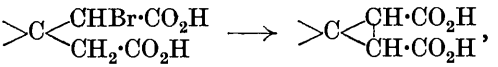
CLXXV.—*The Hypothesis of Valency-deflexion.*

By Christopher Kelk Ingold and Jocelyn Field Thorpe.

In a recent issue of the *Fortschritte der Chemie, Physik und physikalischen Chemie* (Bd. **19**, Heft. 4, 1927) Hückel discusses our view that the disparity between the space-requirements of the several groups attached to a central carbon atom modifies the angle between the valencies of that atom. The discussion includes a partial statement of experimental data which have been interpreted by ourselves and others in the light of the hypothesis mentioned, and a criticism which, since it reveals lack of understanding of the essentials of the hypothesis, will briefly be considered here.

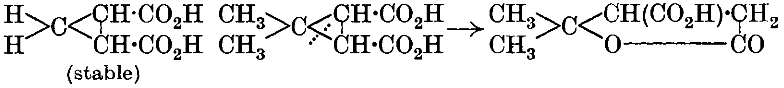
In the first place, it must be remarked that the calculations of the angles between the valencies of an atom from molecular volume data have never been regarded by us as otherwise than illustrative of the qualitative implications of the theory, and of the manner in which it might be developed when the constitution of the combined carbon atom is more fully worked out. The theory is, in fact, intended to be translated as our knowledge of the constitution of the atom grows, and it therefore need scarcely be said that the assumption of distorted valencies does not imply, as Hückel asserts, that the forces of valency are assumed to be of gravitational type governed by the law m_1m_2/r^2. The details of this, the principal subject of Hückel's criticism, require no further comment.

Hückel's further criticism regarding the applications (which he regards as arbitrary) of the hypothesis fails for two reasons. In the first place, whilst we have consistently endeavoured to restrict the applications of the hypothesis to cases which are comparable in the sense that polar disturbances are at a minimum, Hückel endeavours to extend the comparisons on the same purely spatial basis to examples in which polar influences would be expected to act powerfully and very differently, and, in commenting on the recognition of the necessity for taking count of polar influences, asks "Wozu diese ad hoc gemacht Annahme?" We are not aware that the existence of polar influences in Organic Chemistry has previously been disputed, and it is certainly true that modern work has yielded much definite information with regard to them. Two examples may be given to illustrate the difference between our comparisons and those of Hückel. The ease of formation of a series of *cyclo*propanedicarboxylic acids from glutaric acids by monobromination and subsequent hydrolysis under comparable conditions,



$$>C<\begin{matrix}CHBr\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix} \longrightarrow >C<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix},$$

has been shown to follow the anticipated order (for example, glutaric acid 47%, ββ-dimethylglutaric acid 84% of ring-formation). This comparison is a just one, for the β-alkyl groups would be expected to have only second-order polar effects on the α-hydrogen and α-bromine, and the possibility that polar disturbances might affect the result is still further diminished by the circumstance that they will be of opposite sign for the two atoms indicated. Hückel, however, seeks to produce a parallel case pointing in the opposite direction by comparing the stability of *cyclo*propane-**1** : 2-dicarboxylic acid with the tendency of the 3 : 3-dimethyl derivative to yield terebic acid :



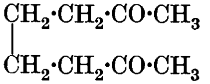
$$\begin{matrix}H\\ H\end{matrix}>C<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix} \quad \begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix} \rightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}CH(CO_2H)\cdot CH_2\\ O\text{———————}CO\end{matrix}$$

(stable)

