

another element than the distortion or displacement to which Dr. Chapman very properly refers, namely, the position in which the brain is held or placed. In Dr. Chapman's figures, the organ rests upon the medulla, and upon the ventral aspects of the frontal and temporal lobes; were it brought into something approximate to its natural position, or to the position of the human brain, the occipital lobes would surely project beyond the cerebellum to an appreciable extent. It would be well if the next Orang's head should be sawn into sections parallel with the mesial plane, and the brain figured *in situ*.

It is gratifying to find Dr. Chapman, like Humphrey and Barnard, insisting that the "scansorius" muscle of Traill is really the entoglutæus. But Dr. Chapman does not seem to have observed the curious little muscle passing over the capsule of the acetabulum which Prof. Barnard has called "ilio-femoralis subrectus," and which, in the opossum, Coues seems to have mistaken for the unlucky "scansorius."

A novel and significant suggestion is that, "morphologically speaking, the laryngeal pouch of the anthropoids would be homologous with and replace the two layers of the cervical fascia in man."

This otherwise very commendable paper is marred by some important misspellings, as of *ilium* which is made *ileum* twice on page 4, and by an occasional obscurity of style which sometimes renders the author's meaning doubtful.

B. G. W.

ON THE CONSTITUTION OF THE NAPHTHALINES AND THEIR DERIVATIVES.

(Translated from the German.)

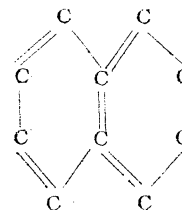
BY M. BENJAMIN, PH. B., AND T. TONNELÉ, PH. B.*

Among the many aromatic hydrocarbons, naphthalene is one of the most interesting. The causes and laws of isomerism may be studied from the numerous isomeric compounds on one hand, while on the other, much information is derived from the consideration that many of these have acquired a great importance in the technical arts. In consequence of this, a great number of memoirs exist on this subject, and they are scattered abroad among the numerous scientific journals. It is, therefore, no simple matter for one to obtain a clear survey of the naphthalene question. We hope that the following pages, comprising material originally collected for our own information, will be welcomed by such of our professional colleagues as may have occasion to study this subject, for we feel assured that by consulting this article much of their time and labor will be economized.

CONSTITUTION OF NAPHTHALINE.

Naphthalene was discovered in 1826, by Garden, and subsequently widely studied by many investigators; yet its constitution remained undetermined for more than forty years. In the year 1866, Kékulé¹ published his ingenious and fertile theory of the aromatic compounds, considering them as derivatives from a single hydrocarbon, benzol. Soon after Erlenmeyer² so extended this

theory as to include naphthalene, which he considered as having been derived from two benzol rings possessing two carbon atoms in common.



Graebe³ was the first to demonstrate the correctness of this theory, in the course of his remarkable researches on the chinones of benzol and naphthalene. Since then this theory has been sustained by a large number of facts, while no satisfactory objections have been brought forward against it.

Other formulæ have been proposed by Berthelot⁴, and later by Ballo⁵, and also by Wreden⁶, but none of these have received the approval of chemists.

The following are the principal facts which support the formula given by Erlenmeyer and Graebe:

I. The bichloronaphthochinon (C_6H_4) ($C_4Cl_2O_2$) yields on oxidation phthalic acid $C_6H_4 \begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$ and it is also transformed by the action of pentachloride of phosphorus into the pentachloride of naphthalene (C_6H_2Cl) (C_4Cl_4) and this on oxidation produces tetrachlorophthalic acid $C_6Cl_4 \begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$.

These facts prove that naphthalene is composed of two symmetrical rings, and that it can only have the formula of Erlenmeyer by the acceptance of Kékulé's benzol scheme.

