydroxyl radicals in ortho position, showed the most powerful halochromy, while the 3,5-compound, which has all the substituents in meta position, was the least halochromic. The 2,6- and 3,5-dinitrophenols with naphthylamines, which formed a less halochromic compounds than the *m*-dinitrobenzene, notwithstanding the presence of the hydroxyl radical, were found to be another type of molecular compound, as already shown (with 2,6-dinitrophenol and its derivatives) by Hertel[7].

Experimental.

(1) α-Naphtol—*o*-dinitrobenzene (Fig. 1).

Dinitrobenezene: 8.0 mg.

Mol% dinitrobenzene	100.0	87.4	72.5	56.4	41.9	32.0	20.4
Melting point	117.0	112.0	103.0	89.0	72.0	74.0	84.0
Thawing point	116.0	72.0	65.0	64.0	64.5	65.2	65.0

Naphthol: 6.7 mg.

Mol% naphthol	83.9	66.2	53.1	38.3
Melting point	86.5	72.0	76.3	92.0
Thawing point	64.5	65.0	65.0	65.0

Eutectic point: 64.5°, 61.8 mol% α-naphthol.

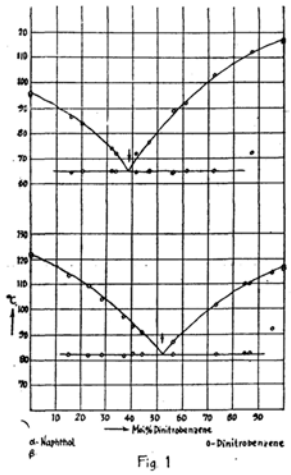


Fig. 1

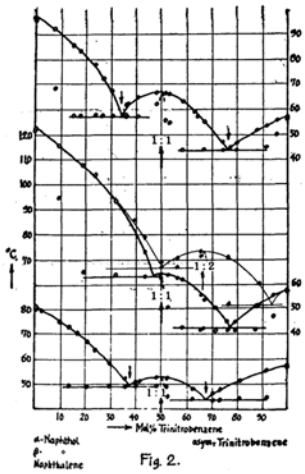


Fig. 2.

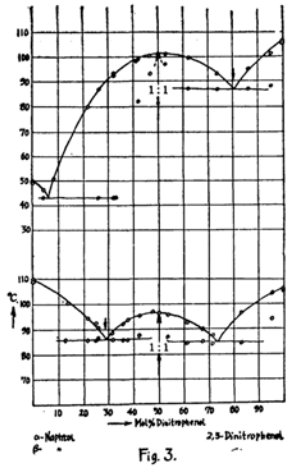


Fig. 3.

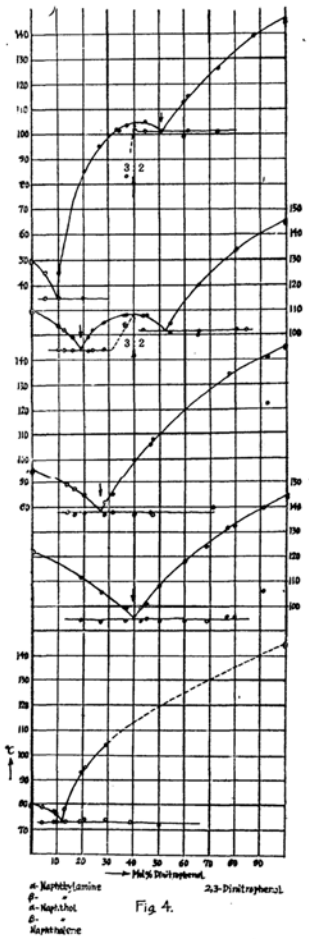


Fig. 4.

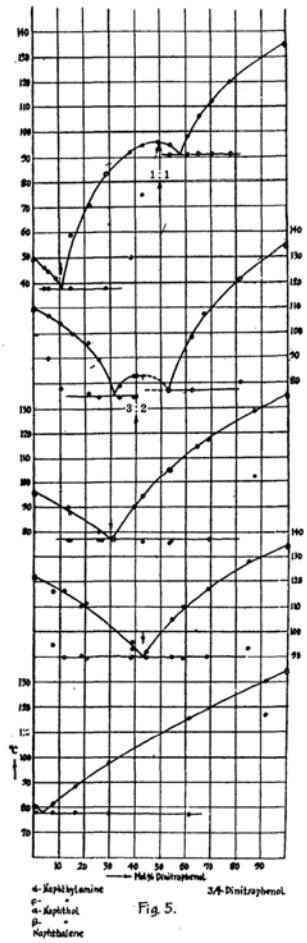


Fig. 5.

