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

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Graduation of Molecular Compound Formation. Organic "molecular compound formation" is discussed in this paper, with the binary solid—liquid phase equilibrium diagram as basis. The aromatic—nitroaromatic molecular compound formation studied by the writer is summarised schematically in Fig. 1.

Curve $A_1C_1B_1$ indicates a stable compound type with a congruent melting point C_1. Curves A_1DB_2, A_2UB_1, and $A_2E_6B_2$ in the diagrams illustrate the successive changes that occur with the decrease of the tendency of compound formation.(1) A_1DB_2 is a dissociation type,

(1) For simplicity, only a single compound of the type AB (1 : 1) is considered. The argument, however, can readily be extended to other types.

A_2UB_1 an incongruent type, and $A_2E_6B_2$ a simple eutectic type, for which last named no compound is found in the diagram.

The Existence Range of Molecular Compounds. In the ideal case, the crystallisation curve A_2E_6 represents the ideal solution equation, namely

$$\ln x = -\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where x is the mol fraction of A_2 in the saturated solution at temperature T, Q the differential mol heat of solution of A_2, T_0 the melting point of pure A_2, and R the gas constant. Curve B_2E_6 is also of a similar nature. E_6, the intersection of the two curves, is the eutectic point of this system.

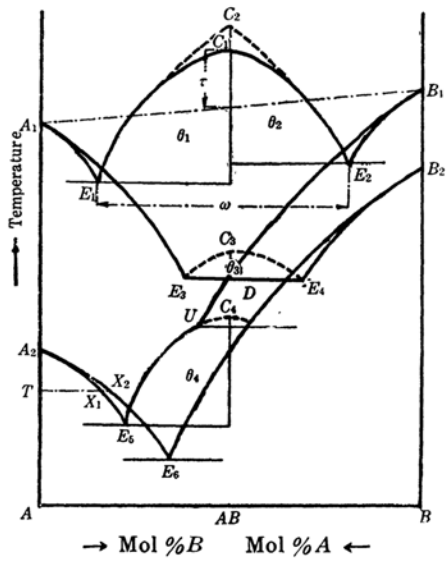


Fig. 1.

Kendall and his co-workers,[2] who studied the various factors that induce deviations from the ideal solubility curve in polar systems, concluded that the predominant disturbing factor is the "addition compound formation" between the components of the systems. The essential point to be noted is the depression of the crystallisation curve (AE or BE) from its ideal position, which is made necessary by compound formation in the solution.[3]

"If only a part of the total A in solution exists as uncombined A, then the total mol fraction of A in the saturated solution must exceed the ideal value by an amount depending on the stability of the compound AB in the liquid state, since the solution will not become saturated with respect to A until the mol fraction of uncombined A reaches this ideal value." Consequently, in Fig. 1, at any fixed temperature T under the melting point of A_2, the solubility of A_2 in the system A_2UB_1 is larger than that in $A_2E_6B_2$, as also the solubility of A_1 in the system $A_1C_1B_1$ is larger than that in A_1DB_2.

Increasing solubility and increasing tendency of compound formation, therefore, for one fixed component (A_1) in a series of different anothers (B_1 or B_2, etc.), proceed in parallel. Since it is the same when we take B in place of A, the increased solubility necessitates an enlarged range of existence of compounds ($E_1E_2 = \omega$ in the system $A_1C_1B_1$) in the solid—liquid equilibrium state.

(2) J. Kendall, A. W. Davidson, H. Adler, *J. Am. Chem. Soc.* **43** (1921), 1481.

(3) Curve A_2E_6 is asymptotic to the ordinate at B ($x = 0$), and curve A_1E_1 is asymptotic to the ordinate at AB ($x = 0.5$). In the remaining case, AE assumes an intermediate position between the two.

The Melting Point of Molecular Compounds[4]. Increasing stability of the compound and elevation of its melting point also proceeded in parallel. In the system $A_1C_1B_1$, the virtual point C_2 indicates the melting point of the compound, not dissociated into its components in the fused state, the system consisting, indeed, of two simple eutectic systems of type $A_2E_6B_2$ compressed into one composition range. Point C_1 is the dystectic point of an actual compound in which some degree of dissociation is realized on fusion,

$$AB \rightleftarrows A+B.$$

In the less stable A_1DB_2 system, further dissociation takes place, the crystallisation curve $E_3C_3E_4$ becomes flatter, and, finally, in the case of complete dissociation, it coincides with the straight line E_3DE_4.