On the other hand, the ortho- (1, 2) position of phthalic acid is likewise shown which was corroborated by the examination of the benzol bi-derivatives (Graebe).⁷

Ladenburg⁸ and Wreden⁹ have objected to Graebe's method of proof, on account of the derivation of tetrachlorophthalic acid from phthalic being uncertain. It can just as well be obtained from tere or isophthalic acid. This is improbable, because the tetra-chlorophthalic acid used, agrees in all its properties (formation of anhydrides, etc.), with phthalic acid, and not with its two isomers.*

II. Naphthalinetetrachloride (C_6H_4) ($C_4H_4Cl_4$), by oxidation gives phthalic acid $C_6H_4 \begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$ (Laurent). On submitting it to dry distillation it becomes converted into the α and β dichloronaphthalene (C_6H_4) ($C_4H_2Cl_2$) and the latter (β) produces, on oxidation, dichlorophthalic acid $C_6H_2Cl_2 \begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$ (Atterberg).¹⁰

III. Monochloronaphthalinetetrachloride C_6H_4 ($C_4H_2Cl_4$) may be converted into ordinary phthalic acid by oxidation. (P. and E. Depouilly¹¹ and Widman¹².) Monochloronaphthalene, C_6H_4 (C_4H_3Cl) which is the basis of the above compounds may be converted into

* Das Naphtal'n und seine Derivate. Braunschweig (1870).

¹ Deutsche Chem. Ges., IX, 593 (1876.)

² Ann. Chem. Pharm., CXLIX, 1 (1869.)

³ Theorie der aromatischen Verbindungen Braunschweig. 1876, p. 36.

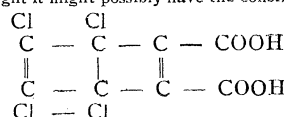
⁴ Deutsche Chem. Ges., IX, 547 (1877).

⁵ Deutsche Chem. Ges., IX, 547, (1877).

⁶ Soc. Chim., Paris, IV, 10, (1865).

⁷ Om Naphtalins Klorföreningar, Upsala, 1877, p. 16. Soc. Chim. Paris, XXVIII, 505, (1877).

⁸ Wreden thought it might possibly have the constitution,



that is to say, be derived from an isometric hypothetical benzol. This is however, extremely improbable.

* NOTE.—The following memoir, written by MM. F. Reverdin and E. Nütting, was published in Geneva early this year. In addition to the text herewith given, the original pamphlet was supplemented with several valuable tables. These showed the derivation and behavior with reagents of the various substitution products. It is with regret that we are obliged to omit them. The space which they would occupy, together with the fact that they are not of general interest, does not seem to warrant their insertion. The entire article is undoubtedly the best resumé of the different theories concerning the formation of the naphthalenes in existence. (Translators.)

¹ Annalen der Chemie und Pharmacie, vol. CXXXVII, p. 129 (1866).

² Ann. Chem. Pharm., CXXXVII, 346 (1866).

³ Ann. Chem. Pharm., CXLIX, 1 (1869).

⁴ Ann. Chem. Pharm., CXLII, 251 (1867). Comptes Rendus, LXXIII, 788 and 834.

chloronitrophthalic acid $C_6H_2Cl(NO_2)$, $\begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$ (Atterberg).¹⁰

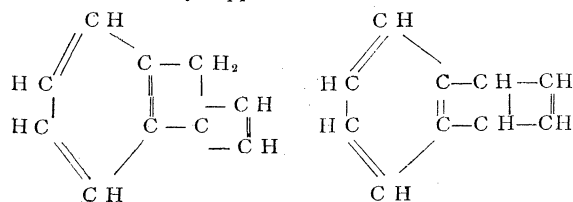
IV. This same monochloronaphthalinetetrachloride yields on saponification with alcoholic potash the α trichloronaphthalene $C_{10}H_4(Cl_3)$ melting at 81° , and this, by oxidation, produces trichloronitrophthalic acid, $C(NO_2)Cl_3$, $\begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$. (Widman.¹³)

V. Mononitronaphthalene $C_{10}H_7(NO_2)$ (C_4H_4) produces, by oxidation with chromic acid, nitrophthalic acid $C_6H_3(NO_2)$, $\begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$ melting at 212° , which can also be obtained directly from phthalic acid by the action of nitric acid. (Beilstein and Kurbatow.¹⁴)

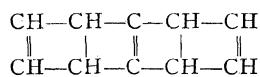
On the other hand, naphthylamine $C_{10}H_7(NH_2)$ (C_4H_4) which corresponds to this nitronaphthalene may be oxidized, by means of permanganate, into ordinary phthalic acid¹⁵ (Graebe.¹⁶) C_6H_4 , $\begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$.

