

Passons maintenant à la démonstration que la condition 2^o, figurant dans le théorème IV est suffisante pour que le cas irréductible se présente.

Le facteur arithmétique est égal à un produit infini $\prod_p Q(p, t)$, qui est étendu aux nombres premiers p et qui converge absolument et uniformément par rapport à t . Si ξ est le nombre des ν ($1 \leq \nu \leq n$) tels que y_ν appartienne à la première famille,

$$p^{(n-m)\beta} \left(1 - \frac{1}{p}\right)^\xi Q_\beta(p, t)$$

est égal au nombre de solutions du système

$$\sum_{\nu=1}^n b_{\mu\nu} f_\nu(y_\nu) \equiv t_\mu \pmod{p^\beta} \quad (\mu = 1, \dots, m),$$

$$y_\nu \equiv a_\nu \pmod{A_\nu} \quad (\nu = 1, \dots, n)$$

et

$$\prod_\nu y_\nu \not\equiv 0 \pmod{p}.$$

Pour démontrer que le cas irréductible se présente il suffit de démontrer que $Q_\beta(p, t)$ est positif pour chaque nombre premier p et pour chaque nombre naturel β . Cela résulte immédiatement de la condition 2^o du théorème IV dans le cas où β est $\equiv 2\xi + 1$. Une proposition de VAN DER CORPUT¹⁴⁾ apprend que $Q_\beta(p, t)$ est indépendant de β pour chaque $\beta \equiv 2\xi + 1$, de sorte que $Q_\beta(p, t)$ est positif pour chaque $\beta > 2\xi + 1$.

Le raisonnement utilisé à la fin du § 3 (p. 411), où nous donnons la démonstration du théorème II, appliqué avec $\beta_0 = 2\xi + 1$, nous apprend que dans la condition 2^o du théorème IV le facteur arithmétique est compris entre deux nombres positifs indépendants de t et le théorème IV est démontré.

¹⁴⁾ Proposition 3 de son article: „Sur quelques systèmes de congruences”, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 42, 328—335 (1939).

Chemistry. — *On the mobility of the saturated six- and seven-ring and the configuration of the cycloheptane diols 1.2.* By J. BÖESEKEN.

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It may be considered well known that, as a general result of the researches on the influence of the polyols on the electric conductivity of boracic acid, the increase observed there is due to the formation of complex polyol boracic acids, in which the boron atom forms part of a ring of five or six atoms.

According as two hydroxyl groups in the dynamic equilibrium position *) of the polyol are situated more favourably for the formation of this ring, the increase in conductivity is larger, since in the aqueous solution of boracic acid and polyol under for the rest comparable conditions more of the very strong borocomplex will be present.

This consequence, which is of importance in determining the configuration of a large number of compounds, was first checked by aromatic orthodiphenols, which indeed all exerted a positive influence, in contrast with the meta- and para-diphenols which all appeared to be indifferent.

Subsequently the alicyclic polyols were examined. In complete agreement with the expectation all *cis-cyclopentane diols 1.2* appeared to produce an increase, all isomeric transdiols being indifferent.

It may be remarked that meanwhile it had been found that the common 1.2 glycols did not give an increase (no more than the 1.3 and 1.4 diols) and that this was explained by assuming a mutually repulsive action of the hydroxyl groups in these diols, so that in the dynamic equilibrium position they could stand apart as far as possible and consequently were in an unfavourable position for the formation of borocomplexes.

It was likewise demonstrated that, according as the number of vicinal hydroxyl groups increases, the influence on the conductivity is raised, which is a consequence of the previous theorem, since upon mutual repulsion of the hydroxyl groups in the alcohols with more than two of these groups these must come to lie two by two constantly more favourably for the formation of borocomplexes.

The expectation that in the *cis-cyclopentane diols 1.2* the hydroxyl

*) We assume that the atoms and groups of atoms of the molecules in liquid or dissolved condition are in constant motion, rotating round the single bonds as axes. Owing to repulsive and attractive forces there will be favoured positions, thus causing the movements to acquire the character of oscillations. These favoured positions I have called "dynamic equilibrium positions".

groups take a favourable position was based on the hypothesis of VAN 'T HOFF concerning the constant valency angles of $109^{\circ}28'$ of the carbon atom. The five atoms of the ring will then form a regular five-ring with a small tension. By the ring-closure the intermolecular movements are very strongly inhibited and the hydroxyl groups are retained in a fixed position. For the cis-diol 1.2 this is favourable for the formation of the borocomplex.