Generallization is used here in order to compare the compound formation in systems of various types. It has been shown that—

(a) Compound formation and its stability decreases in the order,[5] congruent type $>$ dissociation type, incongruent type $>$ simple eutectic type.
(b) In the first three types, where compound crystals are perceived, the order of compound formation is generally parallel to the solubility of the mutual components, which spreads the existence range of the compound: ω.[6]
(c) In the congruent melting type, stability is related to the curvature of the crystallisation curve near the dystectic point.

In the non-dissociation type, the dystectic point C_2, which designates the melting point of a pure solid compound, is on the apex of $E_1C_2E_2$, although usually in the case of organic molecular compounds in the fused state, dissociation takes place to a certain extent, so that, the crystallisation curve becomes progressively flat with the depression of the melting point, whence the greater the dissociation, the lower the melting point.

Regardless of this consideration, actually, the melting point of the molecular compound is higher or lower than that of the component, depending on other intermolecular factors. At present, these factors are so complicated that no satisfactory resolution has yet been accomplished. However, if we take the following value τ from a large number of congruent systems, consisting of analogously constituted components, we can conveniently compare the sequence of compound formation, namely,

$$\tau = t_c - \frac{mt_A + nt_B}{m+n},$$

where t_A, t_B, and t_C are respectively the melting points of the binary components and their compound, $m:n$ is the compound mol ratio ($A:B = m:n$), and τ is provisionally called the "melting point elevation."

(4) R. Kremann, *Monatsh.*, **25** (1904), 1215; *Z. Elektrochem.*, **12** (1906), 259.
(5) Crystallisation velocity is greatly diminished in viscous liquids.
(6) Area θ in Fig. 1 may be taken for this comparison.

The Molecular Compounds between Naphthalene, Naphthols, and Aromatic Nitrobenzenes[7]. In recent crystal chemistry, the crystal lattices of typical organic compounds have gradually been found to belong to the molecular lattice type. Benzene,[8] naphthalene,[9] anthracene,[9] and the series of the aromatic condensed ring compounds with simple substitution radical[10] have been determined as having the flat molecular structure. Fixation of the lattices by intermolecular force is generally weakened by melting. At the melting point, the crystal lattice structure being disturbed, a freer molcular state follows, in which the molecular compounds usually dissociate into their components. In this sense, it is possible to discuss the formation and stability of molecular compounds in fusion together with the structure of their components. Tables 1 and 2[7] give the essential data of molecular compounds between naphthalene, naphthols, and aromatic nitrobenzenes.

Table 1. Binary Systems of Trinitro and Tetranitro Compounds.

Mol ratio A : B (τ) / ω — A / B	α-Naphthol	β-Naphthol	Naphthalene
sym-Trintrobenzene	1 : 1 (84.0) 90·6	1 : 1 (36.0) 76·7	1 : 1 (51.0)* 83·4
Picric acid	1 : 1 (81.5) 92·8	1 : 1 (34.3)** 78·7	1 : 1 (50.5)* 86·4
Picramide	1 : 1 (52.3) 71·3	1 : 1 (7.3) 56·0	1 : 1 (34.8)* –
2, 4, 6-Trinitrotoluene	1 : 1 (37.8) or (3 : 2) 73·2	1 : 1 (8.3)* –	1 : 1 (17.3)* 72·7
Picryl chloride	1 : 1 (34.5) 71·9	1 : 1 (3.5) 52·3	1 : 1 (10.5)* –
2, 4, 6-Trinitroanisol	1 : 1 (−4.0) 49·0	∨	∨ or 1 : 1 (−20.0) 22·3
2, 4, 6-Trinitrophenetol	1 : 2 (−16.0) 32·3	1 : 2 (−17.2) 29·4	1 : 2 (−5.7) 45·1
Trinitrocresol	1 : 1 (58.8) or (3 : 2) 91·0	1 : 1 (15.3) 66·9	1 : 1 (32.8)* 87·2
Styphnic acid	1 : 1 U* –	1 : 1 U* –	2 : 1 (26.0) or (1 : 1)* 17·5
1, 2, 4, 6-Tetranitrobenzene	1 : 1 (26.0) 73·5	1 : 1 (6.5) 64·6	3 : 2 (41.1) 84·7
Tetryl	3 : 2 (−29.0) 19·7	m : n (−46.3) D –	1 : 1 (−17.5)* –

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

** Asahina, Yokoyama, *J. Chem Soc. Japan*, **56** (1925), 415.

(7) T. Asahina and C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 341; C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 833, 922; **60** (1939), 170.

