[Contribution from the Chemical Laboratory of The University of Tennessee]

A STUDY OF MOLECULAR ORGANIC COMPOUNDS. II. THE MOLECULAR ORGANIC COMPOUNDS OF 2,4-DINITROANILINE, 2,4-DINITROCHLOROBENZENE AND 2,4-DINITROBROMOBENZENE[1]

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This paper is a continuation of the study[2] of the molecular organic compounds of *m*-dinitrobenzene and some monosubstituted *m*-dinitrobenzenes. In the present investigation the effect upon molecular compound formation of introducing amino, chloro and bromo groups into *m*-dinitrobenzene has been determined. Quite a few compounds were isolated, some of their properties were determined, and the substitution compounds, into which some were easily converted, were identified.

Experimental Part

The molecular compounds were prepared for the most part as described previously. In a few cases it was not possible to purify by recrystallization due to decomposition. In two cases—the naphthols with 2,4-dinitrobromobenzene—carbon tetrachloride was found to be the best solvent for purification by crystallization. Substitution compounds were frequently obtained with the dinitrohalogenobenzenes. These were easily recognized by their color, solubility and melting points.

Table I

Molecular Compounds of 2,4-Dinitrochlorobenzene

				From literature		
Second component	M. p., °C. (corr.)	Color	Mol. ratio	M. p., °C.	Mol. ratio	Method of prepn.
α-Naphthylamine	72.0	Blood-red	1:1	69[a]	1:1	Soln.
				71.5	1:1[b]	F. p.
β-Naphthylamine	65.3	Garnet-red	1:1	65[a]	1:1	Soln.
Benzidine	68.8	Black	1:1[c]	......	..	...
Pyridine	189.6[d]	White	1:1	170–210[e]	1:1[e,1,2,3]	Soln.
Naphthalene	76.8	White	1:1	78[f]	1:1	Soln.
Fluorene	39[g]	Straw yellow	1:1	......	...	...
Diphenyl	31[g]	White	1:1	......	...	...
α-Naphthol	104.9	Deep yellow	1:1	......	...	...
β-Naphthol	91.2	Deep yellow	1:1	......	...	...

[a] Buguet, *Compt. rend.*, **151,** 312 (1910).

[b] Giua, Marcellino and Curti, *Gazz. chim. ital.*, **50**, II, 300 (1920).

[c] It was not possible to obtain this compound in a quantity sufficient for an analysis. A few black crystals separated out with the bright red substitution compound, 2,4-dinitrophenylbenzidine. Since the latter is likely formed through the molecular com-

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[1] This paper is an abstract of the Master's Theses presented by Alan Hisey and Jesse H. Wood at the University of Tennessee.

[2] Buehler and Heap, This Journal, **48,** 3168 (1926).

pound as an intermediate, it has been assumed that the former has a molecular ratio of 1:1.

[d] The melting point of this compound was not definite, due to decomposition.

[e] (1) The melting point of this compound was reported variously in the literature. Reitzenstein, *J. prakt. Chem.*, **68**, II, 251 (1903), gave it as 201°; Gail in a Marburger Institute dissertation gave it as 210° according to Reitzenstein. (2) Zincke, *Ann.*, **333**, 296 (1904), stated that the compound decomposed into its constituents at 200°. (3) Desvergnes, *Mon. sci.*, **15**, 73 (1925), reported a melting point of 170°.

[f] Willgerodt, *Ber.*, **11**, 601 (1878).

[g] This melting point was an approximation. It could not be determined accurately by the ordinary method since the value is so near room temperature.

TABLE II

MOLECULAR COMPOUNDS OF 2,4-DINITROBROMOBENZENE

Second component	M. p., °C. (corr.)	Color	Mol. ratio	From literature M. p., °C.	From literature Mol. ratio	Method of prepn.
α-Naphthylamine	64.5	Blood-red	1:1	......	...	...
β-Naphthylamine	61.7	Blood-red	1:1	......	...	...
Pyridine	214[a]	Yellow	1:1	225 (dec.)[b]	1:1	Soln.
Naphthalene	72.0	Straw yellow	1:1	......	...	...
α-Naphthol	97.9	Deep yellow	1:1	......	...	...
β-Naphthol	83.0	Orange yellow	1:1	......	...	...

[a] The melting point of this compound was not definite, due to decomposition.