In the case of the cyclohexane diols 1.2 neither with the cis-diol 1.2 nor with the trans-isomer increases in conductivity were stated. With regard to the material already collected at that time, it could be concluded that likewise in the cis-diol the hydroxyl groups are not situated favourably for the formation of the boron-containing five-ring¹⁾.

If VON BAYER's opinion that the six atoms of the saturated six-ring lie in the same plane were correct, this behaviour would be incomprehensible. In that case there would have to be a higher tension in this ring than in the five-ring; the two hydroxyl groups would have to be still more strongly fixed to their places and the formation of the borocomplex would have to take place even more easily.

This not being the case, the two hydroxyl groups appear to lie further apart; consequently they may respond to the tendency of mutual repulsion, which is only possible if the six C-atoms do *not* form a tense flat ring, but have another position with respect to each other.

In order to explain this possibility, I have assumed that the ring has become more *supple* (l.c.). On the ground of the theory of SACHSE, who retaining the valency angle of $109^{\circ}28'$ showed that the six-ring may assume several different positions, one of which, the chair position, is characterized by the fact that it has to trespass an energy threshold in order to pass into a series of other positions which may gradually change into one another, none of these configurations may be so stable that the molecule — at any rate in liquid or gaseous condition — is fixed, for if this were the case, a number of stereo-isomers would be possible, which have never been found.

The suppleness of the six-ring, therefore, is necessary and then the vicinal hydroxyl groups in the dynamic equilibrium of these rings may diverge so far that the formation of a boro-complex is difficult.

The *suppleness* of the ring was now further demonstrated by means of the acetone method of CHR. VAN LOON²⁾. The latter had proved that the cis-cyclopentane diols with acetone yielded cyclic ethers and had pointed out that the study of the formation of these acetone-ethers might form a welcome amplification of the boracic acid method. By applying this method to cyclohexane diols 1.2, DEX³⁾ found that the cis-diol easily yielded an

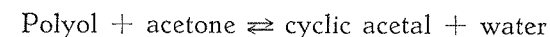
¹⁾ J. BÖESEKEN and J. VAN GIFFEN, *Rec. Trav. chim.*, **39**, 185 (1920).

²⁾ CHR. VAN LOON, *Dissertation Delft* 1919.

³⁾ H. D. DEX, *Rec. Trav. chim.*, **41**, 312 (1922).

acetone compound, which is not possible unless the hydroxyl groups may be placed in a position favourable to the formation of this ether (the trans-diol, as was expected, did not enter into reaction).

On the other hand HERMANS⁴⁾ in his studies on the equilibria:



found that this equilibrium in the cis-cyclohexane diol lay far to the left, indicating that in the dynamic equilibrium position the hydroxyl groups lie indeed unfavourably for this acetal formation, in agreement with the absence of an increase in conductivity of boracic acid.

However, the examination of the cycloheptane diols 1.2, likewise by DEX (l.c.), caused a surprise. The cis-diol as well as the trans-diol yielded a cyclic acetal and both caused an increase in conductivity of the boracic acid.

By means of atom-models, DEX demonstrated that in the trans-diol the hydroxyl groups bound to vicinal carbon atoms may come to lie rather favourably for the formation of cyclic acetals with acetone, in contrast with the trans-cyclohexane diol, where in all possible positions they lie unfavourably. The preparation of this compound, therefore, is conceivable and at the time was of great importance, being the *first* example of the trans-binding of two saturated rings with two vicinal common carbon atoms and producing tangible evidence of SACHSE's hypothesis that the atoms of rings with more than five atoms do not lie in the same plane. The positive effect on boracic acid, however, was unexpected and for the time being inexplicable.

If we assume, namely, that the six-ring is pliable and makes rhythmical movements, this hypothesis, if it has any value at all, must be no less applicable to the seven-ring. The general hypothesis of mutual repulsion of the hydroxyl groups must apply here as well.

Owing to these two conditions, by which the hydroxyl groups, responding to the repulsion, may assume a position as unfavourable as possible, we may neither of the trans-diol nor of the cis-diol expect an increase in the conductivity of boracic acid.