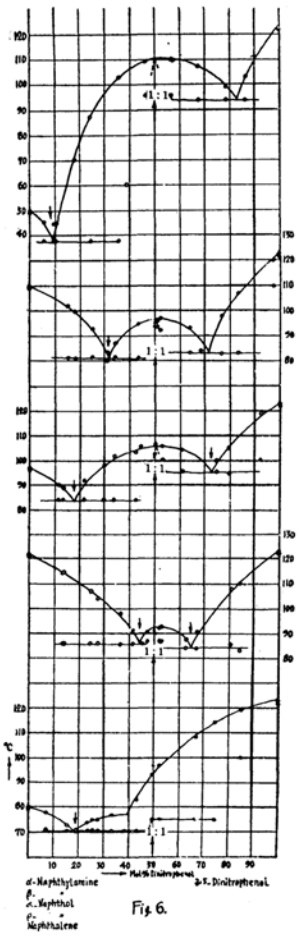


Fig. 6.

(2) β-Naphthol—*o*-dinitrobenzene (Fig. 1).

Dinitrobenzene: 12.0 mg.

Mol% dinitrobenzene	84.4	59.2	40.5	23.0
Melting point	110.5	92.5	93.0	109.5
Thawing point	82.5	82.5	82.3	82.0

Dinitrobenzene: 9.8 mg.

Mol% dinitrobenzene	95.4	86.6	73.1	56.4	44.0	37.0	28.3	15.1
Melting point	114.5	110.0	101.5	87.0	91.0	97.0	104.0	113.5
Thawing point	92.0	82.5	81.8	82.0	82.0	81.8	82.0	82.0

Eutectic point: 82.0°, 48.0 mol% β-naphthol.

In the binary systems of *o*-dinitrobenzene, remarkable halochromic phenomenon was seen in the liquid state, which, however, vanished on solidification.

(3) α-Naphthol—*asym*-trinitrobenzene.

Trinitrobenzene: 9.5 mg.

Mol% trinitrobenzene	95.6	87.7	77.2	64.1	53.0	48.2	40.3	35.4	30.0	23.2	17.3
Melting point	55.8	52.0	45.0	57.0	66.0	66.5	64.8	62.0	67.0	77.3	83.0
Thawing point	50.0	—	—	—	54.5	62.0	57.0	57.8	57.0	57.5	57.0

Trinitrobenzene: 2.0 mg.

Mol% trinitrobenzene	100.0	77.2	62.8	51.0	36.0	26.2	14.8	7.4
Melting point	57.0	45.5	59.0	66.0	62.0	72.0	85.5	92.0
Thawing point	56.0	—	—	55.0	57.0	57.0	57.0	68.0

Trinitrobenzene: 4.7 mg.

Mol% trinitrobenzene	91.7	79.8	74.1	66.5	58.0
Melting point	53.5	46.5	47.2	55.0	63.0
Thawing point	45.0	43.5	43.7	43.8	43.8

Eutectic point: 57.0°, 43.7°; 66.5 mol%, 24.0 mol% α-naphthol.
Compound (1:1): brown red powder, melting at 67.0°.

(4) β-Naphthol—*asym*-trinitrobenzene.

Trinitrobenzene: 2.3 mg.

Mol% trinitrobenzene	72.0	58.4	52.7	39.3	24.1	9.5
Melting point	50.5	61.5	63.0	(85.0)	103.2	115.2
Thawing point	41.0	42.0	50.0	—	—	94.0

Trinitrobenzene: 9.7 mg.

Mol% trinitrobenzene	88.9	76.5	65.8	56.3	49.8[8]	43.2	32.0	19.1
Melting point	49.5	45.0	55.0	62.0	63.5	72.0	92.5	107.5
	(60.0)	(70.8)	(73.0)	(70.0)	(68.5)	(78.0)		
Thawing point	—	41.0	41.0	—	62.5	62.0	63.0	64.0
	(51.0)	(51.5)	(71.0)	(66.5)	(66.5)			

Trinitrobenzene: 5.1 mg.