Binitronaphthol $C_{10}H_6(OH)(NO_2)_2$ (C_4H_4), produced from naphthylamine, also yields, by oxidation, phthalic acid. (Liebermann and Dittler.¹⁷)

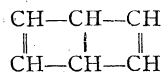
This last proof is indisputable, as it shows conclusively that no matter which half of the naphthalene ring is oxidised the same phthalic acid results. Naphthalene must therefore possess an absolutely symmetrical structure, and hence the following formulæ, proposed by Wreden, lose every support.



Berthelot,¹⁸ and latter Ballo,¹⁹ deduced from the formation of naphthalene from benzol or styrol and aethylene the formulæ:



The above formula explains very clearly, the corresponding syntheses and is also symmetrical but it cannot be accepted because it would give the following formula for benzol:



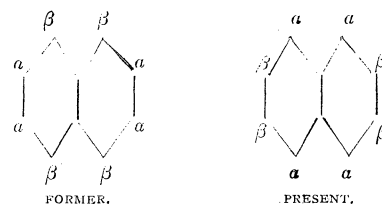
in which the six hydrogen atoms have not all the same value. The univalence of the same is positively shown from the examination of Ladenburg, Hübner and Petermann, Hubner and Wroblewsky.

ISOMERISM OF THE NAPHTHALINE DERIVATIVES.

Faraday²⁰ observed while investigating the sulpho-acids of naphthalene that two isomeric mono derivatives were formed. Since then an entire series of others have been discovered. Almost all of the biderivatives exist in two modifications, and the number of isomers among the higher substitution products is very numerous. The formula now used to represent naphthalene explains this fact in a very satisfactory manner.

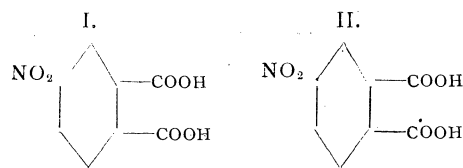
One observes, therefore, that it is not indifferent whether the hydrogen consecutive to the four combining carbon atoms are replaced or whether the four combining positions furthest removed from them, are replaced. On the other hand it is evident that the hydrogen atoms in groups of four possess equal values. In order to distinguish between these two varieties of hydrogen atoms Merz²¹ has designated them by the letters α and β , and distinguishes the isomeric series as the α and β derivatives. He did not, however, state to which of the positions of the hydrogen atoms belonged the α and which the β series.

Wichelhaus,²² soon after, forming a theory on the analogy between the α naphthol with phenol, assumed that the substituting hydrogen atoms were combined with the carbon atoms in both compounds alike (*i.e.* in a similar manner) and hence the α position must correspond to the combining place furthest removed from the carbon atoms. Especially as they are more like the benzol carbon atoms. Subsequently when it was shown that naphthachinon was an α - α derivative (Liebermann and Dittler²³) and the para (1, 4) position of ordinary chinon was definitely settled, the notation was changed.



This demonstration is untenable however, for Stenhouse and Groves,²⁴ have discovered a second naphthachinon, viz.: the β , which likewise contains the two atoms of oxygen in the same ring; hence it follows that there are chinons which do not have their oxygen atoms in the paraposition (1, 4). Consequently the constitution of ordinary naphthachinones, as well as the position of the α and β atoms again becomes doubtful. Fortunately however other experiments, made under different conditions, permit the final answering of this question.

We have seen how Beilstein and Kurbatow²⁵, by the oxidation of nitronaphthalene, which is an α derivative, have obtained ordinary nitrophthalic acid, melting at 212° . Theoretically, there are but two isomeric nitrophthalic acids possible, both of which have been prepared.



The first melts at 212° ; the other, discovered by O. Miller, melts at 165° .

