Chemistry. — *A mathematical analysis of the single and double six-ring.* By P. COHEN HENRIQUEZ. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of September 29, 1934).

Very little is known as yet concerning the spatial configuration of the ring systems. For a long time the ring systems were merely assumed to be plane. Since in plane carbon rings the angles between the valences can never be equal to the tetraeder angle, it was supposed that "tension" occurred in the rings.

In 1918 MOHR[1]) pointed out that only in carbon rings with fewer than six C-atoms, tension must of necessity occur. He demonstrated that a spatial model could be constructed from the six-ring without any tension.

If, however, we make a model from the six-ring in which the C-atoms are represented by little wooden balls and the valences by little brass rods (in such a manner that rotation with a valence as axis remains possible), not only *one* spatial configuration will prove to be possible, but an infinite number. We find namely one fixed form and one mobile form which can occupy a continuous series of tensionless positions.

A mathematical demonstration, however, of the existence of the mobile form has never been given yet. On account of this it is therefore impossible to link up calculations with the mobile form. In the literature we mostly find the fixed form designated as the "chair position" and the mobile form as the "bed position".

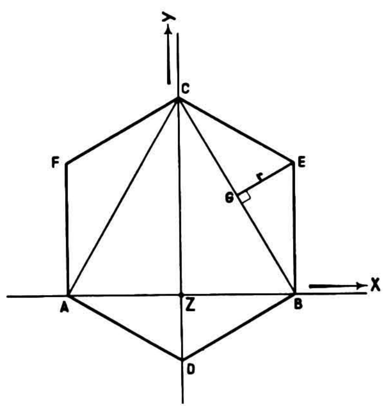

Fig. 1.

In the following we shall try to find out *all* possible forms of the six-ring on strictly mathematical grounds, postulating only the fixed angle between the valences.

If we state the problem very generally, we get:

"To construct in space all possible forms of a six-ring, given equal sides and equal angles".

Let us now approach the six-ring problem stated above.

By distortion of the angles of the spatial six-ring in such a manner that the whole six-ring lies in *one* plane, we get fig. 1.

1) J. Prakt. Chem. (2), 98, 352 (1918).

If we connect the vertices A, B and C, we get an equilateral triangle Whatever form the six ring may assume now, the form and size of triangle ABC will constantly remain the same. If we call one side of the triangle: q, one side of the hexagon: p and the angle between two sides of the hexagon: ψ, then $q = 2p \sin \frac{1}{2}\psi$. We shall assume the triangle ABC to lie in the plane of drawing. The small triangles BEC, CFA and ADB in the spatial six-ring now make all three an angle with the plane of drawing; let these angles be φ_1, φ_2 and φ_3.

The angles φ_1, φ_2 and φ_3 must now be in such a relation to one another that the six-ring angles DBE, ECF and FAD are equal to ψ, in other words the distances DE, EF and FD must be equal to q.

Now, if we express DE, EF and FD in terms of the angles φ_1, φ_2 and φ_3, and if we set these to be equal to q, we obtain three equations from which we can get the required relation between φ_1, φ_2 and φ_3, which enables us to calculate all possible formations of the six-ring. For the sake of facility we shall assume for a moment the system of coördinates XYZ, where X and Y lie in the plane of drawing, and to which plane Z is perpendicular. Working out analytically the distance between F and E we get

$$\tfrac{3}{4}\, q^2 = 2\, r^2 + r^2 \cos\varphi_1 \cos\varphi_2 - 2\, r^2 \sin\varphi_1 \sin\varphi_2 + \tfrac{1}{2}\, q\, r \sqrt{3}\,(\cos\varphi_1 + \cos\varphi_2).$$

If, for the sake of simplicity, we suppose $\frac{1}{2}\, q \sqrt{3} = kr$, where $k = \sqrt{3} \,.\, tg\, \frac{1}{2}\psi$, we get:

$$k^2 - 2 = \cos\varphi_1 \cos\varphi_2 - 2 \sin\varphi_1 \sin\varphi_2 + k\,(\cos\varphi_1 + \cos\varphi_2).$$

In this equation nothing is found any more of the system of coördinates, hence we get equations of the same form for the distances DE and DF.

