211. *Structure of Benzene. Part I. The Problem and Experimental Method.*

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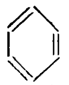
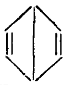
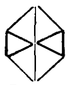
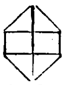
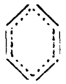
(1) *Theory.*—The structure of benzene has long been one of the foremost of the unsolved problems of organic chemistry, the fundamental difficulty being that of reconciling the transformations of the aromatic nucleus with its stability. The following formulæ will be a sufficient reminder of the lengthy period of historical development extending from 1867 to within the last decade :

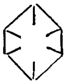

Kekulé.


Dewar.


Claus.


Ladenburg.


Thiele.


Baeyer.

Concerning the chemical transformations of the nucleus, Kekulé's expression is undoubtedly the best single representation, and Dewar's is a permissible addition if a dynamical system be postulated; neither structure, however, satisfactorily interprets the stability of the ring, nor do the saturated but highly strained alternatives. Formulæ which employ imperfectly defined symbols merely convert the problem into that of defining the symbols. There is, moreover, a stereochemical criterion to be satisfied: no formula, static or dynamic, is satisfactory which does not provide the ring with at least the approximate planarity demanded by the evidence of crystal analysis.

The more recent developments of the theory of benzene form a special case of that general extension of our conceptions of valency which has received the name mesomerism. This has been recognised as an objective phenomenon since 1926, and as a projection of the exchange theory of valency, involving, like the latter, a non-classical negative energy term, since 1929 (for a summary see *Chem. Reviews*, 1934, **15**, 225). In the case of benzene Hückel (*Z. Physik*, 1931, **70**, 204; **72**, 310; 1932, **76**, 628) and, more directly, Pauling and Wheland (*J. Chem. Physics*, 1933, **1**, 362) have given semi-quantitative status to the theory. In these calculations it is assumed that the atomic nuclei occupy the corners of a plane regular hexagon. Then, as the last-mentioned authors show, two Kekulé and three Dewar formulæ (derived from each other by rotations through ± 60°) represent the complete set of unperturbed structures from the wave functions of which the new wave functions may be composed. Neglecting all electron interactions except amongst six $2p$-electrons assigned one to each carbon atom, a "zeroth" approximation is calculated to the new wave functions and new energy levels. For the ground state the wave function is

$$\psi = 0{\cdot}6246(\underset{2}{\Sigma}\psi_K + 0{\cdot}4341\underset{3}{\Sigma}\psi_D)$$

The corresponding energy lies $1{\cdot}1055\alpha$ below the "Kekulé energy," α being an undetermined exchange energy integral for carbon $2p$-electrons. Pauling and Wheland estimated α by equating $1{\cdot}1055\alpha$ to the difference between the observed heat of combustion of benzene and the heat calculated by the additive method on the basis of the Kekulé formula; the value obtained was $\alpha = 1{\cdot}5$ e.v. (= 34·5 kg.-cals.).

In spite of its success in bringing the stability of the ring into line with its chemical transformations, this theory has still to face certain difficulties: (1) Pauling and Wheland's value of α does not agree with the value, $\alpha = 0{\cdot}72$ e.v., calculated by Penney from the twisting frequency of ethylene (*Proc. Physical Soc.*, 1934, **46**, 333). (2) It is not particularly clear why *cyclo*butadiene and *cyclo*octatetraene, which can be treated by the same method and with qualitatively similar results, are as unstable as they appear to be. This question has also been discussed by Penney, whose work suggests that the answer is to be found by taking into account some of the electronic interactions which the elementary treatment neglected (*Proc. Roy. Soc.*, 1934, *A*, **146**, 223). (3) Pauling and Wheland's scheme of energy levels for the excited states of the benzene molecule places only one such level in the near ultra-violet, although we have known for more than a decade that there are two electron terms in this region and it is shown in Part V that actually there are three. (4) Again, benzene possesses a prominent frequency of about 161 cm.$^{-1}$, and although no conclusive argument can be derived from this, one's knowledge of vibrational force constants in general makes it hard to see how a fundamental of such a small frequency could be present in the model proposed. (5) Quite the most notorious of all these difficulties, however, is that which arises from the observation of identical frequencies in the Raman and infra-red spectra of benzene. As this question will be discussed in detail later, it will suffice here to refer to the spectroscopic selection rule which states that no fundamental, overtone, or combination tone can appear both in the Raman and in the infra-red spectra of a molecule possessing a centre of symmetry.