In these considerations, therefore, something must have been overlooked. Already in 1922 DEX (l.c. p. 330) pointed out that the negative behaviour of the cis-cyclohexane diol might be explained by the fact that the molecule is almost completely in the chair position, in which the hydroxyl groups lie unfavourably. I shall revert to this later on and will merely observe here that this assumption in itself is at variance with the absence of a number of stereo-isomers which would have to be the result of the rigid condition of the six-ring (see above). Besides, the behaviour of the trans-cycloheptane diol remains unexplained, here being only a very small region where the hydroxyl groups are in a moderately favourable position and

⁴⁾ P. H. HERMANS, *Z. f. phys. Chem.*, **113**, 337—384 (1924).

where they would be very rarely, owing to the mutual repulsion. Moreover, for ring-systems we should have to introduce an auxiliary hypothesis, viz. that these hydroxyl groups cannot lie so unfavourably as in the non-cyclic compounds.

In an interesting paper P. H. HERMANS and CHR. J. MAAN⁵⁾ recently published a sterical analysis of the saturated six- and seven-ring and of the two cycloheptane diols 1.2. For this purpose they made use of the accurate data on the atomic distances C—C, C—H and C—O; the obtained results were explained with the aid of the STUART atom-models. Probably for the sake of clearness, they assumed a chair- and bed-position in the seven-ring; it should however be emphasized that a chair position, as found by SACHSE in the six-ring and distinguished from the other possible positions by the fact that the molecule has to trespass an energy threshold in order to attain the bed position, does *not* exist in the seven-ring. All possible positions may gradually change into one another.

In their calculations HERMANS and MAAN found that by the intramolecular movements of the six-ring and particularly of the cyclohexane diols a sufficiently large space is left for the hydrogen atoms and for the hydroxyl groups. In the seven-ring this space appeared to be not sufficient; for the H-atoms on the C-atoms 1 and 4 (2 and 5 or 3 and 6 resp.) in most of the possible positions of the molecule no sufficient space was available and this was even more the case if one of the H-atoms was replaced by a hydroxyl group, as in the cycloheptane diols.

It was found that there was only a very small region (see table II, p. 651 between b' and c'), where this sterical inhibition did not occur and that in this small strip lie the positions (3'.4 trans and 6'.7 trans resp.) where two vicinal trans-placed hydroxyl groups are lying moderately favourably towards boracic acid.

HERMANS and MAAN considered this fact a perfectly satisfactory explanation of the positive influence of the trans-diol on the conductivity of the boracic acid, since it may be expected that this free region will be occupied by preference by the molecule.

Without further considerations, however, the behaviour of the *cis*-cycloheptane diol 1.2 remains inexplicable, the position of the vicinal *cis*-placed hydroxyl groups in the inhibition-free area being unfavourable.

The elaborate investigation on the borocomplexes does not leave any doubt that the increase in conductivity is a measure for the position of the hydroxyl groups in space. The fact of this positive influence, exerted by the *cis*-diol, proves that in the dynamic equilibrium position it forms fairly easily a borocomplex ($\Delta_{\text{mol}} = 161$) and that consequently the molecule cannot be situated entirely in the inhibition-free region. This implies that the sterical disturbances cannot *prevent* the intramolecular movements but at most can *retard* them. As a matter of course this applies as well to the

⁵⁾ P. H. HERMANS and CHR. J. MAAN, Rec. Trav. chim., 57, 643—652 (1938).

movements of the trans-diol, but in the extensive area of motion the *cis*-diol finds two very favourable positions (see Table I, 4.5 config. e; and Table II, 4.5 config. a') for the formation of borocomplexes and besides a moderately favourable position (Table I, 4.5 config. e), the trans-diol there finding nothing but unfavourable positions.

For both isomers the inhibition-free area will have a certain preference, but considering the fact that the intramolecular movements are only retarded and that the region favourable to the *cis*-diol is very extensive, there may be a good deal of borocomplex present in the dynamic equilibrium position.

This more precise description of the mobility of the seven-ring requires an amplification of the simple statement of the negative behaviour of *cis*-cyclohexane diol 1.2.

According to the calculations by HERMANS and MAAN no sterical inhibitions may be expected here (see above). In the region of the bed positions, just as in the cycloheptane diol, *two* very favourable positions of the hydroxyl groups for the formation of the borocomplexes occur. Although there is not a separate moderately favourable area, yet in the *cis*-cyclohexane diol 1.2 a probably small increase of the conductivity of boracic acid might be expected.

The original explanation of the negative behaviour of the *cis*-cyclohexane diol was based upon the mutual repulsion of the hydroxyl groups, so that they were able to lie as far apart as is the case in the non-ring-shaped 1.2 glycols and, as we have seen above, on this the expectation was founded that the cycloheptane diols do not exert any influence either on the conductivity of boracic acid.