We thus get three equations with φ_1, φ_2 and φ_3 as unknown quantities, viz.:

$$k^2 - 2 = \cos\varphi_1 \cos\varphi_2 - 2 \sin\varphi_1 \sin\varphi_2 + k\,(\cos\varphi_1 + \cos\varphi_2) \quad . \quad (1)$$

$$k^2 - 2 = \cos\varphi_1 \cos\varphi_3 - 2 \sin\varphi_1 \sin\varphi_3 + k\,(\cos\varphi_1 + \cos\varphi_3) \quad . \quad (2)$$

$$k^2 - 2 = \cos\varphi_2 \cos\varphi_3 - 2 \sin\varphi_2 \sin\varphi_3 + k\,(\cos\varphi_2 + \cos\varphi_3) \quad . \quad (3)$$

In general, only a few very particular values of the unknown quantities satisfy three equations with three unknown quantities.

This will not be so, if the equations are dependent, in that case an infinite number of solutions is possible.

Thus, in order to ascertain whether a mobile form of the six-ring is possible, we must investigate whether the equation (3) is dependent on (1) and (2).

For this purpose we proceed as follows:

φ_2 and φ_3 we represent both by φ'. From (1) as well as from (2) it is then found:

$$sin\ \varphi' = \frac{-b \pm \sqrt{b^2 - 4\ ac}}{2a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$cos\ \varphi' = \frac{-b' \pm \sqrt{b'^2 - 4ac'}}{2a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $a = (k + cos\ \varphi_1)^2 + 4\ sin^2\ \varphi_1$

$b = 4\ sin\ \varphi_1\ (k^2 - 2 - k\ cos\ \varphi_1)$

$c = \{(k^2 - 2)^2 + k^2\ cos^2\ \varphi_1 - 2\ k (k^2 - 2) cos\ \varphi_1 - (k + cos\ \varphi_1)^2\}$

$b' = 4\ cos\ \varphi_1 + 2\ k\ cos^2\ \varphi_1 - 2\ k\ (k^2 - 2)$

$c' = (k^2 - 2)^2 - 4\ sin^2\ \varphi_1 + k^2\ cos^2\ \varphi_1 - 2\ k\ (k^2 - 2)\ cos\ \varphi_1$

For each value of φ_1 we now find two values of φ' (between $+90°$ and $-90°$).

In the most general case we have $\varphi_2 \neq \varphi_3$; we must therefore assign one of the values of φ' to φ_2 and the other value to φ_3.

Now, if we substitute the values thus obtained from *sin* φ_1, *sin* φ_2, *cos* φ_1 and *cos* φ_2 in (3), we get, after working out, $0 = 0$, from which it follows that equation (3) is dependent on the equations (2) and (1), and the relations which φ_1, φ_2 and φ_3 must satisfy, are therefore always completely given by the equations (1) and (2).

Let us imagine a system of rectangular coordinates XYZ in space and let φ_1 be set off on the X-axis, φ_2 on the Y-axis and φ_3 on the Z-axis, then equation (1) represents a closed area parallel to the Z-axis, equation (2) an area parallel to the Y-axis and equation (3) an area parallel to the X-axis.

The equations (1) and (2) together represent a line in space, viz. the intersection of the areas represented by (1) and (2).

Equation (3) must now also contain the spatial line represented by (1) and (2), *which line symbolizes the mobile form of the six-ring.*

The projection of the line on a plane which cuts off equal pieces from the X- and the Y- and the Z-axes, is a circle.

The spatial line passes through all the octants, with the exception of the first octant and the seventh octant (which lies diametrically opposite the first one).

We can see this as follows:

If we consider form (4), we see that for a positive value of φ_1, b is always positive (for the carbon six-ring). Hence we obtain either two negative roots for φ' or one positive root and a negative one for φ'. From this it is plain that the spatial line cannot contain any points for which φ_1, φ_2 and φ_3 all three have *simultaneously* the same sign. Consequently, the line does not pass through the first and the seventh octant.

In the table 1 we indicated several values belonging together of φ_1, φ_2 and φ_3 for the carbon six-ring.

TABLE I.