Mol% trinitrobenzene	94.5	87.5	79.3	67.0
Melting point	55.0	51.0	45.0	53.0
Thawing point	46.5	41.5	41.0	42.0

In the stable system,
Eutectic point: 62.5°, 42.0°; 52.5 mol%, 22.8 mol% β-naphthol.
Compound (1:1) orange red powder, melting at 63.5°.

In the metastable system,
Eutectic point 66.5°, 51.0°; 49.2 mol%, 6.0 mol% β-naphthol.
Compound (1:2) brown red crystals, melting at 73.0°.

(5) Naphthalene—*asym*-trinitrobenzene.

Trinitrobenzene: 2.0 mg.

Mol% trinitrobenzene	70.3	52.3	41.4	23.6	16.7	9.1	2.4
Melting point	46.0	—	50.8	63.0	70.0	74.5	79.0
Thawing point	43.5	44.5	—	—	—	—	—

(8) At 63.5° the compound crystal disappeared, and upon stirring, the fused liquid soon solidified again to a more coloured mass, the thawing and melting points of which were 66.5° and 68.5° respectively.

Trinitrobenzene: 13.1 mg.

Mol% trinitrobenzene	91.8	80.6	73.0	62.1	52.2	48.1	39.7	35.4	29.2	20.6	13.1
Melting point	55.0	51.0	47.5	48.0	52.0	52.5	50.5	52.0	58.0	67.0	72.5
Thawing point	44.5	44.0	43.0	43.5	48.5	49.0	49.0	48.8	49.0	49.0	49.0

Eutectic point: 49.0°, 43.5°; 62.7 mol%, 32.8 mol% naphathalene.
Compound (1:1): yellow powder, melting at 52.5°.

Three systems of *asym*-trinitrobenzene are given in Fig. 2. The order of solubility of trinitrobenzene in naphthalene and naphathols did not quite agree with that of the value τ. In the diagram of β-naphthol—trinitrobenzene, a metastable compound (1:2) was once found by keeping the fused liquid for a long time above its melting point [8].

(6) α-Naphthylamine—2,5-dinitrophenol (Fig. 3).

Dinitrophenol: 8.1 mg.

Mol% dinitrophenol	95.4	86.3	74.0	62.3	53.0	47.0	41.5	32.6	22.3
Melting point	101.0	95.0	93.0	99.5	101.0	100.0	98.0	92.0	80.0
Thawing point	88.0	87.0	86.5	87.0	97.0	93.0	—	43.0	—

Naphthylamine: 9.8 mg.

Mol% naphthylamine	95.4	91.4	73.3	67.5	57.6	39.4
Melting point	46.3	51.0	87.0	93.5	99.0	101.0
Thawing point	43.0	—	43.0	43.0	70.0	100.0

Eutectic point: 43.0°, 87.0°; 93.5 mol%, 19.5 mol% α-naphthylamine.
Compound (1:1): long black needles, melting at 101.0°.

(7) β-Naphthylamine—2,5-dinitrophenol (Fig. 3).

Dinitrophenol: 4.3 mg.

Mol% dignitrophenol	67.6	47.5	35.8	24.8	12.3
Melting point	90.0	97.0	92.5	93.0	—
Thawing point	85.0	—	86.0	86.0	86.0

Dinitrophenol: 8.2 mg.

Mol% dinitrophenol	95.5	83.2	71.8	61.4	53.7	50.3	42.6	37.6	31.2	25.4	21.3	13.9
Melting point	104.0	96.5	87.8	92.5	95.5	96.2	95.5	94.0	89.0	91.0	95.0	101.0
Thawing point	94.0	84.0	84.0	84.5	87.0	94.0	88.0	86.0	86.5	87.0	86.0	86.0

Eutectic point: 86.0°, 85.0°; 70.8 mol%, 16.5 mol% β-naphthylamine.
Compound (1:1): black prisms or needles, melting at 96.5°.

2,5-Dinitrophenol forms a stable molecular compound with naphthalene and its derivatives.

(8) α-Naphthylamine—2,3-dinitrophenol.

Dinitrophenol: 5.2 mg.

