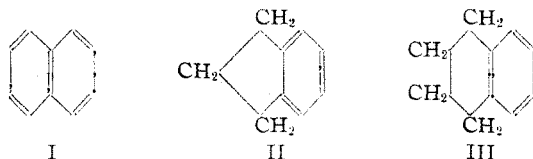


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

## The Structure of Some Naphthalene, Hydrindene and Tetralin Derivatives

BY R. B. SANDIN AND T. H. EVANS<sup>1</sup>

The problem which has to do with the fixation or the non-fixation of the Kekulé ring in such compounds as naphthalene has been attacked from numerous and different viewpoints.<sup>2</sup> There is much chemical evidence in favor of the idea that the double bonds of naphthalene are not free to migrate and that the Erlenmeyer formula (I) is



to be preferred.<sup>3</sup> The investigations of Fieser and Lothrop,<sup>4</sup> and Baker and Carruthers,<sup>5</sup> provide evidence of this kind. Also recently McLeish and Campbell,<sup>6</sup> working from the standpoint of the reactivity of the halogens in halogenated nitronaphthalene compounds, provide additional evidence in favor of the Erlenmeyer formula. Using Fuson's<sup>7</sup> theory of vinylogy, they have shown that the reactivity of the bromine atom in aromatic bromonitro compounds can be used to detect the presence and position of double bonds in bromonitro derivatives of naphthalene. They have also extended their work to derivatives of hydrindene and tetralin.

The authors of this paper call attention to another reaction which might prove of value in detecting ring stabilization and which, as far as the authors are aware, has never been used specifically for this purpose. The reaction involved is one studied by Nicolet<sup>8</sup> and co-workers. They showed that certain compounds containing bromine or iodine in the benzene ring could undergo hydrolysis in such a way that the halogen was re-

placed by hydrogen, the solution acquiring oxidizing properties as evidenced by the liberation of free halogen or by the formation of more highly halogenated derivatives. The halogen which reacted in this manner was always ortho or para to an amino or hydroxyl group. In studying the removal of such halogens it was found by Nicolet to be more convenient to perform the hydrolysis in the presence of stannous chloride in order to obviate effects due to resubstitution and oxidation. The important point in connection with the present work is that an arrangement in an aromatic compound of a bromine atom and an amino group in such a way that they are separated by a double bond or a conjugated system of double bonds, gives rise to a so-called "positive" bromine atom. This type of structure might also be added to the list of examples given by Fuson in his theory of vinylogy. A number of aminobromo derivatives of naphthalene have therefore been prepared and their behaviors examined with respect to an acid solution of stannous chloride at the boiling point. This work likewise has been extended to similar derivatives of hydrindene and tetralin. The measurements make no claim to accuracy, but are sufficient to show the relative reactivities of the bromine atom in the compounds examined. The results are found in Table I. The experimental details are given later in this paper.

Franzen and Stauble<sup>9</sup> have done considerable work on the effect of tin and hydrochloric acid and of an acid stannous chloride solution on brominated  $\beta$ -naphthols and  $\beta$ -naphthylamines. Their results are recorded in Table II.

If the Erlenmeyer formula for naphthalene is correct, the first three compounds in Table I should contain reactive bromines, whereas the bromine in 3-bromo-2-naphthylamine should be non-reactive. Also in 1,3-dibromo-2-naphthylamine the 1-bromo atom should be reactive, whereas the 3-bromo atom should be non-reactive. However, if there is no bond fixation, then the bromine in 3-bromo-2-naphthylamine should give rise to oxidizing properties and in the same way both bromines in compound (IV) should be substituted by hy-

(1) Present address: 2063 Stanley Street, Montreal, Quebec.  
 (2) See excellent discussion of this topic, by Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 70.  
 (3) On the other hand, all of the physical evidence points to the existence of valence isomers which contain a double bond at C-3. Arnold and Sprung, *THIS JOURNAL*, **60**, 1163 (1938); Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933), etc.  
 (4) (a) Fieser and Lothrop, *THIS JOURNAL*, **57**, 1459 (1935); (b) **58**, 2050 (1936).  
 (5) Baker and Carruthers, *J. Chem. Soc.*, 479 (1937).  
 (6) McLeish and Campbell, *ibid.*, 1103 (1937).  
 (7) Fuson, *Chem. Rev.*, **16**, 1 (1935).  
 (8) (a) Nicolet, *THIS JOURNAL*, **48**, 2081 (1921); (b) Nicolet and Sampey, *ibid.*, **49**, 1796 (1927); (c) Nicolet and Ray, *ibid.*, **49**, 1801 (1927); (d) Nicolet and Sandin, *ibid.*, **49**, 1806 (1927); (e) Nicolet, *ibid.*, **49**, 1801 (1927).