φ_1^0	φ_2^0	φ_3^0
+ 0	+ 63	— 63
+ 10	+ 57	— 67
+ 20	+ 49	— 73
+ 30	+ 40	— 74
+ 35	+ 35	— 74
+ 40	+ 30	— 74
+ 49	+ 20	— 73
+ 57	+ 10	— 67
+ 63	+ 0	— 63
+ 67	— 10	— 57
+ 73	— 20	— 49
+ 74	— 30	— 40
+ 74	— 35	— 35
+ 74	— 40	— 30

Fig. 2 gives the graphical representation of formula (1).

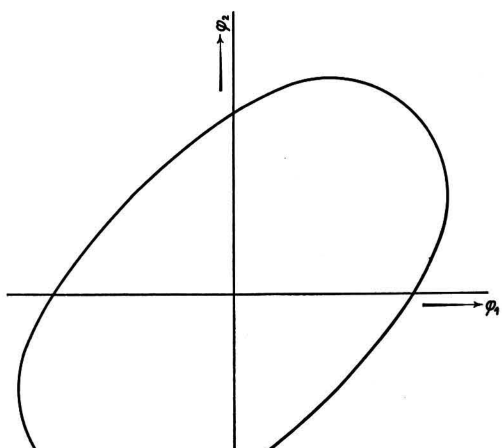

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Fig. 2.

In the case of the carbon six-ring we have:

$$k = tg\,\tfrac{1}{2}\,\psi\sqrt{3} = \sqrt{6} = 2.45.$$

Not all the points common to the areas given by the equations (1), (2) and (3) are given by the spatial line, which is here considered. We get another particular solution of the three equations if we suppose that $\varphi_1 = \varphi_2 = \varphi_3$. We then get as solution: $\varphi_1 = \varphi_2 = \varphi_3 = \pm$ *arc.* cos $- {}^1/_3\, k$ and $\varphi_1 = \varphi_2 = \varphi_3 = \pm$ *arc. cos* $- k$. For the carbon six-ring only the former solution is possible, for which we calculate: $\varphi_1 = \varphi_2 = \varphi_3 = \pm 35^\circ$.

According to the foregoing (viz. that the spatial line cannot contain any points for which φ_1, φ_2 and φ_3 have simultaneously the same sign), the particular point which is found cannot lie on the spatial line. It is equally impossible that it forms part of another line, for only in the case of one of the equations being dependent on the two others, a *line* is at all possible. Hence, the particular point which is found is an isolated point in space, *which symbolizes the fixed configuration of the six-ring.*

Thus, along strictly mathematical lines, we have deduced the fixed as well as the mobile form from the carbon six-ring. In the case of a diagrammatical representation in a system of coördinates with φ_1, φ_2 and φ_3 as axes, the mobile form is symbolized by a spatial line passing through all the octants, with the exception of the first and the seventh octant, and the fixed form is symbolized by a point in the first octant and a point in the seventh octant.

In order to gain some insight in the various possibilities of motion of the six-ring, we shall now deduce and make a drawing of some particular positions.

The fixed configuration.

Of this only one formation is naturally possible.

$$\varphi_1 = \varphi_2 = \varphi_3 = arc.\cos {}^1/_3\, k = \pm 35^\circ.$$

If we number the vertices of the six-ring (see fig. 3) from 1 up to 6

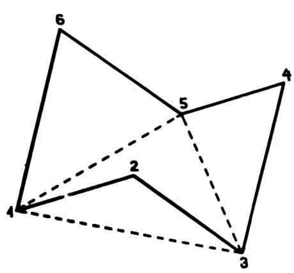

Fig. 3.

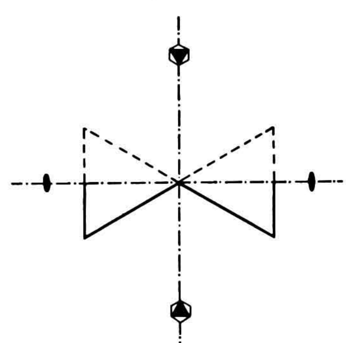

Fig. 4.

inclusive and project the six-ring on a plane which bisects the line 1—4 perpendicularly and if we denote what lies before the plane by means of drawn lines and what lies behind the plane by means of dotted lines, then we get what is easy to see: fig. 4.

At the same time it can be demonstrated very simply that the opposite sides run parallel in pairs.

Symmetry elements: m III′ 3 II (3 I′) 3 S [1]).

Classification: ditrigonal skalenoedric.