[b] Zincke, *Ann.*, **333**, 296 (1904).

TABLE III

ANALYSES OF NEW MOLECULAR COMPOUNDS

( )-2,4-Dinitrochlorobenzene	Formula	Calcd., %		Found, %	
Fluorene-	$C_{13}H_{10}\cdot C_6H_3(NO_2)_2Cl$	Cl	9.63	9.55	9.43
Diphenyl-	$C_6H_5C_6H_5\cdot C_6H_3(NO_2)_2Cl$	Cl	9.95	9.64	9.53
α-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Cl$	Cl	10.23	10.30	10.32
β-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Cl$	Cl	10.23	10.30	10.35
( )-2,4-Dinitrobromobenzene					
α-Naphthylamine-	$C_{10}H_7NH_2\cdot C_6H_3(NO_2)_2Br$	Br	20.48	20.26	20.39
β-Naphthylamine-	$C_{10}H_7NH_2\cdot C_6H_3(NO_2)_2Br$	Br	20.48	20.21	20.16
Naphthalene-	$C_{10}H_8\cdot C_6H_3(NO_2)_2Br$	Br	21.31	21.26	21.40
α-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Br$	Br	20.44	20.59	20.67
β-Naphthol-	$C_{10}H_7OH\cdot C_6H_3(NO_2)_2Br$	Br	20.44	20.56	20.41

The analyses for halogens were carried out by Pringsheim's method.[3] The amount of silver halide was determined in some cases gravimetrically and in others volumetrically. The melting points were taken by Mulliken's[4] capillary tube method with a thermometer calibrated by the Bureau of Standards.

No molecular compounds of 2,4-dinitro-aniline were isolated.

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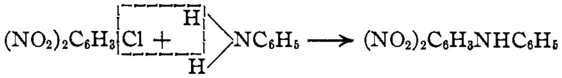
[3] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, **1927**, 4th ed., Vol. I, p. 147.

[4] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Vol. I, p. 218.

Substitution Compounds of 2,4-Dinitrochloro- and 2,4-Dinitrobromobenzenes.—Second components containing amino groups did not readily form molecular compounds with the 2,4-dinitrohalogenobenzenes. Instead, substitution compounds were usually formed with the elimination of the hydrogen halide according to the scheme



$$(NO_2)_2C_6H_3\boxed{Cl + \begin{matrix}H\\ \end{matrix}}\begin{matrix}\\ H\end{matrix}\!\!>NC_6H_5 \longrightarrow (NO_2)_2C_6H_3NHC_6H_5$$

Aniline,[5] methylaniline,[6] diethylamine,[7] *p*-toluidine,[8,5] *o*-toluidine,[5] *p*-aminophenol,[9] *o*-,[10] *m*-[6] and *p*-phenylenediamines[11] reacted in this manner. Dimethylaniline reacted with the elimination of the methyl halide to form a substitution compound identical with that formed with methylaniline.[12] Benzidine[5,8] gave a few crystals of the molecular compound with the chloro compound, but substituted completely with the bromo compound. The α- and β-naphthylamines[13] formed fairly pure molecular compounds but these were readily converted into the corresponding substitution compounds by simply refluxing them for several hours in alcoholic solution. Of the two, the α-molecular compound was the more resistant to decomposition.

Discussion

Molecular Compounds are Intermediates in the Formation of Substitution Compounds.—The idea that reactions between organic compounds are due to an attraction between molecules resulting in an initial combination is not new.[14] Cases similar to those mentioned in this investigation are those of the addition compounds of picryl chloride with the α- and β-naphthylamines,[15] which readily lost hydrochloric acid to

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[5] Reitzenstein, Table I, Ref. *e*1.

[6] Leyman, *Ber.*, **15**, 1233 (1882).

[7] Romburgh, *Rec. trav. chim.*, **2**, 40 (1883).

[8] Willgerodt, *Ber.*, **9**, 977 (1876).

[9] Nietzki, *ibid.*, **28**, 2973 (1895).

[10] Borsche and Rantscheff, *Ann.*, **379**, 169 (1911).

[11] Nietzki and Ernst, *Ber.*, **23**, 1852 (1890), gave the melting point of 2,4-dinitrophenyl-*p*-phenylenediamine as 177°; Morgan and Micklethwait, *J. Chem. Soc.*, **93**, 610 (1908), stated that the compound melted at 190°. Our result (177.8°) obtained repeatedly agreed more closely with the former. In addition the monoacetyl derivative, melting at 238°, checked the former's value.