Mol% dinitrophenol	100.0	87.0	59.9	34.8	20.6
Melting point	145.0	139.0	113.0	101.0	85.0
Thawing point	144.0	—	99.0	—	35.0

Dinitrophenol: 5.3 mg.

Mol% dinitrophenol	73.3	61.3	50.7	44.7	37.4	33.2	26.4	10.6	5.7
Melting point	126.0	115.0	101.0	105.0	103.0	101.5	95.0	45.0	44.5
Thawing point	101.0	101.0	101.0	101.0	83.0	—	—	35.0	35.0

Eutectic point: 35.0°, 101.0°; 90.0 mol%, 49.3 mol% α-naphthylamine.
Compound (3:2): black powder, melting at 105.0°.

(9) β-Naphthylamine—2,3-dinitrophenol.

Dinitrophenol: 7.5 mg.

Mol% dinitrophenol	83.9	65.3	45.1	36.4	23.7	15.8	10.3
Melting point	—	—	108.0	108.0	102.0	99.0	104.0
Thawing point	102.0	100.0	—	104.5	94.0	94.0	94.0

Dinitrophenol: 6.0 mg.

Mol% dinitrophenol	80.9	66.0	54.5	43.7	36.7	28.1	22.1	12.2
Melting point	134.0	120.2	104.5	107.8	108.0	105.0	99.3	102.0
Thawing point	102.0	101.5	101.0	102.0	103.5	94.0	93.5	94.0

Eutectic point: 94.0°, 101.5°; 80.5 mol%, 47.0 mol% β-naphthylamine.
Compound (3:2): black needles or powder, melting at 108.0°.

(10) α-Naphthol—2,3-dinitrophenol.

Dinitrophenol: 6.8 mg.

Mol% dinitrophenol	92.9	78.0	47.8	40.0	28.6	16.4
Melting point	140.5	134.0	108.0	100.0	82.0	87.0
Thawing point	122.0	92.0	77.0	77.0	77.0	77.0

Dinitrophenol: 5.4 mg.

Mol% dinitrophenol	71.4	46.4	31.8	20.1	13.8
Melting point	—	106.0	85.0	86.0	89.0
Thawing point	80.0	78.0	78.0	78.0	78.0

Eutectic point: 78.0°, 73.0 mol% α-naphthol.

(11) β-Naphthol—2,3-dinitrophenol.

Dinitrophenol: 5.0 mg.

Mol% dinitrophenol:	76.6	44.4	27.0	15.8
Melting point	132.0	101.0	105.0	112.0
Thawing point	96.0	95.0	96.0	96.0

Dinitrophenol: 12.4 mg.

Mol% dinitrophenol	90.6	79.5	68.3	59.9	49.8	42.2	35.4	26.7	18.7
Melting point	140.0	132.5	124.0	118.0	108.0	99.5	99.5	105.5	110.8
Thawing point	106.0	95.8	94.0	94.0	94.0	94.0	94.0	93.8	94.5

Eutectic point: 95.0°, 60.3 mol% β-naphthol.

(12) Naphthalene—2,3-dinitrophenol.

Dinitrophenol: 3.8 mg.

Mol% dinitrophenol	76.6	50.5	39.2	19.6	10.0	4.4
Melting point	—	—	—	93.0	76.0	79.0
Thawing point	100.0	72.0	73.0	73.0	73.0	73.0

Dinitrophenol: 4.6 mg.

Mol% dinitrophenol	29.3	21.1	13.3	9.0
Melting point	104.0	95.0	78.0	77.5
Thawing point	74.0	74.0	73.0	73.0

Eutectic point: 73.0°, 87.7 mol% naphthalene.

Owing to the considerable sublimation of naphthalene, melting points above 100° could not observed.

Six diagrams of 2,3-dinitrophenol are shown in Fig. 5.

(13) α-Naphthylamine—3,4-dinitrophenol.

Dinitrophenol: 4.4 mg.

Mol% dinitrophenol	100.0	14.6	6.1
Melting point	134.5	59.0	45.0
Thawing point	133.5	38.0	38.0

Naphthylamine: 10.0 mg.