The mobile configuration.

In order to calculate various particular positions of this configuration, we again recall form (5), viz.

$$\sin \varphi' = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad . \; . \; . \; . \; . \; . \; . \; , \qquad (5)$$

where a, b and c, indicated elsewhere, represent functions of φ_1.

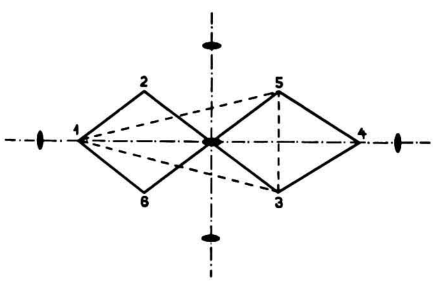

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Fig. 5.

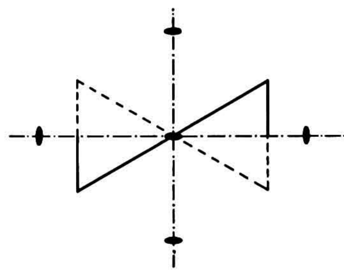

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Fig. 6.

$\varphi_1 = 0$.

For $\varphi_1 = 0$ we calculate $\varphi_2 = \pm 63°$ $\varphi_3 = \mp 63°$.

Elements of symmetry: II II II. (see fig. 5 and 6, projection in fig. 6 as in fig. 4).

Thus classification: Rhombic-bisfenoidic.

$\varphi_2 = \varphi_3$.

For $\varphi_2 = \varphi_3$, we find from form. (3) and also from form. (5)

$$\varphi_2 = \varphi_3 = \pm 35°.$$

From form. (5) it follows for $\varphi_2 = \varphi_3$: $\sqrt{b^2 - 4ac} = 0$.

Let the value belonging to φ_1, be φ_m. In case of φ_1 becoming greater than φ_m, $(b^2 - 4ac)$ would become negative. Since this would yield imaginary values for φ_2 and φ_3, φ_m represents the maximal value of φ_1.

We calculate: $\varphi_m = \mp 74° \, 15'$.

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1) m = centre of symmetry; III = axis of threefold symmetry; II = axis of binary symmetry. S = plane of symmetry; III′ = axis of sixfold complex symmetry; I′ = axis of binary complex symmetry.

Elements of symmetry II^p SS[1]. Classification: Rhombic-pyramidal.
It is easy to demonstrate that 2—3 runs parallel to 5—6 (see fig. 7 and 8).

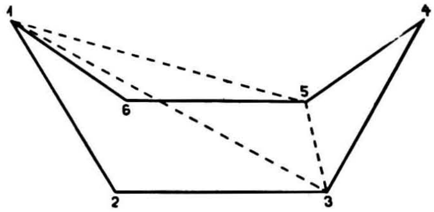

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Fig. 7.

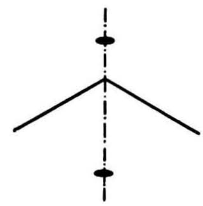

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Fig. 8.

The case $\varphi_2 = -\varphi_3$ can be transferred to the case: $\varphi_1 = 0$. The case $\varphi_1 =$ maximal up to the case $\varphi_2 = \varphi_3$.
In the general case, when $\varphi_1 \neq \varphi_2 \neq \varphi_3$ is true, the six-ring has only one element of symmetry, namely a polar axis of binary symmetry.

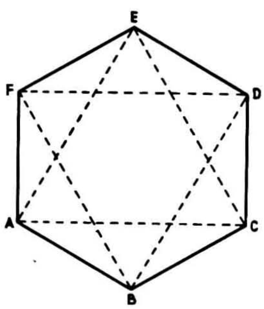

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Fig. 9.