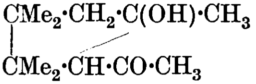
In our view this comparison is unjust, because the first-order polar effect of the methyl groups would be in the direction of increasing the vulnerability of the quaternary carbon atom in the reaction considered, and this might be expected to outweigh the spatial influences. Again, Hückel considers the evidence to be derived from the dissociation constants of the alkylmalonic acids, and points out that the results do not fall into the regular sequence which might be expected if the spatial hypothesis advanced by us were the only factor in the situation. This, however, need not occasion surprise; but it is to be noted that Hückel does not attempt a corresponding analysis of the data relating to the β-alkylated glutaric acids in which the polar effect of the alkyl groups would be expected to be diminished (see Spiers and Thorpe, J., 1925, **127**, 538). Even this series would not be expected to conform *exactly* to the requirements of our hypothesis, but it should certainly conform much more closely than the series of malonic acids; and although the available data for the second dissociation constants (which are required for the application of the Bjerrum calculation) are rather few, there is already evidence that the anticipated closer conformity exists, and we confidently expect that further measurements will substantiate this conclusion. It must be confessed that many examples exist in which it is impossible in the present state of knowledge to foretell the effect of polar influences on the angular relations of the valencies—for instance, in the Dieckmann–Komppa synthesis of *cyclo*pentanedionedicarboxylic esters, in which a concentration of highly polar groups is produced. In these circumstances, we do not pretend to be able to foretell the conditions of substitution which will produce the system having greatest stability. In such examples, the examination of the effect of series of substituents of increasing bulk often reveals a maximum of stability at some intermediate member, with falling-off in both directions. There is, however, nothing in this behaviour which is demonstrably inconsistent with the theory (as Hückel asserts), although it must be admitted that the full explanation cannot yet be given.

The remaining point relates to the theory of the strainless forms of the 6- and 7-membered rings. Hückel's contention is expressed in the assertion that our hypothesis " steht und fällt mit der willkürlich Annahme eines ebenen gespannten Sechsrings." It is true that in our first memoir (J., 1915, **107**, 1080) the *cyclo*hexane ring was assumed to be uniplanar; but the whole application of the valency distortion hypothesis to 6- and higher-membered rings was modified in 1923 (Baker and Ingold, J., **123**, 122) contemporaneously with, and independently of, the publication by Hückel and others of the first experimental evidence relating to the existence of isomerides of the decahydronaphthalene type. This explicit modification, ignored by Hückel, may be restated as follows. The intrinsically probable existence of strainless multiplanar forms (Sachse, 1890; Mohr, 1918) of the *cyclo*hexane ring, combined with the non-existence of isomerides which should arise if such forms were static, leads to the suggestion that these forms (*cis* and *trans*) are to be regarded as limiting states of a vibrating framework, the average condition of which is between the uniplanar and strainless condition. (The occurrence of isomeric decahydronaphthalenes in which each ring " locks " the other merely proves that the multiplanar forms *can exist*, not that they represent a permanent condition in the absence of locking.) It was a natural corollary that the further a uniplanar form departed from the strainless condition, as, for example, in 7- and 8-membered rings, the more would the average condition recede from the uniplanar state. This view, which was subsequently emphasised by Baker and others, is in excellent agreement with the available data, and Hückel's statement quoted above is thus seen to be unwarranted.

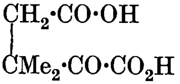
In justice to the views discussed by Hückel, it should be remarked that this memoir contains no constructive suggestion as to any alternative to the hypothesis on the basis of which we have consistently endeavoured to collate a large body of data; yet observations continue to accumulate which obviously require interpretation. Reference may be made to Vogel's recent demonstration (J., 1927, 594) that, whereas αδ-diacetylbutane exists in the open-chain form, its ββγγ-tetramethyl derivative reacts in the cyclol form only :



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \\ | \\ CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \end{array}$$



and to Rothstein and Shoppee's elaboration (*ibid.*, p. 531) of the earlier observations of one of us relating to the progression and substitution of the stability of the lactolone forms of the α-ketoglutaric acids :



$$\begin{array}{l} CH_2{\cdot}CO{\cdot}OH \\ | \\ CMe_2{\cdot}CO{\cdot}CO_2H \end{array}$$

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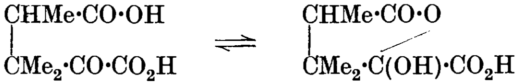

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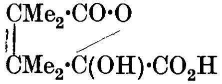

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The facts which have been accumulated during the past 13 years are now so numerous that the hypothesis by which we have endeavoured to collate them cannot lightly be brushed aside unless some alternative view can be advanced. Some of the points dealt with in this communication were raised also by Sidgwick in his work "The Electronic Theory of Valency," Oxford, Clarendon Press, 1927.

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