Mol% naphthyl-amine	95.5	90.9	78.6	71.2	62.9	56.8	50.7	45.7	38.9	34.5	29.2	22.0
Melting point	46.3	42.0	71.0	83.5	92.0	94.8	96.0	95.0	98.0	106.0	112.0	120.0
Thawing point	38.0	—	viscous	38.0	50.0	75.0	93.0	91.0	91.0	91.0	91.0	91.0

Eutectic point: 38.0°, 91.0°; 88.8 mol%, 41.8 mol% α-naphthylamine.

Compound (1:1): yellowish brown powder, melting at 96.0°.

(14) β-Naphythylamine—3,4-dinitrophenol.

Dinitrophenol: 4.0 mg.

Mol% dinitrophenol	81.4	67.2	49.9	40.2	21.4	10.4
Melting point	121.5	107.5	viscous	83.0	96.0	104.0
Thawing point	80.0	—	viscous	75.0	76.0	78.0

Naphthylamine: 9.8 mg.

Mol% naphthylamine	94.0	84.6	74.6	66.1	60.1	53.7	46.8	37.6
Melting point	107.0	99.5	89.0	79.0	83.0	viscous	77.0	98.5
Thawing point	90.0	—	74.7	74.5	74.3	viscous	—	77.0

Eutectic point: 75.0°, 77.0°; 68.6 mol%, 47.0 mol% β-naphthylamine.

Compound (3:2?): yellowish brown prisms, melting at 83.0°.

In this system, the compound crystal was obtained, although with difficulty, by rubbing the viscous liquid at 50–60° with the thermometer inserted, but in the range of 47–59 mol% of β-naphthylamine, neither rubbing nor seeding had any effect.

(15) α-Naphthol—3,4-dinitrophenol.

Dinitrophenol: 3.4 mg.

Mol% dinitrophenol	86.8	64.0	52.6	39.5	26.9	13.2
Melting point	128.5	114.5	105.5	90.0	—	90.0
Thawing point	102.0	—	75.5	—	77.0	77.0

Naphthol: 6.8 mg.

Mol% naphthol	86.1	74.4	69.0	57.2	46.7	31.2
Melting point	88.0	80.0	78.0	94.0	105.0	117.0
Thawing point	77.0	77.0	77.0	76.0	76.0	77.0

Eutectic point: 77.0°, 69.3 mol% α-naphthol.

(16) β-Naphthol—3,4-dinitrophenol.

Dinitrophenol: 5.6 mg.

Mol% dinitrophenol	84.4	58.6	38.6	20.4	11.7
Melting point	128.5	110.0	96.0	111.5	116.5
Thawing point	93.5	89.5	90.0	89.0	90.0

Naphthol: 5.1 mg.

Mol% naphthol	92.7	81.2	61.4	55.7	45.5	31.5
Melting point	116.0	110.0	93.0	92.2	105.0	117.0
Thawing point	95.0	90.5	89.8	89.8	90.0	90.0

Eutectic point: 90.0°, 57.2 mol% β-naphthol.

(17) Naphathalene—3,4-dinitrophenol.

Naphthalene (mg.)	101.0	12.0	19.6	13.0	10.0	3.5
Mol% naphthalene	99.3	92.5	83.4	70.0	38.5	8.4
Melting point	80.0	81.0	88.0	97.5	115.5	130.0
Thawing point	77.5	77.5	77.5	77.5	77.0	117.0

Eutectic point: 77.5°, 96.3 mol% naphthalene.

In order to avoid considerable loss of naphthalene by sublimation, this system was observed by the capillary method.

Six diagrams of 3,4-dinitrophenol are shown in Fig. 4. They resemble somewhat the diagrams of 2,3-dinitrophenol. The solubility curve of dinitrophenol in α-naphthylamine and in α-naphthol almost agrees with that in the β-isomer.

(18) α-Naphthylamine—3,5-dinitrophenol.

Dinitrophenol: 8.0 mg.

Mol% dinitrophenol	100.0	78.5	56.9	46.3	35.1	24.0	10.1
Melting point	123.0	99.0	110.0	109.0	103.0	87.0	55.0
Thawing point	121.5	94.0	96.0	96.0	38.0	38.0	38.0

Dinitrophenol: 4.0 mg.

Mol% ditrophenol	86.1	67.4	57.4	38.3	17.4	9.4	5.6
Melting point	103.0	107.5	109.5	—	70.0	45.0	46.0
Thawing point	94.0	94.0	103.0	60.0	—	38.0	38.0

Eutectic point: 38.0°, 94.0°; 91.1 mol%, 17.2 mol% α-naphthylamine.