We can demonstrate this as follows: (see fig. 9).
If we project *ED* and *BC* on a plane perpendicular to *DC* and call the angle between these projections β (see fig. 12), we can deduce a relation between φ_1, being the angle between the plane of $\triangle$ *ABC* and the plane of $\triangle$ *ACE* and β. (The deduction is given later on, see form (8)).
The same relation we find for φ_1', being the angle between the plane of $\triangle$ *FED* and the plane of $\triangle$ *FBD*.
Thus $\varphi_1 = \varphi'_1$ (only for the fixed configuration we have: $\varphi_1 = -\varphi'_1$) and also $\varphi_2 = \varphi'_2$, $\varphi_3 = \varphi'_3$.
Now, the reader can easily understand that a polar axis of binary symmetry must be possible; this axis standing perpendicular on a plane, which bisects the angle between the planes of $\triangle$ *ACE* and $\triangle$ *FBD*.
We find thus in the case $\varphi_1 \neq \varphi_2 \neq \varphi_3$ one element of symmetry, namely: II^p.
Classification: sfenoidic.

In the literature the fixed configuration is being constantly denoted by "chair position" and the mobile configuration by "bed position". These names are very characteristic and clear and can therefore safely be preserved. It is, however, to be borne in mind that the "bed position" is

[1]) With *p* we denote that the axis is a polar axis of symmetry.

only one of the possible formations to which the mobile configuration is liable (viz. the formation for which $\varphi_2 = \varphi_3$ and $\varphi_1 =$ maximal) and that therefore "bed-position" and "mobile configuration" are not to be identified (as is often done).

In many cases the so-called "bed-position" is even the most improbable of all possible formations of the mobile configuration (e.g. in the case of molecules with equal atoms in the 1.4 places). BÖESEKEN, who introduced the here-mentioned names had a clear conception about this. To quote him: [1]) "Es kommt darauf an, dass diese Ringsysteme fortwährend in Bewegung sind, verschiedene Lagerungen im Raum einnehmen, symmetrische und unsymmetrische, aber immer so, dass der Winkel zwischen den Affinitäten 109° 28′ bleibt".

It only remains for us to invent a characteristic name for the particular formation, where $\varphi_1 = 0$ and $\varphi_2 = -\varphi_3$. For lack of better we shall designate this formation for the present as "crossed formation".

In table II we give a survey of the various configurations and formations of the single six-ring.

TABLE II.
The single six-ring.

Configuration	Formations	φ_1	φ_2	φ_3	Elements of symmetry	Classification
fixed	chair	± 35°	± 35°	± 35°	m III′ 3 II (3 I′) 3 S	ditrigonal skalenoedric
mobile	irregular				II^p	sfenoidic
	crossed	0	± 63°	∓ 63°	II II II	rhombic-bisfenoidic
	bed	± 74°	∓ 35°	∓ 35°	II^p S S	rhombic-pyramidal

Let the mobile configuration of the six-ring occupy successively all possible formations, then the angle φ_1 moves between its maximum (with the carbon-ring $+74°$) and its minimum (with the carbon-ring $-74°$). Hence, if we let the ring carry out a continuous motion and if we set off φ_1 on the one axis, and the time on the other axis, we obtain the motion of the ring diagrammatically represented as a wave-line.

The wave-line, however, can take up various possible forms, for we are at liberty to let φ_1 move according to whatever equation of motion we want. The angles φ_2 and φ_3 will describe some wave line or other, just as φ_1. If, however, we want to class φ_1, φ_2 and φ_3 in *one* diagrammatical representation, it will be good, for the sake of surveyability, to choose the equation of motion of φ_1 in such a manner as to render φ_2 and φ_3 capable of satisfying the same equation of motion, in other words such that φ_1, φ_2 and φ_3 describe three equal and similar wave-lines, which, however, don't coincide.

[1]) B. **58**, 1472 (1925); see also: B. **56**, 2411—2413 (1923).

This will only be possible in the case of *one* particular equation of motion, which can be found as follows:

As we have already discussed, the spatial line denoting the relation between the φ_1, φ_2 and φ_3 projects itself as a circle on a plane cutting off equal pieces from the X-, Y- and Z-axes. Now, if we let a radius vector revolve in this circle with uniform velocity, we are able to find for each angle of deflection of the radius vector: α an accessory value for φ_1. Thus, we can express φ_1 in terms of the angle α which the radius vector makes with a fixed radius of the circle. It is now easy to see that for φ_2 and φ_3 the same function must be found, on the understanding that for α: $(\alpha + 120°)$ and $(\alpha + 240°)$ are to be written respectively.

Consequently, the diagrammatical representation of the motion of the six-ring is given by three wave lines with mutual phase differences of 120^{c}.