The latter, according to the exact researches of this investigator, corresponds to the oxyphthalic acid of Baeyer. On the other hand, Schall,²⁷ in the course of his researches on the hydroxylated benzoldicarboxylic acids, demonstrat-

¹³ Loc. Cit., p. 59. Soc. Chim., Paris, XXVIII, 505, (1877).

¹⁴ Deutsche Chem. Ges. XII, 688, (1879).

¹⁵ Naphthylamine gives, with potassium chromate and sulphuric acid, phthalic acid and naphthachinon, (R. & N.)

¹⁶ Private papers.

¹⁷ Ann. Chem., CLXXXIII, 228, (1876).

¹⁸ Ann. Chem. Pharm. CXLI, 251 (1867.) Comptes Rendus LXIII,

788 and 834.

¹⁹ Das Naptalin und seine Derivate.

²⁰ Ann. Chim. Phys. XXXIV, 164.

²¹ Zeitschrift für Chemie, NF. IV, 399 (1868).

²² Ann. Chem. Pharm. CLII, 311 (1869).

²³ Ann. Chem. CLXXXIII, 228 (1876).

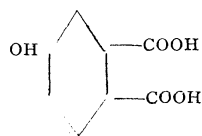
²⁴ Ann. Chem. Pharm. CLXXXIX, 145 (1877.)

²⁵ Deutsche Chem. Ges. XII, 688 (1879).

²⁶ Deutsche Chem. Ges. XI, 1191 (1878).

²⁷ Deutsche Chem. Ges. XII, 816 (1879.)

ed that the corresponding oxyphthalic acid has the following constitution.



Nitrophthalic acid, melting at 165° , has the second (II) formula, while the one melting at 212° , has the first (I) formula. As stated above, these are both produced from nitronaphthalene, which is itself an α compound, and so it is demonstrated that the α position is the one next to the two common carbon atoms. The hydrogen atoms in naphthalene are combined in groups of four, each of which is equivalent; this follows naturally from the observed facts in benzols.

Atterberg, in his masterly researches on the chlorinated naphthalenes, found that in naphthalene, the four α positions are of equal value without any reference to the benzol formula. According to de Koninck, Marquardt and Atterberg, nitronaphthalene may be converted into α monochloronaphthalene. Therefore, in these compounds, the nitro and chloro groups hold the same position. The monochloronaphthalene may, however, be converted into a nitro compound and that into a β dichloronaphthalene. Nitronaphthalene may be converted into two different dinitronaphthalenes, and those into two different dichloronaphthalenes γ and δ . Hence all three dichloronaphthalenes β , γ , δ , contain a chlorine atom in the position of the nitro group of the nitronaphthalenes. The three remaining chlorine atoms of the three compounds must take different positions with reference to the first, since otherwise the three compounds could not be different. All of the chlorine atoms of these compounds possess an α position, consequently the naphthalene molecule must possess four α positions of equal value.

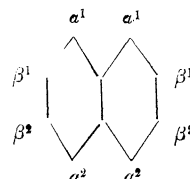
DETERMINATION OF THE CONSTITUTION OF THE NAPHTHALINE DERIVATIVES.

The constitution of naphthalene derivatives is ascertained by converting them by a simple reaction into another of known position. The nitro derivatives may, for instance, be converted into the chlorine or bromine derivatives by the chloride or bromide of phosphorus, and then by reduction into the amido derivatives. These latter may, by means of their diazo-compounds, be converted into phenols, chlorine, bromine (and perhaps iodine) derivatives, and by means of formic acid into nitriles, and consequently into carbon acids. The bromine derivatives produce, with ethyl and methyl iodide, ethyl and methyl compounds, and with chlorocarbonic acid ether carbon acids are produced. The sulpho-acids give with potassium cyanide, cyanates. With penta chloride and bromide of phosphorus, chlorine and bromine derivatives are obtained with sodium formate, carbon acids; and with sodium at a high temperature phenols are formed. On the other hand the oxidation often shows whether the substituting groups are in the same ring, or are divided among both; in the first case phthalic acid is formed, and in the second substitution products of phthalic acid are formed.

CONSTITUTION OF THE NAPHTHALINE DERIVATIVES.

