ON THE STRUCTURE OF NAPHTHALENE NUCLEUS.

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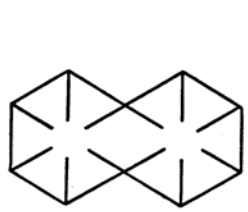
Received April 2nd, 1935. Published August 28th, 1935.

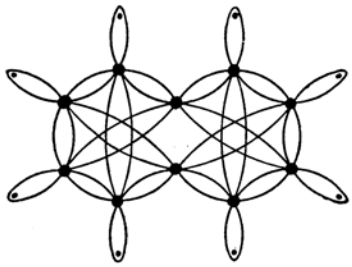
Although many attempts were made to assign a structural formula to naphthalene, there is much uncertainty in this problem. As an introduction to my own experiments,[1] on which I will report shortly, I have tried to obtain a clear notion on the status of the problem.

(1) *Ber.*, **64** (1931), 2059.

The structural arrangement of the carbon atoms is proved by many syntheses, but the distribution of the five double bonds is very doubtful. This question is identical with the problem of the aromatic nature of the naphthalene system. Bamberger,[2] signifying the analogy between benzene and naphthalene, proposed formula (I) with centric valencies, which in terms of the modern electronic theory of valency is the renewed formula by L. Pauling (II).[3] But these formulæ give no account of the well-known fact that naphthalene does not possess the same degree of aromatic nature as benzene. By the usual substitution reagents naphthalene is very easily attacked, and our model must explain such irregularities.



I



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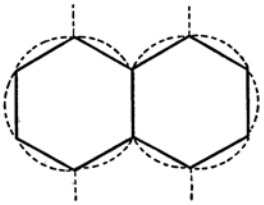


III

The application of Thiele's theory of partial valencies to naphthalene formula (III) can doubtlessly account for the unusual reactivity of the α-positions. But, since the properties of anthracene are not explained by Thiele's theory without the hypothesis that the meso-carbon-atoms are tervalent, it seems also uncertain to work with Thiele's theory in the naphthalene series. Furthermore, formula (III), cannot account for the very surprising fact that the 3-position is not an ortho-position to the 2-position. For instance, 2,3-dihydroxy-naphthalene cannot be converted into a quinone, while the 1,2-compound can and, on coupling with diazonium-compounds, β-naphthol reacts at an α-position, but by no means at any of the β-positions. The very profound spectrochemical data, collected on naphthalene compounds by K. v. Auwers and his collaborators,[4] lead to the conclusion that the physical and chemical properties of this hydrocarbon are explained by Erlenmeyer's formula (IV) with nuclei, one aromatic and the other partly hydroaromatic. The investigation by Bhatnagar and Singh[5] on the parachor value of

(2) *Ann.*, **257** (1890), 1.

(3) *J. Am. Chem. Soc.*, **48** (1926), 1140.

(4) Auwers and Frühling, *Ann.*, **422** (1920), 192; Auwers and Krollpfeiffer, *ibid.*, **430** (1923), 230.

(5) *J. Indian Chem. Soc.*, **6** (1929), 263.

IV V VI a VI b

naphthalene seems also to demonstrate that it is not a homogeneously aromatic system, but really consists of two different rings. However, formula IV is interpreted by Auwers as not representing a rigid system, but as being in a mobile equilibrium with formula V, in which the ring on the right is aromatic, whereas in the system IV the left ring has a benzenoid character. This interpretation corresponds to the oscillation hypothesis for explaining the fact that only one *o*-dichloro-benzene exists (VI a, VI b). The generalization proposed by Auwers is by no means a progress in the naphthalene chemistry. The previously mentioned fact that the 1,2-, but not the 2,3- positions are really ortho-positions cannot be understood if we assume the equilibrium between IV and V. Only when we make the special assumption that those exclusively combined by a double linkage are ortho-positions and when we, in the second place, attribute the rigid formula IV to naphthalene, we can explain the anomaly in question, an anomaly, indeed, which induced Obermiller[6] to deny the existence of a real bond between the carbon atoms 2 and 3 and between carbon atoms 6 and 7. The difficulty is deepened by the observation of H. de Làszlò[7] that the carbon atoms 2 and 6 are not wholly identical with the carbon atoms 3 and 7 respectively.

There is another question concerning the stereochemical behaviour of naphthalene. Are all the carbon atoms of each ring placed on one plane or are the two rings in our system on the same plane? The observation of Bragg[8] that naphthalene has only one center of symmetry in its crystal is interpreted by E. Bergmann and Mark[9] on the basis of the fact that benzene in its crystalline state is represented by a puckered ring, in which carbon atoms lie alternatingly in two planes. The same assumption for the naphthalene nucleus gives really a centrosymmetrical model. But we must add that the carbon atoms can vibrate between the two possible extreme positions.[10] This statement is confirmed by Mack[11] on measurements of

(6) *J. prak. Chem.*, (2), **126** (1930), 257.
(7) *J. Am. Chem. Soc.*, **50** (1928), 892.
(8) W. H. and W. L. Bragg, " X-Rays and Crystal Structure ", p. 230.
(9) *Ber.*, **62** (1929), 750.
(10) Cf. Richard Kuhn, *Ann.*, **475** (1929), 13.
(11) *J. Am. Chem. Soc.*, **47** (1925), 2468.