Complicated higher exponents appear to be found for the functions; it

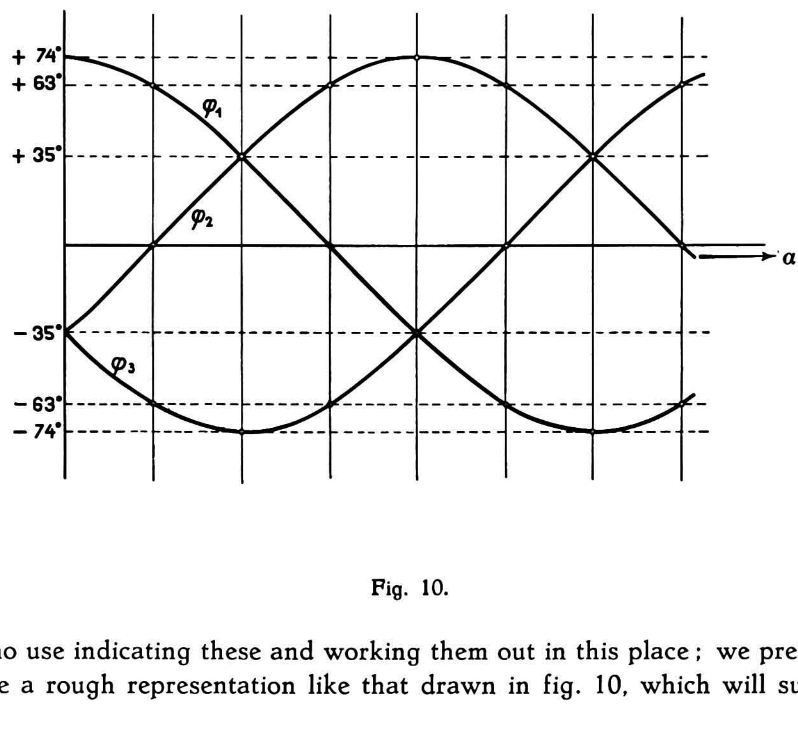

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Fig. 10.

is no use indicating these and working them out in this place; we prefer to give a rough representation like that drawn in fig. 10, which will suffice.

The double six-ring.

Now that we have ascertained all the possibilities of the single six-ring, we shall deduce from these what combinations of formations are possible for two six-rings, which have two carbon atoms in common.

For this purpose we shall project the valences of the carbon atoms A and B (see fig. 11) on a plane perpendicular to the line AB (see fig. 12). The three valences of A, not being perpendicular to the plane of projection, will project themselves as three lines making angles of $120°$ with one another. This is equally true for B. We shall denote the valences of A by 1, 2 and 3 and the valences of B by $1'$, $2'$ and $3'$. Now we shall first consider the general case that 1 makes any angle β ($< 60^\circ$) with $1'$. Let us suppose

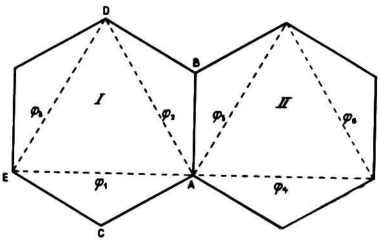

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Fig. 11.

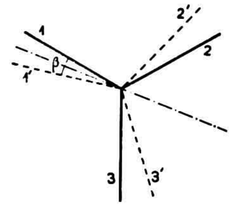

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Fig. 12.

that we fix 1 and $1'$ in ring I, then we have the following valence pairs for ring II at our disposal: (see fig. 12) $22'$ and $33'$ (*cis*) and $32'$ and $23'$ (*trans*) [1].

Let us first consider the *cis-combinations*. As it is easy to see, case $22'$ yields the same as case $33'$. Hence we must construct ring I on the valences 1 and $1'$ and ring II on the valences 2 and $2'$; and we must ascertain how many possibilities present themselves with a given position of 1 and $1'$.

Of ring 1 (see fig. 11) AB, AC and BD are fixed, hence the distance DC is given. This means that the angle φ_1, which the plane of $\triangle ACE$ makes with the plane of $\triangle EAD$ is determined.

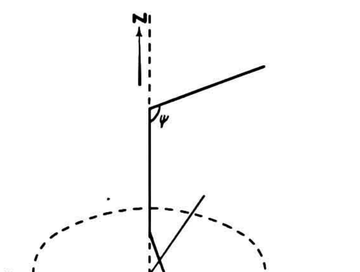

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Fig. 13.