(2) *Experimental Method.*—The configuration of the normal benzene molecule represents a problem in experimental stereochemistry which has not as such been seriously attacked hitherto—except by the method of crystal analysis under the conditions of which the molecule is inevitably disturbed by lattice forces. The two methods available for the

investigation of the individual molecule are those of electron interferometry and long-wave spectroscopy. Observations in the former field have been published by Wierl (*Ann. Physik*, 1931, **8**, 521) and Jones (*Trans. Faraday Soc.*, **1935**, **31**, **1036**), but it is doubtful whether the problem can be carried very far forward by this method without considerable further refinements of technique : probably many models, provided that they are annular and roughly flat, could be found which would give agreement with the diffraction density curve to within the error of measurement. In the following papers we take up the study of the matter by the method of long-wave spectroscopy, which includes the study, not only of infra-red and Raman spectra, but also of the vibrational structure of bands arising from electron transitions.

Considered as a tool for the elucidation of molecular configuration, the method of long-wave spectroscopy has recently obtained a new access of power in its application to hydrogen-containing compounds from the discovery and isolation of deuterium. The replacement of an element by its isotope leaves unaltered all nuclear charges, therefore all electron wave-functions, and therefore substantially all vibrational force constants, so that practically the whole effect of the substitution on the vibration frequencies arises from the known changes of certain atomic masses. Having assumed some molecular model, we can, on account of this consideration, calculate definite numerical relationships between the frequencies of corresponding normal vibrations in the two isotopically related molecules. Comparison with the observed frequency shifts then serves the double purpose of assisting in or confirming the identification of the normal vibrations concerned, and of testing the model; for the theoretical relations governing the frequency changes naturally depend on the model assumed, and therefore a model which always gives the correct relations is proved.

It transpires that one cannot, without making assumptions about the force system and merely from the knowledge that it remains unaltered by an isotopic substitution, calculate every frequency shift individually : some vibrations can be treated individually whilst others have to be taken in groups. However, as 13 different benzenes can be built up from protium and deuterium, the total number of verifiable frequency relations is large.

The complexity of the vibrational spectra will naturally increase as the symmetry of the benzene molecule is destroyed by dissymmetric arrangements of the isotopic hydrogen atoms. The most feasible procedure is therefore to start with a comparison of the two most symmetrical benzenes, C_6H_6 and C_6D_6, and interpret their spectra as fully as possible so that the results are available to assist analysis of the next case in order of symmetry, which is that of *s*-$C_6H_3D_3$. The sequence continues with *p*-$C_6H_4D_2$ and its symmetry equivalent 1 : 2 : 4 : 5-$C_6H_2D_4$, and then with all the other deuterobenzenes, except 1 : 2 : 4-$C_6H_3D_3$ which is the least symmetrical. It is a general consequence of high symmetry, however, that certain normal vibrations are prohibited by selection rules from appearing in the spectra, so that in C_6H_6 and C_6D_6, for instance, there are quite a number of fundamental frequencies which cannot be directly observed; this fact places a difficulty in the way of the identification of combination tones. As symmetry is progressively removed by dissymmetric substitution, more and more of the frequencies previously " forbidden " become " allowed," and hence we expect that the study of the spectra of the less symmetrical modifications of benzene should help to clear up those details of the spectra of the more symmetrical forms which have at first to be left aside; this applies especially to the interpretation of combination frequencies.

In pursuance of the programme indicated, we first evolved a convenient exchange reaction by means of which C_6D_6 can be prepared in a high degree of purity, and took the opportunity to study its more easily measured physical properties such as density, refraction, and vapour pressure. We then examined comparatively for C_6H_6 and C_6D_6 the following four spectra : the near infra-red absorption spectrum, the Raman spectrum, the ultra-violet fluorescence spectrum, and the ultra-violet resonance spectrum. All these spectra afford information about the vibrations of the normal molecule; we have not studied the ultra-violet absorption spectrum because the vibrational structure of this relates primarily to the electronically excited molecule, which from our present point of view is of secondary interest. The work up to this stage is recorded in the parts immediately following.* As indicated in our various preliminary notes, similar studies with *s*-$C_6H_3D_3$, *p*-$C_6H_4D_2$, and C_6H_5D are in progress, though they are not yet complete enough for detailed report (cf. *Nature*, 1934, **134**, 734, 847; 1935, **135**, 1033; **136**, 301, 680; 1936, **137**, 70).

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