In non-ring-shaped glycols there is only *one* very favourable position of the hydroxyl groups; in the *cis*-diols of the six- and seven-ring there are *two* and in my opinion this is the main reason why the *cis*-cycloheptane diol, in spite of the inhibitions (see below) in the dynamic equilibrium position yet fairly easily forms borocomplexes, just as, as was explained above, we should expect a, probably small, positive influence of the *cis*-cyclohexane diol on the boracic acid, particularly since the passage-disturbances do not occur in this six-ring.

However, in contrast with the seven-ring, the latter molecule may assume a tension-free, energetically very peculiar position, from which it can only pass into the other tension-free conditions by trespassing an energy threshold. This, the chair position, will undoubtedly be taken by preference and, since the hydroxyl groups in this position lie as far apart as possible, this particular minimum of potential energy coincides with the configuration which the molecule, owing to the mutual repulsion of the hydroxyl groups, tends to assume.

In the cyclohexane itself this preference is less pronounced; the interference-spectrum of the electron rays passing through the dilute vapour (R. WIERL, Ann. der Physik I p. 1) consisted of two sharp lines, cor-

responding with the constant atomic distances of the vicinal C-atoms: $\pm 1.53 \text{ \AA}$ and of those at 1.3 (2.4 and 3.5 resp.): $\pm 2.5 \text{ \AA}$, which distances during all movements of the six-ring indeed remain constant; the third line, corresponding with the distances between the C-atoms 1.4, 2.5 and 3.6, was vague, indicating that these distances were *not* constant, as could be expected in a succession of chair and bed positions. For cyclopentane two sharp images were observed at ± 1.53 and 2.5 \AA and for benzene three on the calculated distances for the aromatic C—C-bond 1.39 , $2 \times 1.39 \cos 30^\circ$ and $2 \times 1.39 \text{ \AA}$.

Recapitulating we may say the following:

Parts of molecules (atoms) may rotate round the bonds as axes.

By mutual repulsion of equal groups (e.g. hydroxyl groups) favoured positions are formed, owing to which fact the movements acquire the character of oscillations round those positions as points of oscillation.

In the *non-cyclic diols* (in general) this point of oscillation has an unfavourable position for the formation of borocomplexes and among the other possible positions there is only *one* which is highly favourable for this purpose.

In the *cyclopentane diols* the rotating movement is almost entirely (but not completely) stopped, owing to the ring-closure; consequently the amplitudes of the oscillations of the hydroxyl groups have become small and in the *cis*-diols these remain favourable to the formation of borocomplexes; in the *trans*-diols very unfavourable for that purpose.

In the *cyclohexane diols* the rotating movement has indeed decreased, owing to the ring-closure, but the groups bound to the C-atoms can describe fairly large tracts.

In the *trans*-diols, however, the hydroxyl groups remain constantly very unfavourable to the formation of borocomplexes; in the *cis*-diols the hydroxyl groups pass *two* very favourable positions.

The H-atoms and OH-groups have sufficient space to pass each other; however, in the six-ring one position occurs which is characterized by the fact that the molecule has to trespass an energy threshold in order to pass into other tension-free positions. From the negative behaviour towards boracic acid we may conclude that the inhibition caused by the energetic condition in the six-ring must be of greater importance than the inhibition caused by lack of space (i.e. sterical conditions) in the seven-ring (see below).

With regard to the latter we observe that the binding axes must have some space to move, so that the angle of $109^\circ 28'$ may somewhat vary. This is apparent in the first place from the possibility of substances such as camphane and isocamphane and their derivatives, which consist of two five-rings with *three common C-atoms*. Of the *two* five-rings the carbon atoms cannot be situated in one plane, since the angles 6-1-2 and 5-4-3 cannot be $= 0^\circ$.

In these molecules there is a struggle between the mentioned angles,

which try to become $109^\circ 28'$ but do not reach that figure, and the C-atoms of the five-ring which try to extend in one plane since the angles between their affinities likewise try to become $109^\circ 28'$ and do not attain this either.

For the further considerations on the suppleness of the saturated five-ring I refer to an investigation on the cyclic hydroxy acids⁶⁾. This kind of suppleness will exist in the larger rings as well and then it is evident that the effect of the varying affinity angle will be greater in a ring with seven atoms than in one of five.

The greater possibility of moving in the six-ring, however, must then be powerfully counteracted by energy conditions in the chair position (see above).