(8) E. G. Cox, *Proc. Roy. Soc.* (London), A, **135** (1932), 491.

(9) J. M. Robertson, *Proc. Roy. Soc.* (London), A, **142** (1933), 674; **140** (1933), 79.

(10) R. C. Evans, "An Introduction to Crystal Chemistry", 335–349, Cambridge (1939).

Table 2. Binary Systems of Dinitro and Mononitro[11] Compounds.

Mol ratio A : B (τ) — A / B	α-Naphthol	β-Naphthol	Naphthalene
2, 4-Dinitrobenzoic acid	1 : 1 U	1 : 2 U or ∨	1 : 1 U
2, 4-Dinitrochlorobenzene	1 : 1 (35.7)	1 : 1 (6.7)	1 : 1 (13.2)
2, 4-Dinitrophenol	1 : 1 (14.7)	1 : 1 (−8.3)	1 : 1 (−4.0)
2, 4-Dinitrobromobenzene	1 : 1 (12.3)***	1 : 1 (−15.7)***	1 : 1 (−5.7)***
2, 4-Dinitrotoluene	1 : 1 (15.0)	1 : 1 (−19.5)	1 : 1 (−14.5)
m-Dinitrobenzene	1 : 1 (7.0)	1 : 1 U*	1 : 1 (−34.2) D*
2, 4-Dinitroanisol	1 : 1 (2.0)	1 : 1 (−22.0)	1 : 1 (−33.5)
2, 4-Dinitroaniline	1 : 1 (2 : 3) or U	2 : 3 U	1 : 3 U
Dinitromesitylene	∨	∨	∨
2, 6-Dinitrophenol	1 : 1 (0.8)	1 : 1 (−16.7)	1 : 1 (−13.8)
2, 6-Dinitrotoluene	1 : 1 U	∨	∨*
2, 6-Dinitroaniline	1 : 1 U	1 : 1 (12.0)	1 : 1 U
3, 5-Dinitrobenzoic acid	1 : 1 (41.5)	1 : 1 (22.0)	1 : 1 (39.5)
3, 5-Dinitroanisol	1 : 1 (−7.3)	∨	1 : 1 U
2, 5-Dinitrophenol	1 : 1 (17.4)	1 : 1 (3.4)	3 : 2 (10.1) or (1 : 1
2, 5-Dinitrotoluene	1 : 1 (11.9)	1 : 1 (−8.5)	1 : 1 (−19.6)
p-Dinitrobenzene	1 : 1 U	1 : 1 (−11.8) or (3 : 2)	1 : 1 (−7.5)*
p-Nitrobenzoic acid	1 : 1 U	1 : 2 U	1 : 1 U
m- ,,	1 : 2 (3.3)	∨ or 1 : 1 (−24.3)	1 : 2 (10.2)
o- ,,	∨	∨	∨
p-Nitrobenzaldehyde	3 : 2 (−21.6)	1 : 1 (−37.0)*	∨
m- ,,	1 : 1 (−29.0)	1 : 1 U*	∨
o- ,,	1 : 1 U	∨*	∨
p-Nitrochlorobenzene	2 : 3 (−37.0)	∨	∨
m- ,,	∨	∨	∨
p-Nitrophenol	∨	∨	∨*
m- ,,	∨	∨	∨
o- ,,	∨	∨	∨*
p- or *m*-Bromobenzene	∨	∨	∨
p-Nitrotoluene	∨	∨	∨*
m- ,,	—	—	∨*
Nitrobenzene	—	—	∨*
p-Nitroaniline	∨	∨	∨
m- ,,	∨	∨	∨*
o- ,,	∨	∨	∨
p-Nitroanisol	∨	∨	∨

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

*** Data of the molecular compound obtained from the solution by Buehler, Hisey, Wood (*J. Am. Chem. Soc.*, **52** (1930), 1940.).

