[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

# A STUDY OF MOLECULAR ORGANIC COMPOUNDS. I. THE MOLECULAR ORGANIC COMPOUNDS OF META-DINITROBENZENE, 2,4-DINITROTOLUENE AND 2,4-DINITROPHENOL[1]

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## Introduction

The literature shows that molecular-compound formation is quite common among certain types of organic compounds. Probably the most common are the picrates, the first of which were prepared by Fritzsche.[2] Later, it was found that this property was characteristic of other nitro compounds,[3] as well as phenols,[4] amines, quinones[5] and hydrocarbons.[6] It is evident, therefore, that large numbers of these compounds must be prepared and carefully studied if an insight is to be gained into their structure.

In this investigation, the molecular compounds[7] of the structurally related compounds, *m*-dinitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrophenol, were isolated[8] and their melting points and molecular ratios were determined. From the number of molecular compounds formed in each case it was hoped to gain some information in regard to the structure of these compounds.

## Experimental Part

**Materials.**—The materials, most of which were obtained from the Eastman Kodak Company, were C.P.

**Method of Preparation.**—The molecular compounds were prepared by dissolving equimolecular quantities of the two constituents in hot absolute alcohol and allowing the solution to cool. Recrystallization was

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[1] This paper is an abstract of a thesis presented by Alice G. Heap in partial fulfilment of the requirements for the degree of Master of Arts at the University of Tennessee.

[2] Fritzsche, *Ann.*, **109,** 247 (1859).

[3] Hepp, *Ann.*, **215,** 344 (1882).

[4] Dyson, *J. Chem. Soc.*, **43,** 466 (1883).

[5] Hebebrand, *Ber.*, **15,** 1973 (1882).

[6] Kuriloff, *Z. physik. Chem.*, **23,** 547 (1897).

[7] An attempt was made to form a combination with each of the following compounds: α-naphthylamine, β-naphthylamine, naphthalene, benzidine, α-naphthol, β-naphthol, aniline, *p*-toluidine, *o*-toluidine, dimethylaniline, hydroquinol, pyrogallol, resorcinol, phenol, pyridine, catechol, *o*-cresol, fluorene, phloroglucinol, *o*-phenylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, benzamide, diphenyl, anthracene, triphenylmethane, *p*-aminophenol, carbazole, methylaniline, diethylamine (not tried with 2,4-dinitrophenol), triethylamine, anisole, phthalimide, *p*-bromo-acetanilide and diphenylamine.

[8] The authors are aware of the fact that molecular compounds incapable of isolation may exist in some of these cases.

carried out with absolute alcohol on a watch glass until the molecular compounds had a sharp melting point or until they began to dissociate. In cases where one of the constituents was a liquid, the molecular compounds were prepared most easily by fusing the two constituents together in equimolecular ratios.

**Method of Analysis and Melting Points.**—The analyses for nitrogen were carried out by Dumas' method. Melting points were taken by the capillary-tube method with a thermometer calibrated by the Bureau of Standards, and stem corrections were applied in each case.

**Tabulated Results.**—A great portion of the compounds described below had not been isolated previously from solution but their melting points were determined by the "freezing-point" method. By this method, freezing-point curves of the two compounds were constructed and the melting points of the respective molecular compounds were obtained from the maximum points on the intermediate curves, which were always present in the

TABLE I

MOLECULAR COMPOUNDS OF *m*-DINITROBENZENE

| Second constituent | M. p., °C. (corr.) | Color | From literature | | | Ref. |
|---|---|---|---|---|---|---|
| | | | M. p., °C. | Mol. ratio | Method of prepn. | |
| $\alpha$-Naphthylamine | 65.1–65.7 | Red | 63.8 | 1:1 | Freezing pt. | 9 |
| | | | 67 | 1:1 | Solution | 10 |
| $\beta$-Naphthylamine | 53.9–55.7 | Red | 53.3 | 1:1 | Freezing pt. | 9 |
| | | | 57 | ... | .... | 11 |
| Naphthalene | 50.7–51.6 | Greenish-yellow | 50.8 | 1:1 | Freezing pt. | 12 |
| | | | 52–53 | 1:1 | Solution | 13 |
| Benzidine | 127.6–128 | Jet black | 128 | 1:1 | .... | 10 |
| Aniline | 38.3–39.3 | Red | 40 | 1:1 | Freezing pt. | 12 |
| | | | 41–42 | 1:1 | Modified fusion[a] | 10 |

[a] Compound was prepared by heating aniline directly with *m*-dinitrobenzene.