the area of the gaseous naphthalene molecule. The centrosymmetry of naphthalene excludes also the possibility that the two rings do not lie in the same plane, an assumption made by Kaufler[12] many years ago. But we must remember the possibility that not all naphthalene derivatives have the same structure, a supposition already expressed by Willstätter.[13]

It seems desirable to make new experiments for elucidating the state of affairs. The method applied by me to the problems in question is the measurement of dipole moments, which has led to very interesting results in the field of organic chemistry.[14]

The moments measured are given in Table 1. The experimental details will be published elsewhere. The comparison between the α-substituted naphthalenes and the corresponding benzene derivatives (nitrobenzene 3.96, fluorobenzene 1.45, chlorobenzene 1.56, bromobenzene 1.49[15]) leads to the very surprising conclusion that only the α-positions of the naphthalene nucleus have an aromatic character. The moments of the isomeric β-compounds are higher, and since the aliphatic halogen atoms have higher moments than the aromatic, we must conclude that the β-positions of naphthalene have aliphatic character. The carbon atoms 2 and 3 are ethanoid, and here is the explanation for the mentioned anomaly of the 2,3-compounds, an explanation which demonstrates, I believe, the correctness of formula IV.

Table 1.

Substance	Dipole moment in 10^{18} electrostatic units	Substance	Dipole moment in 10^{18} electrostatic units
α-Nitronaphthalene	3.88	1,4-Dichloronaphthalene	0
α-Fluoronaphthalene	1.42	1,5-Difluoronaphthalene	~0
α-Chloronaphthalene	1.50	1-Bromo-5-nitronaphthalene	2.49
α-Bromonaphthalene	1.48	2,8-Dichloronaphthalene	2.58
β-Fluoronaphthalene	1.49	2,6-Dichloronaphthalene	0.60
β-Chloronaphthalene	1.57	1-Bromo-2-fluoronaphthalene	2.34
β-Bromonaphthalene	1.69	1-Bromo-2-iodonaphthalene	1.80

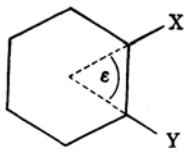
The centrosymmetry of naphthalene is demonstrated by the moments of 1,4-dichloronaphthalene, 1,5-difluoronaphthalene and 1-bromo-5-nitronaphthalene. In a centrosymmetrical model the partial moments of the

(12) *Ann.*, **351** (1907), 151; *Ber.*, **40** (1907), 3250.
(13) *Ber.*, **56** (1923), 1407.
(14) Cf. E. Bergmann and L. Engel, *Z. physik. Chem.*, (B), **8** (1930), 111.
(15) Bergmann, Engel, and Sándor, *Z. physik. Chem.*, (B), **10** (1930), 106, 397.

substituents in the α-positions must be additive, and in the former two compounds they compensate one another; the moments of the latter substance must be equal to the difference of the nitro-group and bromine, namely $3.98-1.49=2.49$, what comes true indeed. The moment of 2,8-dichloronaphthalene has also the expected value. It results from the moments of chlorine in α- and β-positions, respectively, by vectorial addition in an angle of 60°, postulated by the model.

Therefore, it is very surprising that 2,6-dichloronaphthalene has not a zero moment.[16] If other compounds of the same type, which are under investigation, have also a definite moment, we must conclude that in these compounds the naphthalene system is not "uniplanar", but folded.

The investigation of naphthalene derivatives must be pursued. I believe that the most interesting question is the relation between neighbouring atoms and their mutual influence. Therefore, I have measured also the moments of 1-bromo-2-fluoro- and 1-bromo-2-iodo-naphthalene. Bergmann, Engel, and Sándor have exactly proved that the neighbouring atoms in *o*-dihalogenobenzenes repel one another on account of their "Raumbeanspruchung", which increases in the order $F<Cl<Br<I$. The angle between the ortho-valencies, which is normally 60°, increases, and the dipole moment of the compound therefore decreases. The dipole moment of the compound is calculated by the equation

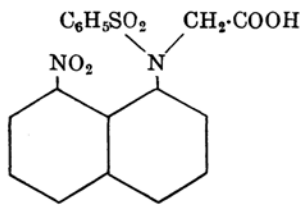


$$\mu^2=\xi^2+\eta^2-2\xi\eta\cos(180-\varepsilon);$$

hence

$$\varepsilon=\arccos\frac{\mu^2-\xi^2-\eta^2}{2\xi\eta}.$$

It is very interesting that on comparison of the two di-halogenated naphthalene derivatives mentioned, with *o*-bromo-fluoro-benzene and *o*-bromo-iodobenzene the angles between the ortho-valencies are almost same (80 and 97° in the benzene series, 76 and 105° in the naphthalene compounds).



It is a well-known fact that also the 1,8-positions in naphthalene are in a certain measure ortho-positions; the very great influence between them is best demonstrated by the resolution of the compound:[17] Höjendahl[18] has measured the moment of 1,8-dinitronaphthalene. If we assume the found value (7.1) to be correct, we must

(16) *Loc. cit.*
(17) Mills and Elliot, *J. Chem. Soc.*, **1928**, 1291.
(18) *Physik. Z.*, **30** (1929), 391.

conclude that the valencies are not parallel to one another, but make—on account of the "Raumbeanspruchung" of the nitro-groups—an angle of ca. 50°. In this question further investigations will bring many interesting informations.

(June 15th, 1934)