(9) (a) Franzen and Stauble, *J. prakt. Chem.*, **101**, 58 (1920); (b) **108**, 352 (1922).

TABLE I  
 REACTION WITH HYDROCHLORIC ACID AND STANNOUS CHLORIDE

	Substance used	Time of hydrolysis, hours	Products recovered and % halogen removed
I	1-Bromo-2-naphthylamine	1.0	90% of $\beta$ -naphthylamine >90% of bromine removed
II	4-Bromo-1-naphthylamine	1.0	90% of $\alpha$ -naphthylamine >90% of bromine removed
III	2,4-Dibromo-1-naphthylamine	1.0	90% of $\alpha$ -naphthylamine >90% of bromine removed
IV	1,3-Dibromo-2-naphthylamine	1.0	95% of 3-bromo-2-naphthylamine >95% of 1-bromo atom removed
V	3-Bromo-2-naphthylamine	10.0	Quantitative recovery of 3-bromo-2-naphthylamine
VI	4,6-Dibromo-5-aminohydrindene	0.5	80% of 4-bromo-5-aminohydrindene, m. p. 54-55° 80% removal of 6-bromo atom
	4,6-Dibromo-5-aminohydrindene	5.0	25% of 4-bromo-5-aminohydrindene, m. p. 54-55°
VII	4-Bromo-5-aminohydrindene	6.0	30% of unaltered material
VIII	5-Bromo-6-aminotetralin	1.0	60% removal of bromine
IX	5-Bromo-6-acetamidotetralin	2.0	85% of 6-aminotetralin, m. p. 34-5°
X	<i>o</i> -Bromoaniline	1.0	56% removal of bromine
	<i>o</i> -Bromoaniline	2.0	75% removal of bromine

TABLE II

Substance used	Conditions of hydrolysis	Result
1,6-Dibromo-2-naphthylamine	Stannous chloride and hydrochloric acid in alcohol; 21 hours	6-Bromo-2-naphthylamine
1,6-Dibromo-2-naphthylamine	Tin and hydrochloric acid	6-Bromo-2-naphthylamine
1,3,6-Tribromo-2-naphthylamine	Tin and hydrochloric acid	3,6-Dibromo-2-naphthylamine
3,6-Dibromo-2-naphthylamine	Tin and hydrochloric acid	Unchanged material
1,6-Dibromo-2-naphthol	Tin and hydrochloric acid	6-Bromo-2-naphthol
1-Nitro-3,6-dibromo-2-naphthol	Stannous chloride and hydrochloric acid	No bromine removed
1,3,6-Tribromo-2-naphthol	Tin and hydrochloric acid	3,6-Dibromo-2-naphthol
1,3,4,6-Tetrabromo-2-naphthol	Tin and hydrochloric acid	3,4,6-Tribromo-2-naphthol
3-Bromo-1-nitro-2-naphthylamine <sup>20</sup>	Tin and hydrochloric acid	3-Bromo-1,2-naphthylenediamine
1,3-Dibromo-2-naphthylamine <sup>20</sup>	Tin and hydrochloric acid; 2 hours	3-Bromo-2-naphthylamine

drogens under the experimental conditions. An examination of Table I definitely points to the Erlenmeyer formula for naphthalene possessing a double bond common to both rings. Attention is called to the high degree of reactivity of the bromine atom in a compound such as 1-bromo-2-naphthylamine and the extraordinary stability of the bromine atom in 3-bromo-2-naphthylamine.