TABLE II

MOLECULAR COMPOUNDS OF 2,4-DINITROTOLUENE

| Second constituent | M. p., °C. (corr.) | Color | Mol. ratio | From literature | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | M. p., °C. | Mol. ratio | Method of prepn. | |
| $\alpha$-Naphthylamine | 62.9–63.7 | Orange-red | | 62 | 1:1 | Freezing pt. | 14 |
| Naphthalene | 60.1–60.9 | White | | 59 | 1:1 | Freezing pt. | 12 |
| | | | | 60–61 | 1:1 | Solution[a] | 13 |
| Benzidine | 77.2–77.5 | Jet black | 1:1 | | | | |

[a] Hepp (Ref. 13) did not state which of the dinitrotoluenes he used but it must have been the 2,4 compound since his melting point checks with that obtained in this investigation.

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[9] Kremann, *Monatsh.*, **37,** 723 (1916).

[10] Van Romburgh, *C. A.*, **6,** 2911 (1912).

[11] Sudborough and Karve, *J. Chem. Soc. Abs.*, **120,** i657 (1921).

[12] Kremann, *Monatsh.*, **25,** 1271 (1904).

[13] Ref. 3, p. 375.

[14] Ref. 9, p. 659.

cases of molecular-compound formation. It will be noted that these melting points are usually considerably lower—which is to be expected—than the melting points, determined by the capillary-tube method, of the compounds prepared from solution.

Table III

Molecular Compounds of 2,4-Dinitrophenol

| Second constituent | M. p., °C. (corr.) | Color | Mol. ratio | From literature M. p., °C. | Mol. ratio | Method of prepn. | Ref. |
|---|---|---|---|---|---|---|---|
| α-Naphthylamine | 107.3–107.7 | Red | | 104.5 | 1:1 | Freezing pt. | 9 |
| β-Naphthylamine | 77.6–77.9 | Red-orange | | 72.3 | 1:1 | Freezing pt. | 9 |
| Naphthalene | 94.7–95.0 | Yellow | 1:1 | ... | ... | Solution[a] | 13 |
| Benzidine | 143.5–143.8 | Brown[b] | 1:1 | | | | |
| Benzidine | 134 (decomp.) | Yellow[c] | | | | | |
| Aniline | 76.7–77.3 | Yellow | 1:1 | 75 | 1:1 | Freezing pt. | 15 |
| *o*-Phenylenediamine | 93.6–94.0 | Yellow | | 85.6 | 1:1 | Freezing pt. | 16 |
| *m*-Phenylenediamine | 107.9–108.2 | Orange-yellow | | 100.0 | 1:1 | Freezing pt. | 16 |

[a] Hepp (Ref. 13) prepared this compound but did not record its molecular ratio or melting point.

[b] This form was obtained by using the constituents and absolute alcohol.

[c] This form was obtained by using the constituents and 90–95% alcohol. It contains water of crystallization as the analysis below shows.

Analytical Results

**Compounds Not Previously Described**

Benzidine-2,4-dinitrotoluene. Calcd. for $NH_2C_6H_4C_6H_4NH_2.C_6H_3(NO_2)_2CH_3$: N, 15.29. Found: 15.14.

Benzidine-2,4-dinitrophenol (brown). Calcd. for $NH_2C_6H_4.C_6H_4NH_2.C_6H_3(NO_2)_2OH$: N, 15.21. Found: 14.94, 14.92.

Benzidine-2,4-dinitrophenol (yellow). Calcd. for $NH_2C_6H_4.C_6H_4NH_2.C_6H_3(NO_2)_2OH.H_2O$: N, 14.51. Found: 14.26, 14.16, 14.26, 14.19.

**Compounds Previously Described But Whose Composition Had Not Been Determined**

Naphthalene-2,4-dinitrophenol. Calcd. for $C_{10}H_8.C_6H_3(NO_2)_2OH$: N, 8.97. Found: 8.78.

Aniline-2,4-dinitrophenol. Calcd. for $C_6H_5NH_2.C_6H_3(NO_2)_2OH$: N, 15.16. Found: 14.79.

## Discussion

The formation of molecular compounds can be explained as being due either to (1) principal valence or to (2) subsidiary valence. Kendall[17] is the chief exponent of the former view. He found that combination takes place between compounds, one of which contained oxygen, providing the difference in acidic strengths was great enough. He assumed that the oxygen in the compound of lower acidity changed its valence from two to four and that the two ions formed from the compound of higher acidity

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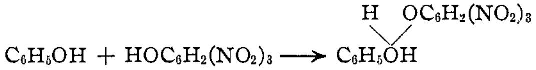
[15] Kremann, *Monatsh.*, **27,** 627 (1906).

[16] Kremann, *ibid.*, **41,** 543 (1921).