(11) Some of the liquidus in systems of simple eutectic type are in fairly good agreement with their ideal crystallisation curves.

(1) Compound ratio usually 1:1, except the following systems:

3 : 2 naphthalene — 1,2,4,6-tetranitrobenzene, α-naphthol — tetryl, naphthalene—2,5-dinitrophenol, α-naphthol — p-nitrobenzaldehyde;

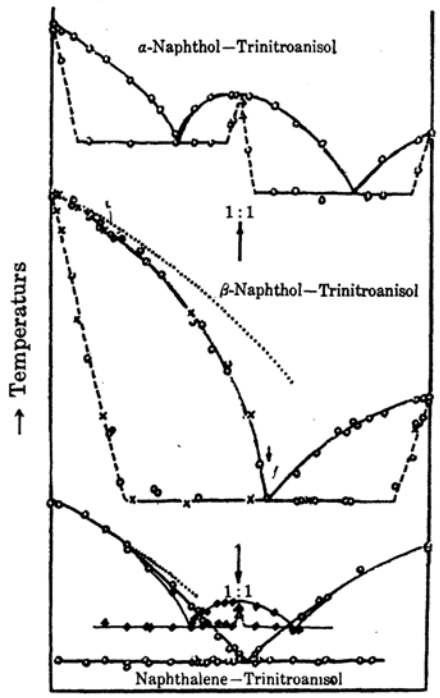
2 : 3 naphthol—2,4-dinitroaniline, α-naphthol—p-nitrochlorobenzene;

1 : 2 naphthol — 2,4,6-trinitrophenetol, naphthalene — 2,4,6-trinitrophenetol, β-naphthol — 2,4-dinitrobenzoic acid, β-naphthol — p nitrobenzoic acid, α-naphthol—m-nitrobenzoic acid, naphthalene —m-nitrobenzoic acid;

1 : 3 naphthalene—2,4-dinitroaniline.

Except a few examples, ratios other than 1:1 are found in the case of rather feeble compound formations, in which case there sometimes happens to be another metastable equilibrium, the molecular ratio of which is given in Tables 1, 2 in parentheses.

(2) From Tables 1, 2, which are arranged in the order of decreasing tendency of compound formation, it will readily be seen by comparing the value of τ or ω that compounds of α-naphthol have higher "melting



○ Stable thawing and melting point.

× Date from the measurement by the cooling method.

◆ Metastable point.

△ Transition point of the crystal obtained in the alcoholic solution.

··· Ideal crystallisation curve calculated from the equation

$$\ln x = -\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where Q is 5.4 or 4.6 kg. cal. respectively in β-naphthol or naphthalene.

Fig. 2.

point elevation" and a wider compound existence range than those of β-isomer (the only exception being β-naphthol—2,6-dinitroaniline). Most of the naphthalene compounds have intermediate values of τ or ω.

It is interesting to compare, of the various feeble compound formation systems, α-naphthol compound with a β-isomer or naphthalene compound. Trinitroanisol which gives a compound of congruent melting point with α-naphthol, fails to give one with β-naphthol, while it gives with naphthalene a simple eutectic or a metastable compound. Analogous examples are to be seen in the compounds of *m*-nitrobenzoic acid..

In *m*-nitrobenzene, 2,4-dinitroaniline, 2-6-dinitrotoluene, 3,5-dinitroanisol, and *p*-, *m*- and *o*-nitrobenzaldehydes, the orders of compound formation are clearly systematized.[12]

(3) In comparing the columns of Tables 1 and 2, the order of compound formation is readily seen to be

trinitro compound $>$ dinitro compound $>$ mononitro compound,

and the effect of second substitution radical in the nitrated benzene nucleus,

sym-Trinitro compounds : $-H > OH > NH_2 > CH_3 > Cl > OCH_3$, OC_2H_5,

2,4-Dinitro compounds : $-CO_2H > Cl > OH > Br > CH_3 > H > OCH_3 > NH_2$,

Mononitro compounds : $-CO_2H$, $CHO > Cl > Br$ - - - .

The tendency of compound formation is the most marked in sym-trinitrobenzene, the substitution of any other radicals into it diminishes the tendency, presumably because of certain hindrances. In the case of less nitrated compounds, the effect of the substituent is profound, whether positive or negative. Of the molecular compounds of mononitrobenzenes, those of naphthalene somewhat differ in nature from those of naphthols.

