

SOME NEW ADDITION COMPOUNDS OF  
POLYNITROPHENOLS

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Although it has long been known that picric acid forms molecular compounds with compounds containing the aromatic nucleus, particularly if several condensed nuclei are present, the corresponding complexes of other polynitrophenols have received less attention. The present work was undertaken to fill in gaps in existing knowledge of such compounds; it deals with previously described ones in only a few cases.

The styphnic acid used was prepared by the nitration of resorcinol; 2,4-dinitrophenol, 2,4,6-trinitro-*m*-cresol, and picric acid were purchased C. P. reagents. Of the other compounds, the naphthyl ethers were left over from a similar previous research (Dermer and Dermer 1938). Dibenzofuran and chrysene were distilled and then recrystallized from benzene-ethanol and *o*-dichlorobenzene respectively. Phenanthrene was distilled from sodium (cf. Jeanes and Adams 1937) and recrystallized from ethanol. Anthracene was the product obtained by Dermer and King (1941). 1-Chloromethylnaphthalene,  $C_{10}H_7CH_2Cl$ , was prepared by Mr. Grover Mullin according to the method of Fieser and Gates (1940). Other naphthalene derivatives, carbazole, and retene were Eastman Kodak C. P. reagents

The addition compounds were made by dissolving about equimolecular amounts of the polynitrophenol and the naphthalene or other condensed-ring derivative in the minimum amount of boiling methanol or ethanol, mixing the solutions, and cooling to cause crystallization. Each was then recrystallized, usually from the alcohol that had not been used in preparing it, for better purification.

After air-drying, each complex was analyzed by titrating 0.1-0.5 g samples, dissolved in ethanol, with 0.1N aqueous sodium hydroxide solution, phenolphthalein being used as indicator. Melting points were located approximately by the new method of Stahl (1941) and then determined more accurately by the usual capillary-tube procedure, a thermometer calibrated with pure naphthalene and benzoic acid being used.

The compounds isolated, along with their melting points, are listed in table I. Under the conditions specified anthracene, chrysene, and carbazole formed either unstable compounds or none at all with the three polynitrophenols studied. 2,4-Dinitrophenol also formed no stable complexes with 2-methylnaphthalene, 1-chloronaphthalene, 1-chloromethylnaphthalene, 2-naphthyl isoamyl ether, phenanthrene<sup>1</sup>, and retene.

The failure of anthracene and others in the group to form any stable compounds is due mainly to great differences in the solubilities of the components in alcohol (cf. Dimroth and Bamberger 1924). In benzene, color changes and other evidence indicate that the stability of the complexes is greater. The smaller activity of 2,4-dinitrophenol as compared to the

<sup>1</sup>Kremann and Hofmeier (1910) reported that these components form no compound, but Kofler (1940) has detected an intermolecular addition product melting at 84°.

other polynitrophenols and the lighter color of its addition compounds are attributable to its fewer nitro groups, but the difference in its ability to unite with 1-chloronaphthalene and 1-bromonaphthalene, for instance, is unaccountable.

It will be noted from the table that the melting point spread among compounds of similar structure is not large, so that these complexes can be recommended as identifying derivatives only in certain cases.

TABLE I  
*Properties of addition compounds*

Compound with	Neutralization equivalent		Melting point <sup>a</sup> °C.	Color <sup>b</sup>
	Found	Calcd.		
Compounds of 2,4-dinitrophenol				
1-Naphthyl methyl ether	355,357	342	52-3 <sup>c</sup>	YT2
2-Naphthyl methyl ether	328,331	342	52-53.5	YT2
Dibenzofuran	339,342	352	63-63.5	YT1-2
1-Bromonaphthalene	397	391	74-5.75	YT2
Compounds of 2,4,6-trinitro- <i>m</i> -cresol				
2-Methylnaphthalene	389,389	386	113-4	YT1
1-Naphthyl methyl ether	403,404	401	102.5-103.5	YO
2-Naphthyl methyl ether	405,407	401	93-4	OY-Y
1-Chloronaphthalene	413,415	406	77-9	Y
Dibenzofuran	413,414	411	126-126.5	Y
1-Chloromethylnaphthalene	420,421	420	81.5-82	YT2
Phenanthrene	418,420	421	111-3	O
1-Bromonaphthalene	451,453	450	75.5-76.5	Y
1-Naphthyl isoamyl ether	452,452	457	76.5-77	OY
2-Naphthyl isoamyl ether	458,460	457	100-101	YT1
Compounds of styphnic acid				
2-Methylnaphthalene	196	194	128-9	Y-YT1
1-Naphthyl methyl ether	203,205	202	125-6	YO
2-Naphthyl methyl ether	204,204	202	141.5-142.5	OY-Y
1-Chloronaphthalene	206,207	204	111-2 <sup>d</sup>	Y
Dibenzofuran	208,209	206	138.5-140	Y
1-Chloromethylnaphthalene	212	210	112.5-113	YT1
1-Bromonaphthalene	223	226	112-3 <sup>e</sup>	YT1
1-Naphthyl isoamyl ether	233,235	230	119-20	YO
2-Naphthyl isoamyl ether	232,234	230	127-8	OY-Y
Compounds of picric acid				
1-Chloromethylnaphthalene	402	406	80-2	Y
Dibenzofuran	396,397	397	96.5-97.5 <sup>f</sup>	Y

<sup>a</sup> All melting point values are rounded off to the nearest half degree.

<sup>b</sup> By comparison with the color standard charts accompanying Mulliken (1904).

<sup>c</sup> Burmistrov (1939) obtained the value 96°.

<sup>d</sup> Efremov (1919) reported a transition point at 109.8° for this binary system at 53.6% styphnic acid, but Ma, Hsia and Sah (1933) found the melting point of the 1:1 compound to be 126.8°.

<sup>e</sup> The value 107.8° was reported by Gibson (1903), and 116.8° by Ma, Hsia and Sah.

<sup>f</sup> Efremov found a transition point at 101.2° and 57.3% styphnic acid.

<sup>g</sup> The value 94° was given by Goldschmidt and von Schmidt (1881).

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