The mono substitution products exist in but two modifications, and it is easy, therefore, to determine their constitution. When in the bisubstitution products, the two substituting groups are equal, ten different isomeric compounds are obtained. If, however, they are unequal, the number is increased to fourteen. The constitution of a given number of the same is exactly known, while with others it is only known that the substituting groups are contained in the same or in two different rings, that they possess an α or a β position, or a similar position.

In the case of the higher substituted naphthalene derivatives, the number of possible isomers is considerably increased, especially when the groups are unequal. When, however, the groups are equal, fourteen tri-derivatives, twenty-two tetra-derivatives, fourteen penta-derivatives, ten hexa, two hepta, and a single octo-derivative, in which all the hydrogen has been replaced, are obtained. There are, for example, seventy-five possible chlorine naphthalenes; of these, however, only twenty-four have been prepared. In order to simplify the nomenclature of these numerous compounds, we will distinguish the two from each other by designating the same position in each ring, as α^1 , α^2 , β^1 , and β^2 .



When a compound contains both of its substituting groups in the same ring, we will combine the latter after Jolin's method, that is, by a simple line, as for example, $\alpha^1-\beta^1$, $\alpha^1-\beta^2$, $\alpha^1-\alpha^2$, etc. When, however, the groups are divided between the two rings, then they are combined by double lines, thus: $\alpha^1=\alpha^1$, $\alpha^1=\beta^1$, $\alpha^1=\beta^2$, etc. The same method of lettering may be used in the higher substituted compounds; thus the compounds $\alpha^1-\beta^1-\alpha^2$, $\alpha^1-\beta^2-\alpha^2$, $\alpha^1-\beta^1-\beta^2-\alpha^2$, have their groups in the same ring. The compounds $\alpha^1-\alpha^2=\alpha^1$, $\alpha^1-\alpha^2=\beta^1$, $\alpha^1=\alpha^1-\alpha^2$, $\alpha^1-\alpha^2=\alpha^1-\beta^1$, have their groups divided between the two rings. We have placed together, in a series of tables, the most important derivatives of naphthalene. In these tables will be found their constitution as far as it is known; some characteristic properties, as their melting point, boiling point, their formation, conversion, and, as complete as possible, a list of the literature.

It is to be hoped that the many vacancies which appear among these tables may soon be filled.

Last of all we would observe that the terms α , β , γ , δ , etc., which we have chosen to represent the naphthalene derivatives have no connection with their constitution with the single exception of the mono derivative. They have been given to the different isomers only in chronological order, and they do not correspond by any means as far as position is concerned to the different α , β , etc., derivatives. This fact is unfortunate, because it may cause confusion. We believe, however, that at present no change should be made in names originally chosen by the discoverers. When the constitution of the naphthalene derivatives is better known, a rational nomenclature according to the above principles will naturally be adopted. Thus for instance the present β , γ and δ dichloronaphthalenes will be designated as $\alpha^1-\alpha^2$, $\alpha^1=\alpha^2$ and $\alpha^1=\alpha^1$ dichloronaphthalene, the α and δ trichloronaphthalene as $\alpha^1-\beta^1-\beta^2$ and $\alpha^1-\alpha^2=\alpha^1$, trichloronaphthalene, the α and β chlorodinitronaphthalenes as $\alpha^1-\alpha^2=\alpha^1$ and $\alpha^1-\alpha^2=\alpha^2$ chlorodinitronaphthalenes, and in a similar manner for all other compounds by which their constitution will be immediately recognized.

NATIONAL ACADEMY OF SCIENCES.

The abstracts of the papers read before the recent meeting at New York were, in all cases, either corrected or rewritten by the authors, and we are under obligation to Professors James Hall, Wolcott Gibbs, E. D. Cope, S. P. Langley, Henry Morton, Elias Loomis, B. Silliman, O. N. Rood, T. Sterry Hunt, Henry Draper, for their assistance in presenting correct reports.

The addresses of Professor Alexander Agassiz and Lieut. Shawatka were delivered *viva voce*, and we made use of the stenographic notes made for the New York