Evidence in favor of the Erlenmeyer formula is also shown from the results presented in Table II. Here again we notice the persistence of the 3-bromo atom such as we have in 1,3,6-tribromo-2-naphthylamine. It might be expected that the 6-bromo atom should have been reactive, as the 6-bromo atom and the amino group are separated by a conjugated system of three double bonds. The fact that this bromine atom shows no reactivity is evidence that the double bond shared by the two rings does not function normally.<sup>6,10</sup>

In connection with the reactivity of the bromine atom in 1-bromo-2-naphthylamine, the proximity of the bromine atom to the adjoining aro-

matic ring may be of some importance. However, this effect is believed by the authors to be negligible. Franzen and Stauble,<sup>9b</sup> for example, have shown that when 1,3,4,6-tetrabromo-2-naphthol is reduced with tin and hydrochloric acid, the 4-bromo atom remains fixed.

Concerning the stability of the bromine atom in a compound such as 3-bromo-2-naphthylamine it is interesting to note that Nicolet<sup>8c</sup> gives as a possible mechanism for the elimination of a "positive" halogen from *o*-aminobenzene derivatives, first of all the formation of a quinoidal intermediate compound, and second a subsequent 1,3-elimination. On the basis of this conception it might be said that 3-bromo-2-naphthylamine is stable because the quinoidal intermediate is not produced. It is a known fact that 2,3-dihydroxynaphthalene does not yield a quinone on oxidation.<sup>11</sup> Evidently the two hydroxyls function independently and not as though they were connected by a double bond.

(11) Marckwald, *Ann.*, **274**, 331 (1893); **279**, 1 (1894); Fries and Schimmelschmidt, *Ber.*, **65**, 1502 (1932); Fieser, *THIS JOURNAL*, **53**, 5219 (1930).

(10) Sampey, *THIS JOURNAL*, **49**, 2849 (1927).

Regarding the structure of hydrindene and tetralin, Mills and Nixon<sup>12</sup> believe that there is bond fixation and give the structure (II) and (III) for these two compounds, respectively. The work of McLeish and Campbell confirms structure (II) for hydrindene derivatives as does also the earlier work of Fieser and Lothrop,<sup>4b</sup> Sidgwick and Springall,<sup>13</sup> and Baker.<sup>14</sup> Although the present work is not conclusive as far as hydrindene is concerned, any inference that might be drawn is in favor of structure (II) being the preferred structure. There is no doubt about the fact that the 6-bromo atom is remarkably reactive. In this respect it is similar to the bromine in 1-bromo-2-naphthylamine. Also the 4-bromo atom has a marked degree of stability although it is not completely unreactive. Similarly, McLeish and Campbell found that the bromine in 4-bromo-5-nitrohydrindene is very slightly reactive. Recently Fieser and Lothrop<sup>2</sup> have found that 5-hydroxy-6-methylhydrindene is capable of forming azo compounds in very weakly alkaline solutions. Also Baker<sup>14</sup> has shown that 5-hydroxy-4-acetylhydrindene is chelated to a certain degree. Finally, it is possible to make 4,6-dibromo-5-aminohydrindene<sup>15</sup> by direct bromination of 5-aminohydrindene. All these facts indicate (as Fieser and Lothrop<sup>2</sup> already have suggested) that the bonds in certain hydrindene derivatives are not fixed so rigidly that the 4-5 and 6-7 bonds cannot, under certain conditions, acquire double bond characteristics. In the authors' work the effect of the alicyclic ring is considered to be negligible, in view of the fact that 2-iodo-4-aminotoluene<sup>3d</sup> shows no evidence of "positive" iodine.

Concerning the structure of tetralin, the present work gives no definite information, since no 7-bromo-6-aminotetralin was available. The present results, however, do show a "positive" bromine in 5-bromo-6-aminotetralin. Contrary to the conclusions that might be drawn from this, McLeish and Campbell<sup>6</sup> found 6-bromo-5-nitrotetralin to be unreactive. Consistent with our results, Schroeter<sup>16</sup> and co-workers have reduced 5-bromo-6-hydroxy-7-nitrotetralin with stannous chloride and obtained a mixture of 5-bromo-6-hydroxy-7-aminotetralin and 6-hydroxy-7-aminotetralin.