Compound (1:1): brownish yellow needles, melting at 110.5°.

(19) β-Naphthylamine—3,5-dinitrophenol.

Dinitrophenol: 6.6 mg.

Mol% dinitrophenol	77.3	64.8	52.7	43.7	34.6	25.5	15.7
Melting point	98.0	93.0	97.0	94.5	87.0	93.0	102.0
Thawing point	82.5	83.0	92.0	81.0	81.5	82.0	81.0

Dinitrophenol: 10.0 mg.

Mol% dinitrophenol	98.0	83.9	69.2	51.8	31.4	18.5
Melting point	120.0	107.0	—	97.0	83.3	100.0
Thawing point	110.0	83.0	84.0	93.0	80.0	81.0

Eutectic point: 81.0°, 83.0°; 68.0 mol%, 28.0 mol% β-naphthylamine.

Compound (1:1): orange yellow needles or powder, melting at 97.0°.

The above two molecular compounds of naphthylamines crystallised with some difficulty, another metastable compounds occasionally forming.

(20) α-Naphthol—3,5-dinitrophenol.

Dinitrophenol: 6.0 mg.

Mol% dinitrophenol	92.1	74.8	49.9	43.9	33.5	21.8	11.6
Melting point	119.0	100.0	106.0	105.0	101.0	91.0	89.0
Thawing point	100.0	95.0	102.0	100.0	83.0	83.0	83.0

Dinitrophenol: 5.0 mg.

Mol% dinitrophenol	79.8	61.0	52.8	42.0	29.8	13.5
Melting point	105.0	104.0	105.0	102.5	97.0	88.0
	(70.0)					
Thawing point	94.0	95.3	99.8	83.0	83.0	83.0

Eutectic point: 83.0°, 95.0°; 82.3 mol%, 27.2 mol% α-naphthol.
Compound (1:1): yellowish orange needles, melting at 107.0°.

(21) β-Naphthol—3,5-dinitrophenol.

Dinitrophenol: 7.1 mg.

Mol% dinitrophenol	81.0	53.6	45.7	35.6	24.6	14.0
Melting point	108.0	93.0	—	98.0	107.0	115.0
Thawing point	86.0	87.0	86.0	85.5	86.0	86.0
	(40)					

Dinitrophenol: 7.1 mg.

Mol% dinitrophenol	84.8	67.2	63.5	52.6	47.2	41.4	27.3	13.9
Melting point	110.0	91.0	88.0	92.5	90.5	91.5	104.0	114.5
Thawing point	83.0	84.0	84.0	87.0	87.0	86.0	86.0	86.0

Eutectic point: 86.0°, 84.0°; 55.3 mol%, 34.5 mol% β-naphthol.
Compound (1:1): orange yellow needles, melting at 93.0°.

(22) Naphthalene—3,5-dinitrophenol.

Dinitrophenol: 7.3 mg.

Mol% dinitrophenol	74.9	49.4	25.7	15.5	7.0
Melting point	114.0	93.0	75.0	—	78.0
Thawing point	75.0	75.0	71.0	70.5	71.0
	(51.0)				

Dinitrophenol: 8.3 mg.

Mol% dinitrophenol	85.2	67.3	52.6
Melting point	119.0	108.0	97.0
Thawing point	100.0	75.0	75.0

Dinitrophenol: 10.4 mg.

Mol% dinitrophenol	43.4	38.6	33.1	27.9	23.9	19.1	15.8
Melting point	83.0	—	77.0	75.0	74.0	71.0	73.0
Thawing point	70.5	70.5	70.5	70.5	70.5	70.5	70.5

Eutectic point: 70.5°, 81.2° mol% naphthalene.
Pertectic point: 77.0°, 60.5 mol% naphthalene.
Compound (1:1): light yellow needles with an incongruent melting point.

Six diagrams of 3,5-dinitrophenol are given in Fig. 6. The crystalline molecular compound was found in every case, although its crystallisation velocity was not great. Sometimes another metastable state was observed.

Summary.

The molecular compounds of various nitrobenenes with naphthylamines, naphthols, and naphthalene were systematically compared and the compound formations discussed by means of solid—liquid phase diagrams.

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