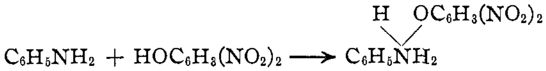
[17] Kendall, This Journal, **36,** 1222, 1722, 2498 (1914); **37,** 149 (1915); **38,** 1309 (1916).

then added onto the free valence bonds of the oxygen. For instance, in the case of phenol and picric acid, Kendall's representation would be as follows.



$$C_6H_5OH + HOC_6H_2(NO_2)_3 \longrightarrow C_6H_5\overset{H\quad OC_6H_2(NO_2)_3}{\overset{\diagdown\,\diagup}{O}}H$$

Our results confirm Kendall's views in certain respects. The greatest number of compounds is formed with 2,4-dinitrophenol which is the strongest acid[18] and the least number is formed with 2,4-dinitrotoluene which is the weakest acid in the group of three. In addition, since all three of the dinitro compounds are very weak acids no compounds were isolated[19] with any compounds other than amines, all of which were basic, and hydrocarbons. To represent the amine compounds according to this view it would be necessary to assume that the nitrogen atom in the amine changes its valence from three to five. For instance, aniline-2,4-dinitrophenol would be represented as follows:[20]



$$C_6H_5NH_2 + HOC_6H_3(NO_2)_2 \longrightarrow C_6H_5\overset{H\quad OC_6H_3(NO_2)_2}{\overset{\diagdown\,\diagup}{N}}H_2$$

Werner, who introduced subsidiary valence in his well-known theory of valence, has applied this idea to molecular organic compounds.[21] After assuming that color change is analogous to molecular-compound formation he concluded from a series of experiments (1) that hydrogen in the nucleus or in an hydroxyl group attached to the nucleus is not responsible for the participation of polynitro compounds in molecular-compound formation; (2) that the aromatic nucleus is not necessary; and (3) that the combination between the hydrocarbons and polynitro compounds is due to the saturation of the subsidiary valence between the unsaturated carbon atoms and the nitro groups. In the case of hydrocarbons and nitro compounds his representation would be as follows: $R.NO_2 —— C_nH_m$.

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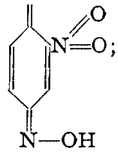
[18] The hydrogen-ion concentration of these compounds is not available. One would expect them to lie in the following order going from the compound with highest hydrogen-ion concentration to that with the lowest: 2,4-dinitrophenol, *m*-dinitrobenzene, 2,4-dinitrotoluene.

[19] Giua and Marcellino [*Gazz. chim. ital.*, **50,** *i*341 (1920)] obtained by the freezing-point method a molecular compound of β-naphthol and 2,4-dinitrotoluene melting at 76.6°.

[20] In the case of *m*-dinitrobenzene and 2,4-dinitrotoluene it is necessary to assume a rearrangement into a quinonoid form such as ; possibly 2,4-dinitrophenol rearranges in a similar manner.

[21] Werner, *Ber.*, **42,** 4324 (1909).

Pfeiffer[22] has extended Werner's ideas. He argued that combination takes place probably in a similar fashion in all cases of molecular-compound formation. Phenols and amines with nitro compounds would therefore be represented as $R.NO_2$——$C_6H_5OH$, and $R.NO_2$——$C_6H_5NH_2$. The fact that deeper colors are obtained in the case of the phenol and amine compounds is used as evidence that the hydroxyl and amine groups are present in the free state. Our results in Tables I, II and III show this variation in color very strikingly.

Thus Kendall's ideas based on principal valence offer a satisfactory explanation for phenol and amine compounds but not for the hydrocarbon compounds. The Werner-Pfeiffer ideas based on subsidiary valence offer an explanation for all molecular combinations. Neither view, however, lends itself satisfactorily to the explanation of the structure of molecular compounds in other than equimolecular ratios.

## Summary

New molecular organic compounds of *m*-dinitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrophenol have been isolated.

A hydrate of a molecular organic compound has been isolated.

The structure of these compounds has been discussed.

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# THE COMPOSITION OF MESQUITE GUM; THE ISOLATION OF *d*-GALACTOSE AND *l*-ARABINOSE

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In two previous publications[1] the authors have described the occurrence, physical properties and partial analysis of mesquite gum as well as the preparation of *l*-arabinose from it. The present contribution deals with further studies as a result of which it is now possible to calculate the approximate composition of the gum.

**The Composition of Mesquite Gum.**—A. W. van der Haar[2] has described the general procedure for determining the composition of plant gums and closely related substances. His monograph has been used freely in the present investigation.

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[22] Pfeiffer, *Ann.*, **412,** 253 (1917); *Z. anorg. Chem.*, **112,** 81 (1920); *Z. angew. Chem.*, **34,** 350 (1921).

[1] Anderson and Sands, (a) Some Plant Gums of the Southwestern U. S., *Am. J. Pharm.*, **97,** 589 (1925); (b) The Preparation of *l*-Arabinose from Mesquite Gum, *Ind. Eng. Chem.*, **17,** 1257 (1925).

[2] van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydesäuren," Gebrüder Borntraeger, Berlin, **1920.**