For the sake of comparison, a study of the be-

havior of *o*-bromoaniline has been included. It will be noticed that the bromine reactivity in this case (two isomeric Kekulé or resonating forms) lies between the reactivity shown in the case of the bromine in 1-bromo-2-naphthylamine (the bromine and the amino groups separated by a fixed double bond), and the nonreactivity shown in the case of 3-bromo-2-naphthylamine (bromine and amino groups separated by a fixed single bond). Sampey,<sup>10</sup> working on the polarity of the carbon-halogen bond, has pointed out the remarkable reactivity of the halogens in ortho or para position to the hydroxyl group in halogen naphthols when the latter are treated with an acid stannous chloride solution. Under the same conditions, similar halogen phenols show little reactivity. Again, Hodgson and Leigh<sup>17</sup> call attention to the fact that the chlorine atoms in 2-chloro- and 4-chloronitrobenzenes are displaced much less easily by alkali than those in the corresponding chloronitronaphthalenes. Is it not possible that the difference in reactivity is connected with a stabilized structure for the naphthalene compounds?

### Experimental Part

**Preparation of Compounds.**—1-Bromo-2-naphthylamine,<sup>18</sup> m. p. 63°, 4-bromo-1-naphthylamine,<sup>19</sup> m. p. 103°, and 2,4-dibromo-1-naphthylamine,<sup>20</sup> m. p. 118–119°, were prepared readily.

1,3-Dibromo-2-naphthylamine,<sup>21</sup> m. p. 119°, was prepared by the bromination of *p*-toluenesulfone-2-naphthalide, followed by hydrolysis with concentrated sulfuric acid. By the acid stannous chloride reduction of 1,3-dibromo-2-naphthylamine, there was obtained 3-bromo-2-naphthylamine, m. p. 169° (Consden and Kenyon<sup>20</sup> report 173°).

4,6-Dibromo-5-aminohydrindene,<sup>16</sup> m. p. 70–71°, was prepared by the bromination of 5-aminohydrindene.<sup>14</sup>

An 80% yield of pure 4-bromo-5-aminohydrindene, m. p. 54–55°, was obtained by reduction of 4,6-dibromo-5-aminohydrindene with stannous chloride and hydrochloric acid.

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>NBr: Br, 37.6. Found: Br, 37.3.

The time of reduction was thirty minutes. Longer periods gave a lowered yield. McLeish and Campbell<sup>6</sup> report a melting point of 50–51°. However, their compound was about 6% too high in bromine content and probably contained some unchanged dibromo compound.

5-Bromo-6-acetamidotetralin,<sup>12,22</sup> m. p. 126–127°, was prepared by the bromination of 6-acetamidotetralin in

(12) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(13) Sidgwick and Springall, *ibid.*, 1532 (1938).

(14) Baker, *ibid.*, 476 (1937).

(15) Borsche and Bodenstein, *Ber.*, **59**, 1909 (1926).

(16) Schroeter, *Ann.*, **426**, 83 (1922).

(17) Hodgson and Leigh, *J. Chem. Soc.*, 1031 (1938).

(18) Morgan, *J. Chem. Soc.*, **79**, 814 (1900).

(19) Morgan, Micklethwaite and Winfield, *ibid.*, **85**, 736 (1904).

(20) Consden and Kenyon, *ibid.*, 1591 (1935).

(21) Bell, *ibid.*, 2732 (1932).

(22) Smith, *ibid.*, **85**, 730 (1904).

glacial acetic acid. Acid hydrolysis of the preceding compound gave 5-bromo-6-aminotetralin, m. p. 52.5°.

**Determination of Halogen Reactivity.**—The method employed was somewhat similar to the one already used by Nicolet.<sup>8</sup> All the compounds were treated under as nearly the same conditions as possible, the only variable factor being the time. It was essential that the acid concentrations should be the same for all runs, since it is known that the rate of halogen removal is directly proportional to the acid concentration but is independent of the stannous chloride concentration.

In this work 0.02 mole of compound was dissolved in a boiling mixture of 25 cc. of glacial acetic acid and 20 cc. of concentrated hydrochloric acid. To this was added enough stannous chloride to give one mole of stannous chloride per gram atom of halogen in the compound being examined. The solution was then boiled in an all-glass apparatus under reflux for a suitable period of time. On boiling, some hydrogen chloride was lost. However, since all the experiments were carried on as nearly as possible under the same conditions, no attempt was made to avoid this loss. The reaction mixture subsequently was transferred to a beaker, treated with concentrated hydrochloric acid and cooled. The precipitated hydro-

chloric acid salt or stannichloride of the amine was filtered off and treated with sodium hydroxide. The liberated amine was either identified as such or as the acetyl derivative. Its weight was determined and sometimes also its halogen content. The mother liquor from the above amine hydrochloride was treated with sodium hydroxide and any precipitate produced was examined from the standpoint of identity, weight and halogen content.