(4) A comparison of isomers of equally nitrated components also gives a number of interesting results in connection with the affinity of molecular compounds. In di- and mono-nitrobenzenes, the orders are,

p-nitro compound, *m*-nitro compound $>$ *o*-nitro compound;
2, 4-dinitro compound, 2, 5-dinitro compound, 3, 5-dinitro compound $>$ 2, 6-dinitro compound.

More detailed results will be given in a later paper.

(5) These compounds[13] showed distinctly halochromic phenomenon, and naphthols were more coloured than naphthalene, owing probably to the presence of the hydroxyl group. Between α- and β-naphthol, most of the α-compounds proved to be more halochromic than the β-isomers.

These molecular compound crystals were prepared from the solution, and most of them showed melting points identical with those obtained in the phase diagrams.

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(12) Incongruent melting point was found not only in feeble combinations but also in systems, one component of which had a much higher melting point than the other.

(13) P. Pfeiffer, " Organische Molekulverbindungen ", 2. Aufl., 338, Stuttgart (1927).

Experimental.

Determination of Solid-Liquid Transion Points. The phase diagram was obtained by improving the thawing and melting point method of H. Reinboldt [14], by which the least quantity of sample (10–100 mg.) could be investigated in a short time.

The apparatus consisted of the following parts.

(a) A thermometer of very small diameter. A rod thermometer about 150 mm. long, 2–3 mm. diameter, with a mercury bulb of the same diameter 2–3 mm. long. Accurary of temperature reading about 0.2°.

(b) Sample tube. The glass tube shown in Fig. 3. The upper stem was made exactly to fit the thermometer inserted in it, in order to prevent the inner wall of the lower bulge from touching the sample throughout the observation.

(c) Heating vessel (not illustrated). To regulate the heating, an air mantle was adopted and immersed in a liquid bath for which liquid paraffin or concentrated sulphric acid was found to be convenient. The bath was provided with a thermometer and a stirrer.

(d) Weighing. To save time, the sample could be weighed with a torsion or a micro spring balance (0.1–100 mg.). The present writer used a quartz spring balance that is a modification of Salvioni's microchemical balance.

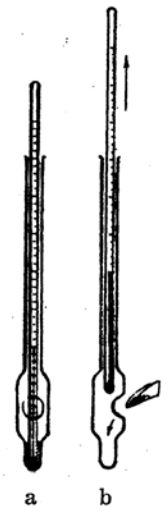

Fig. 3.

The weighed sample was placed through a side hole in the sample tube, and the thermometer introduced. The substance was fused to a homogeneous mixture. After cooling, the sample tube containing the solidified substance was placed in the liquid bath, heated gradually and constantly, and the thawing point observed. The thawed sample was then further heated with a little stirring with the thermometer until it completely melted, when the melting point was observed. (Both thawing and melting point can be frequently observed, their values being usually the same.) Supercooling was avoided by rubbing or crystal seeding, which made it possible to obtain a detailed curve near the eutectic point [15]. The observation was repeated by varying the composition, which was effected by slightly drawing up the thermometer (as in Fig. 3b) and adding one component to the mixture.

The capillary tube method [16] was also used in experimenting with readily sublimable or decomposable material. Some of the data obtained by the cooling curve method are included in the above mentioned tables.

Preparation of the Molecular Compound from the Solution. In the system, the molecular compound formation of which was observed on the diagram, the writer tried to obtain a crystal of the compound from the solution containing its components. From 0.1 to 0.2 g. of the components was weighed in a compound ratio, separately dissolved in alcohol, and the warmed solutions were mixed together, the mixture which, after a short heating, was slowly poured into 50–100 cc. of distilled water with vigorous stirring. The separated crystal was suctioned, washed with distilled water (if permitted), pressed between sheets of filter paper, and dried overnight in a desiccator. The yield of products seems to agree with the compound formation in the diagram.

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(14) H. Reinboldt, K. Henning and M. Kircheisen, *J. prakt. Chem.*, [2], **111** (1925), 246; C. Shinomiya, *J. Chem. Soc. Japan*, **58** (1937), 118.