There are a number of observations which confirm the favouring of this position of a six-ring. As in the *cis*-cyclohexane diol this will take place particularly if the taking of this position is supported by mutual repulsion of equal groups. The dipole momentum of *trans* 1.4 dichloride and *trans* 1.4 dibromide cyclohexane is 0, which is only to be expected when the molecules are almost entirely in the chair position. Similarly the dipole momentum of dioxane hardly differs from 0 and consequently this molecule is for the greater part in the chair position.

In this favoured position the hydroxyl groups in the *cis*-cyclohexane diol lie as far apart as possible (as they tend to do by mutual repulsion) and very unfavourably for the formation of borocomplexes.

In the *cycloheptane diols* the rotating movements are still less inhibited and the area through which the groups of atoms may pass is still larger. Moreover, there is no position which is favoured by its energy conditions. In the *trans*-diol the vicinal hydroxyl groups may take a position which is moderately favourable to the formation of a borocomplex; in the *cis*-diol there is a large region with two very favourable positions and one moderately favourable position of the vicinal hydroxyl groups for the formation of a borocomplex.

In the seven-ring the atoms and groups of atoms in the greater part of the area of motion have not sufficient space to pass each other; there is only a small region for the diols, where they can lie freely. This will be a favoured region but, though the sterical disturbances may retard the intramolecular movements, they cannot prevent them and the inhibitions are less radical than those caused by the energetic conditions in the six-ring. In this small favoured region lies the sole moderately favourable position of the hydroxyl groups in the *trans*-diol. In the *cis*-diol this region is unfavourable for the formation of the borocomplexes, but on the other hand, in the remainder of the region the hydroxyl groups are situated particularly favourably, whereas for the *trans*-diol in the whole further area of motion no favourably situated transpositions occur.

⁶⁾ J. BÖESEKEN, G. SLOOFF, J. M. HOEFFELMANN and H. E. HIRSCH, *Rec. Trav. chim.*, **52**, 881—894 (1932) and J. BÖESEKEN, *Rec. Trav. chim.*, **54**, 101 (1934). ☉

In the light of these considerations and of the sterical analysis of HERMANS and MAAN, who after a correspondence on the subject agree with these explanations, the observed behaviour of *all* diols towards boracic acid and acetone may consequently now be explained very satisfactorily.

The fundamental hypotheses, 1^o. of the constant rhythmical intramolecular movements and 2^o. of the mutual repulsion of the hydroxyl groups, may be maintained unaltered.

Delft, June 1939.

Botany. — *Analysis and Integration of various auxin effects.* I. Bij F. W. WENT. (California Institute of Technology.)

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Three years ago the writer tried to analyze the action of auxin on different developmental processes in terms of a number of elementary reactions (WENT 1936). It was assumed that in root formation, growth, cambial activity, etc., the auxin not only reacted with specific other growth factors, named calines (WENT 1938), but that the auxin also conditioned the distribution of these calines. By consistent application of these two principles most auxin phenomena lined up nicely in a general picture. Nevertheless this theory of a multiple action of auxin had to cope with many difficulties. In the first place very few experiments were available to test the theory. And in the second place there were some rival theories, each accounting for some of the known facts. One of those, most clearly expressed by FITTING (1936), and adopted by BOYSEN-JENSEN (1938), AVERY (1938) and HITCHCOCK and ZIMMERMAN (1938) was that auxin was a "stimulant" for the cell, which practically precluded further analysis. Another theory of THIMANN (1935) was that auxin took part in one master reaction, which then led to either growth, or root formation, or bud inhibition, etc. THIMANN's main point was, that any substance which was found to cause growth by cell elongation also induced root formation or inhibited lateral growth. During the last three years many facts bearing on these theories have been collected and the theory of multiple auxin action has proven to be very fruitful as a working hypothesis. The author's recent papers, all dealing with different aspects of the growth problem in general, could not be published together. This review is intended to integrate these separate papers, to serve as their general discussion. For the experimental evidence on which this discussion is based, the reader is referred to the individual papers. The following subjects will be treated. On the one hand considerable data were collected on the existence of calines (WENT 1938, 1938a, BOUILLENNE 1938, BONNER, HAAGEN-SMIT and WENT 1939). On the other hand it was possible to differentiate each of the developmental processes studied (growth by cell elongation, 1939c, the pea test 1939b, bud inhibition 1939a and root formation 1939) in a chain of at least two successive reactions. And thirdly it was found, that not all substances active in one reaction could take part in other reactions. Lastly extremely interesting facts were published (D. BONNER 1938) substantiating and enlarging the experimental evidence, that in the growth reaction a stoichiometrical relationship exists between the applied growth substance and the resulting