[12] Leyman, Ref. 6, made this observation previously in the case of 2,4-dinitrochlorobenzene.

[13] Heim, *Ber.*, **21**, 589, 2302 (1888).

[14] Kekulé, "Organische Chemie," Ferdinand Enke, Stuttgart, **1867**, Vol. II, p. 730; Guye, *J. chim. phys.*, **8**, 119, 189 (1910); Schmidlin and Lang, *Ber.*, **43**, 2808 (1910); Giua, Marcellino and Curti, Table I, Ref. *b*.

[15] Sudborough and Picton, *J. Chem. Soc.*, **89**, 583 (1906).

form the corresponding substitution products. Amines were particularly susceptible to molecular compound formation, but in most cases in this investigation substitution compounds were obtained. The α- and β-naphthylamines and benzidine were the sole amines which formed molecular compounds capable of being isolated. Since these were disrupted by moderate heat treatment in alcoholic solution, it seems reasonable to assume that molecular compounds were formed as intermediates in all cases of substitution.

Influence of the Substituent in a Dinitrobenzene on the Formation of Molecular Compounds.—Of the six dinitrobenzenes studied[16] each formed a different number of molecular compounds, a fact which shows that the substituent is an influencing factor. The groups arranged in the order of decreasing ability toward molecular compound formation are: $Cl > Br$[17] $> OH > H > CH_3 > NH_2$. This order is the same as the electronegative character of these groups.[18]

Kendall[19] stated, from the results of a series of experiments, that addition compounds will be formed between two components if there is sufficient difference in acidic strength. Increasing the electronegative character of any substituent in a benzene ring should increase the acidic strength of the compound and, therefore, increase the number of possible molecular compounds. The results of this investigation with the amine molecular compounds bear out this relation. In the case of the hydrocarbon and phenol molecular compounds the number obtained was so small that no conclusions can be drawn in regard to this relation.

The Structure of Molecular Organic Compounds.—The electronic conception of valency as introduced by Lewis[20] has been very helpful in that it does account for the differences between inorganic (polar) and organic (non-polar) compounds. Quite recently Sidgwick[21] has applied it to the Werner complexes, solvation and various other chemical phenomena. His success in this work has raised the question: Can molecular compound formation be explained using the electronic interpretation of valency?

Bennett and Willis[22] have proposed formulas for the compounds formed between nitro compounds and amines and hydrocarbons. These investigators assumed that the union takes place by means of co-valent linkages

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[16] Three were reported previously, Buehler and Heap. Ref. 2.

[17] Chlorine and bromine have been placed before the hydroxyl group since it has been assumed that the great number of substitution compounds of the former two implies the previous existence of molecular compounds.

[18] Crocker, *ibid.*, **44**, 1618 (1922).

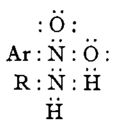
[19] Kendall, *ibid.*, **36**, 1722 (1914).

[20] Lewis, THIS JOURNAL, **38**, 762 (1916).

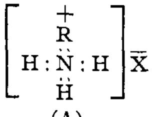
[21] Sidgwick, "The Electronic Theory of Valency," Oxford University Press.

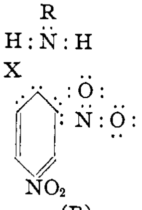
[22] Bennett and Willis, *J. Chem. Soc.*, 256 (1929).

and that the nitro group is the point of attachment[23] in the nitro compound. Their representation of an amine nitro compound would be as indicated. Here the amine is the donor and the nitro compound the acceptor.


$$\begin{array}{c} :\ddot{O}: \\ Ar:\ddot{N}:\ddot{O}: \\ R:\ddot{N}:H \\ \ddot{H} \end{array}$$

There is considerable evidence supporting this coördinate co-valent type of union in molecular compounds. In the first place mention may be made of the low melting points[24] of these compounds—all of them melted lower than the higher-melting component with the exception of the α-naphthol molecular compound. Again, the fact that the great majority of these consist of two molecules in a one-to-one ratio can best be explained upon the basis of a union of a co-valent type between atoms. The color which some of these show may also be interpreted in terms of this type of combination.[22]


$$\left[\begin{array}{c} + \\ R \\ H:\ddot{N}:H \\ H \end{array}\right]\bar{X}$$
(A)