(15) Supercooling is very frequent near the eutectic composition, in which case, supercooled viscous liquid was easily made to crystallise when some crystals of that component (not the other), which should give heterogeneous equilibrium with the liquid, were seeded. In this way, it is easy to determine whether the composition of the mixture lies on the A-component side or on the B-component side of the eutectic composition.

(16) A method devised and modified from the original by T. Asahina. (*Bull. Chem. Soc. Japan*, **9** (1934), 132.)

Special Part.

(1) α- or β-Naphthol—1,2,4,6-tetranitrobenzene.

These system are too unstable to enable a determination of diagrams.

With α-naphthol,

Eutectic point: 74.0°, 111.0°; 87 mol%, 13.5 mol% α-naphthol.
Compound (1:): brown red prisms, melting at 137.0°.

with β-naphthol,

Eutectic point: 95.0°, 110.0°; 82.6 mol%, 18 mol% β-naphthol.
Compound (1:1): brown red powder, melting at 130.5°.

(2) Naphthalene—1,2,4,6-tetranitrobeneze.

Tetranitrobenzene: 5.0 mg.

Mol% tetranitrobenzene	100.0	75.5	59.4	42.9	33.6	19.0	9.2
Melting point	126.0	128.0	135.0	138.0	138.0	129.0	92.0
Thawing point	125.0	—	111.0	129.0	—	73.0	73.0

Tetranitrobenzene: 7.6 mg.

Mol% tetranitrobenzene	88.4	67.7	49.2	34.7	24.1	18.1	12.5	6.4[17]	4.7
Melting point	119.0	132.0	138.0	139.0	—	—	116.5	75.0 ↓	74.0
Thawing point	114.0	114.0	—	108.0	75.0	74.0	74.0	74.0	76.5

Total naphthalene: 21.0 mg.

Mol% naphthalene	80.0	74.0	58.5	48.9	43.0	35.6	28.3
Melting point	—	—	139.5	138.0	139.0	139.0	—
Thawing point	74.0	74.0	134.0	114.0	114.0	120.0	74.0

Eutectic point: 74.0°, 114.0°; 93.7 mol%, 9 mol% naphthalene.
Compound (3:2): orange yellow prism melting at 139.5°.

This system was the most stable of the three, whereas with trinitro or dinitro compounds, α-naphthol usually formed the most stable compound. In Fig. 4, however, the curvature near the melting point is extreamely flat, and considerable dissociation is expected.

The conclusion is that tetranitrobenzene is not a stable substance [18], its tendency of molecular compound formation with naphthalene and naphthols is not so marked as that with *sym*-trinitrobenzene.

(3) α-Naphthol—tetryl (Fig. 5).

Naphthol: 6.7 mg.

Mol% naphthol	95.7	88.1	75.6	69.8	59.0	44.0	34.3	27.0
Melting point	93.0	88.5	79.0	77.5	80.0	97.5	106.0	116.0
Thawing point	84.0	76.0	75.5	75.0	78.0	78.0	78.0	77.0

Tetryl: 7.1 mg.

Mol% tetryl	94.6	54.4	49.1	43.1	39.8	34.7	27.3	17.5	6.5
Melting point	126.0	90.0	83.0	80.0	80.0	79.5	76.0	85.5	92.3
Thawing point	117.0	77.0	77.0	77.0	—	77.0	75.0	75.0	76.0

Naphthol: 12.0 mg.

Mol% naphthol	75.4	66.9	61.3	57.5	52.7	50.4
Melting point	79.0 ↓	79.0	80.0	80.0 ↓	79.5	85.5
Thawing point	76.0	75.5	78.0	78.5	77.0	77.0

Eutectic point: 75.5°, 77.0°; 72.6 mol%, 52.9 mol% α-naphthol.
Compound (3:2): brown red prisms, melting at 80.0°.

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(17) In the sample of 6.4 moles% tetranitrobenzene, its molecular compound crystal was recognized, while in that of 4.7 moles% tetranitrobenzene, naphthalene was seen in the last stage of melting. The arrow indicates the position of the eutectic point.

(18) 1, 2, 4, 6-Tetranitrobenzene was easily prepared by the method of W. Borsche (*Ber.* **56** (1923), 1939.). Instead of trinitrophenetol in alcoholic solution, trinitroanisol in methyl alcohol was used. The crude picryl hydroxylamine immediately nitrated, tetranitrobenzene was formed, which was decomposed considerably by repeated crystallisations in chloroform.