### Summary

Some brominated derivatives of  $\alpha$ - and  $\beta$ -naphthylamine, 5-aminohydrindene and 6-aminotetralin have been examined from the standpoint of "positive" bromine content. It is believed that this reaction is useful in detecting double bond fixation. The results indicate that the structures of the naphthalene derivatives are based on the Erlenmeyer formula, and that the preferred structures for the hydrindene derivatives are based on the Mills and Nixon formula. No definite conclusion was reached regarding tetralin.

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## The Structure of Fluorescein, Sulfonefluorescein and Some of their Halogenated Derivatives

BY R. B. SANDIN, A. GILLIES<sup>1</sup> AND S. C. LYNN

Recently C. G. Le Fèvre and R. J. W. Le Fèvre<sup>2</sup> have determined the dipole moments of xanthone and some of its 2,7-disubstituted derivatives. They conclude that a nearly complete fixation of double and single bonds occurs in the xanthone skeleton (structure (I)). This is in accord with the theoretical prediction of Mills and Nixon:<sup>3</sup> "that fusion of a benzene ring with a 6-membered ring tends toward the stabilization in the former of that Kekulé individual which has a double bond between the points of attachment of the side nucleus."<sup>4</sup>

With the work of Le Fèvre and Le Fèvre in mind, it occurred to the authors of this paper that the xanthene dyes such as fluorescein and sulfonefluorescein and which in the lactoid modifications have a xanthone skeleton, might from a chemical standpoint show ring stabilization.<sup>5</sup>

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(2) Le Fèvre and Le Fèvre, *J. Chem. Soc.*, 196 (1937).

(3) Mills and Nixon, *ibid.*, 2510 (1930).

(4) In the case of tetralin, however, it has been found that tetralin, like all ordinary benzene derivatives, can react in both Kekulé forms. Fieser and Lothrop, *THIS JOURNAL*, **58**, 2050 (1936); Sidgwick and Springall, *J. Chem. Soc.*, 1532 (1936).

(5) For earlier work on the structure of fluorescein and sulfone-

The regulated dibromination of fluorescein has been examined and has been found to occur in the 4,5-positions.<sup>6</sup> This is contrary to what one would ordinarily expect from a consideration of a steric effect.<sup>7</sup> It is believed by the authors that this type of dibromination is an indication of ring stabilization. If the lactoid structure of fluorescein is assumed, then it is believed that structure (II) is the preferred structure. If, on the other hand, it is the quinoid form which is brominated, then it is assumed that either structure (IV) (two resonating negative ions) or structure (VI) (two fluorescein, see (a) Orndorff, Gibbs and Shapiro, *THIS JOURNAL*, **50**, 819 (1928); (b) Gibbs and Shapiro, *ibid.*, **50**, 1755 (1928); (c) Ramart-Lucas, *Compt. rend.*, **206**, 1409 (1937).

(6) Several text-books on organic chemistry give the structure of mercurochrome to be a mercurated dibromofluorescein in which the bromine atoms occupy the 2,7-positions. Orndorff and Hemmer, *THIS JOURNAL*, **49**, 1272 (1927), give the structure of dibromofluorescein as a 4,5-dibromo compound. However, Orndorff and Vose, *ibid.*, **46**, 1896 (1924), give a 2,7-structure for the dibromosulfonefluorescein and diodosulfonefluorescein diacetates.

(7) That the structure of dibromofluorescein is a 4,5-dibromo one has also been shown by Harris, Marriot and Smith, *J. Chem. Soc.*, 1838 (1936). However, they gave no definite proof that the compound they obtained by the alkali fusion of dibromofluorescein was 2-bromoresorcinol which has a melting point of 102–103°. The melting point of 4-bromoresorcinol is almost identical with that of the 2-bromo compound, *viz.*, 103°.