(B)

Assuming a coördinate co-valent type of union, how can the molecular compounds formed in this investigation be best represented? In the case of the amine molecular compounds, the amine is undoubtedly the donor compound. It reacts with acids to form compounds of the type shown (A).[25] In this investigation the dinitrobenzenes were the acids and as such they may be considered as reacting to form ortho or para quinoid inner salts corresponding to the salts which trinitrobenzene forms with potassium methylate.[26] The highly colored compounds resulting from their union with amines may then be represented as shown in diagram (B),[27] where X = Cl, Br, OH,[28] H or CH_3. In cases where X = Cl or Br, this complex was not stable with the more basic amines due to the fact that the halogen was eliminated with one of the hydrogens of the amino group, with the result that the arylimido group occupied the position (1) alone. With pyridine (when X = Cl) this complex seemed to have only a temporary existence.[29] Here, there were no hydrogen atoms attached to the nitrogen atom of the pyridine ring. For that reason the halogen was not eliminated as the halogen hydride but it ionized, resulting in the formation by rearrangement of the complex salt (C). This repre-

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[23] Brewin and Turner, *J. Chem. Soc.*, 334 (1928).

[24] Sidgwick, "The Electronic Theory of Valency," p. 105.

[25] Lewis, "Valency and the Structure of Atoms and Molecules," p. 87.

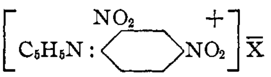
[26] Meisenheimer, *Ann.*, **323**, 205 (1902).

[27] Sudborough and Beard, *J. Chem. Soc.*, **97**, 773 (1910).

[28] The lack of color in some of the amine-2,4-dinitrophenol compounds seems to indicate that the attachment occurs between the lone pair of the amine and the hydrogen atom of the phenolic group. Additional support to this structure is furnished by the numerous amine–phenol compounds that are known.

[29] The compound, at first violet, showed signs of melting below 100°; the red droplets which appeared soon disappeared and the compound turned white and melted as reported above.

sentation explains very well the properties of the pyridine compounds with 2,4-dinitrochloro- and 2,4-dinitrobromobenzenes. They are white or almost so, are soluble in water, have a high melting point and in aqueous solution they precipitate their halide atoms quantitatively with silver nitrate. In other words they are salts and therefore polar compounds.



(C)

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Summary

1. New molecular organic compounds of 2,4-dinitrochlorobenzene and 2,4-dinitrobromobenzene have been isolated; no similar compounds with 2,4-dinitro-aniline could be isolated.

2. It has been shown in some cases that substitution products resulted through the intermediate formation of molecular compounds.

3. The influence of the substituent in the dinitrobenzenes upon molecular compound formation is discussed.

4. An electronic formula is proposed for the amine molecular compounds.

KNOXVILLE, TENNESSEE

[THE RESULTS PRESENTED IN THIS PAPER WERE OBTAINED PRIVATELY IN THE ORGANIC LABORATORY, BUREAU OF SCIENCE, MANILA, PHILIPPINE ISLANDS]

PHENOLIC DECOMPOSITION OF CERTAIN MIXED ETHERS. THE VELOCITY CONSTANT

BY D. M. BIROSEL[1]

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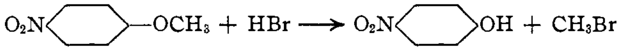
Introduction

It is well known that mixed ethers, *e. g.*, *p*-nitrophenyl methyl ether will give the corresponding phenol as one of the products of reaction according to the scheme



when they are acted upon by hydrogen bromide. Graebe and Martz[2] and also Raiford and Colbert[3] digested certain mixed ethers with 48% hydrobromic acid alone on the steam-bath for two hours and obtained varying degrees of decomposition depending upon the kind and number of substituents actually present in the phenyl residue. Stoermer[4] carried out

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[1] Formerly Research Chemist of the Laboratory Products Company, Cleveland, Ohio.

[2] Graebe and Martz, *Ann.*, **340**, 220 (1905).

[3] Raiford and Colbert, THIS JOURNAL, **48**, 1776 (1926).

[4] Stoermer, *Ber.*, **41**, 321 (1908).