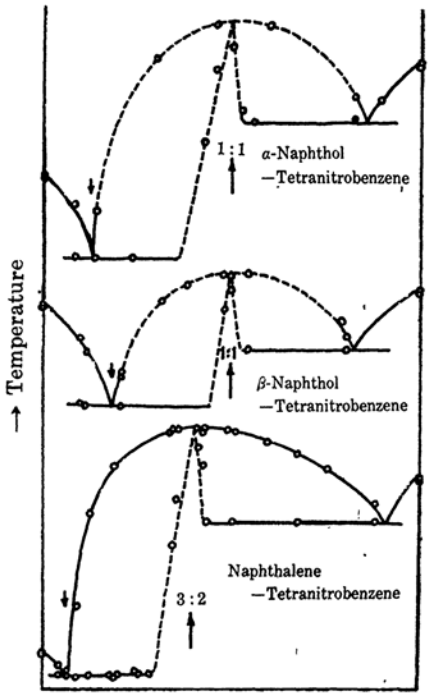

Fig. 4.

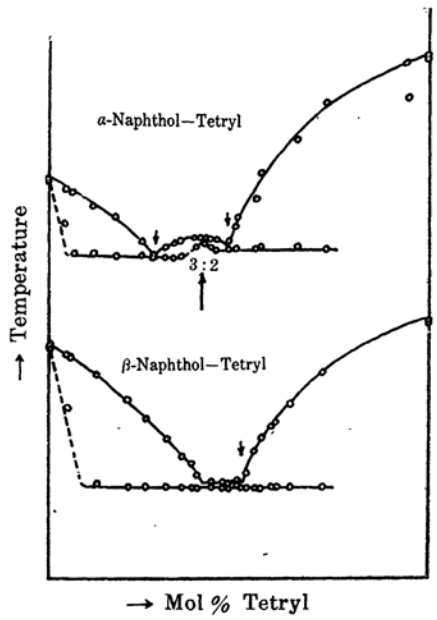

Fig. 5.

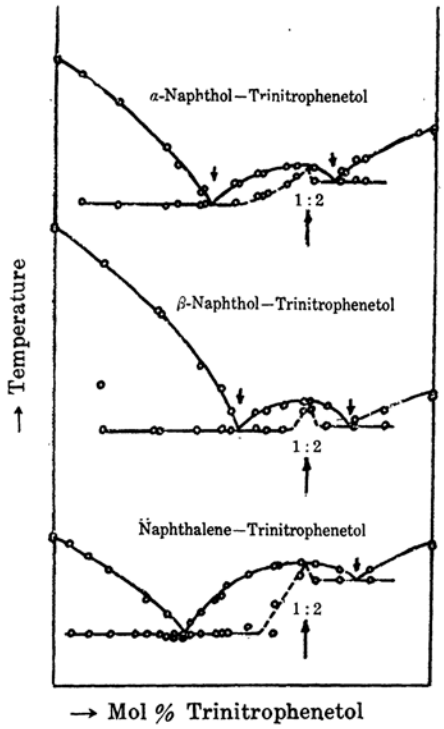

Fig. 6.

(4) β-Naphthol—tetryl (Fig. 5).

Total naphthol: 9.4 mg.

Mol% naphthol	94.5	79.9	87.8	74.8	65.2	54.1	50.6	46.2	40.6	27.9
Melting point	11.85	107.0	114.0	102.0	92.0	85.5	86.0	94.0	101.0	114.5
Thawing point	—	84.0	85.0	84.5	84.0	84.0	85.0	83.8	84.0	84.0

Tetryl: 17.2 mg.

Mol% tetryl	95.9	69.1	62.4	61.7	57.2	53.3	48.4	44.6	41.5	36.9
Melting point	119.0	97.0	90.5	87.0	86.0	85.0	88.0	97.0	100.0	106.0
Thawing point	105.0	84.0	84.0	84.0	84.0	84.0	84.0	83.8	83.8	84.0

This last mentioned system is of dissociation type. In the range of 59.6–49.6 mol% of β-naphthol, the melting curve was a straight line. The compound ratio was indistinct although brownish halochromy was very marked.

Notwithstanding the abundance of nitro groups, two tetranitro compounds have never shown any notable compound formation, probably owing to steric hindrances or ortho nitro effect. In these systems, it is noteworthy that the addition of naphthalene is more marked than that of the two naphthols.

(5) α-Naphthol—2,4,6-trinitrophenetol.

Trinitrophenetol: 5.0 mg.

Mol% trinitrophenetol	100.0	75.6	32.2	16.8	7.0
Melting point	78.0	66.0	68.0	84.8	92.0
Thawing point	77.0	—	57.5	57.8	58.0

Naphthol: 3.2 mg.

Mol% naphthol	60.5	51.3	43.8	35.2	31.8	18.0
Melting point	62.0	63.5	—	67.0	66.8	70.0
Thawing point	58.0	—	60.8	65.0	63.0	64.0

Total trinitrophenetol: 16.3 mg.

Mol% trinitrophenetol	96.0	63.8	55.0	60.9	53.7	47.3	38.5	29.3
Melting point	76.5	67.8	66.3	67.8	65.5	63.3	61.0	73.0
Thawing point	—	65.0	60.0	63.0	60.0	58.0	57.8	57.0

Naphthol: 1.5 mg.

Mol% naphthol	24.5	20.8
Melting point	67.0	70.0
Thawing point	64.3	64.0

Eutectic point: 57.5°, 64.0°; 58.3 mol%, 26.0 mol% α-naphthol.
Compound (1:2): orange prisms or powder, melting at 68.0°.

(6) β-Naphthol—2, 4, 6-trinitrophenetol.

Total trinitrophenetol: 9.3 mg.

Mol% trinitrophenetol	83.4	53.0	67.0	44.2	28.3
Melting point	71.5	73.0	75.0	79.5	99.5
Thawing point	—	68.5	73.0	69.0	68.0

Naphthol: 4.2 mg.

Mol% naphthol	87.2	72.4	61.6	53.1	44.7	39.8	34.5	27.8	20.8	12.8
Melting point	112.0	100.0	85.0	73.0	73.0	74.0	75.5	74.5	71.0	73.3
Thawing point	68.0 (80.0)	68.0	68.0	68.0	68.0	68.0	73.0	69.0	69.0	69.0

Eutectic point: 68.0°, 69.0°; 51.1 mol%, 21.7 mol% β-naphthol.
Compound (1:2): orange yellow prisms or powder, melting at 75.5°.

(7) Naphthalene—2,4,6-trinitrophenetol.

Trinitrophenetol: 6.3 mg.

Mol% trinitrophenetol	58.8	34.8	24.4	15.8	9.3	4.3
Melting point	72.0	54.0	63.0	—	75.0	78.0
Thawing point	62.0 (54.0)	53.0	54.0	54.0	54.0	54.0

Trinitrophenetol: 13.1 mg.

Mol% trinitrophenetol	83.4	75.7	69.3	65.2	59.3	51.8	46.0		
Melting point	71.0	71.0	72.8	73.0	72.0	70.0	67.0		
Thawing point	68.0	68.0	68.0	69.5	—	56.0	54.0		

Trinitrophenetol: 3.1 mg. (19)

Mol% trinitrophenetol	44.5	42.9	39.1	36.3	34.1	29.9	28.1	21.4	14.3
Melting point	64.0	63.0	60.0	57.0	—	59.0	—	64.0	71.0
Thawing point	54.0	54.0	54.0	54.0	54.0	53.0	54.0	54.0	54.0

Eutectic point: 54.0°, 68.0°; 64.9 mol%, 19.8 mol% naphthalene.
Compound (1:2): pale yellow powder or prisms, melting at 73.0°.

Three diagrams of trinitrophenetol are given in Fig. 6. The order of compound formation is naphthalene > α-naphthol > β-naphthol. It is related in character to tetranitro compounds, rather than to trinitroanisol. Substitution of ethyl by a methyl radical somewhat affects addition compound formation.

Summary.

The molecular compound of naphthalene and naphthols with mono-, di-, tri-, and tetra-nitro aromatic compounds are systematically compared, and the compound formation discussed with solid—liquid phase diagrams.

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(19) This datum, together with the value of the cooling method in Fig. 2, is due to Mr. N. Sato, whom the writer wishes to thank for his assistance.