We can now submit the question to ourselves which values of φ_1 belong to a fixed value of β. For this purpose we must express φ_1 in terms of β. We can do this by expressing the distance DC (see fig. 11) which we shall call: s, in terms of β and also in terms of φ_1. By eliminating s from the two equations thus obtained, we find the required relation between φ_1 and β.

In order to express s in terms of β, we introduce a system of coordinates, in which the Z-axis coincides with the line AB (see fig. 11). This is represented by fig. 13.

ψ represents the tetrahedron angle. On working out analytically, we get:

$$s^2 = \frac{41}{9}p^2 - \frac{16}{9}p^2 \cos\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

[1]) The names cis- and trans- may be understood by considering the plane bisecting the angle between the projected valences 1 and $1'$; with the cis- both valences which are in consideration are at the same side of the plane, with the trans- they are each on one side (see fig. 12).

Now we still have to express s in terms of φ_1. If we make a section perpendicular to the plane of drawing, according to DC (see fig. 11) we get fig. 14.

With the aid of fig. 14, we easily find

$$s^2 = \frac{7}{3} p^2 + \frac{2}{3} p^2 \sqrt{6} \cos \varphi_1 \quad \ldots \ldots \quad (7)$$

Through combination of form (6) and (7) we find:

$$10 - 8 \cos \beta = 3 \sqrt{6} \cos \varphi_1 \quad \ldots \ldots \quad (8)$$

Hence if, diagrammatically, we plot β against φ_1, we get fig. 15.

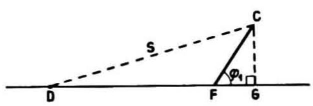

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Fig. 14.

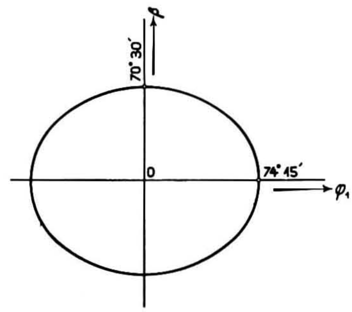

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Fig. 15.

To each value of β thus belong two equal values of φ_1, but of opposite sign. To each φ_1 value belong two φ_2 and two φ_3 values, viz.

$$\varphi_2 = arc.\, sin \frac{b \pm \sqrt{b^2 - 4\,ac}}{2a} \quad \text{and} \quad \varphi_3 = arc.\, sin \frac{b \mp \sqrt{b^2 - 4\,ac}}{2a}$$

(See formula 5).

If, however, β as well as φ_1 are fixed, only *one* φ_2 and *one* φ_3 value will satisfy.

For $\varphi_1 = 0$ $\quad \varphi_2 = \pm\, 63°$ and $\varphi_3 = \mp\, 63°$ holds true.

Now, if φ_2 is the angle which plane ABD makes with plane ADE (fig. 11), then $\varphi_2 = +\,63°$ and $\varphi_3 = -\,63°$ can only satisfy for a *positive* angle β. For a *negative* angle β only $\varphi_2 = -\,63°$ and $\varphi_3 = +\,63°$ can satisfy.

From the foregoing it is clear that for a definite value of β only *one* formation of the ring is possible; that, however, when AB, AC and DB (see fig. 11) are fixed with respect to a spatial system of coordinates, this ring can occupy *two* different positions with regard to the system of coordinates (viz. the position in which φ_1 = positive and the position in which φ_1 = negative).

If one position is denoted by γ and the other by ϑ we have the following possibilities, when combining the two six-rings: $\gamma\gamma$, $\gamma\vartheta$, $\vartheta\gamma$ and $\vartheta\vartheta$.

Now, $\gamma\vartheta$ is identical with $\vartheta\gamma$, for from the one we can get the other by reflecting with respect to a plane perpendicular to the plane of drawing and bisecting the angle between 3 and 3′ (see fig. 12).

$\gamma\gamma$ and $\vartheta\vartheta$ are not identical, for they cannot be obtained from each other by reflection.

Thus, we have only three different possibilities:

$$\gamma\gamma,\ \gamma\vartheta \text{ and } \vartheta\vartheta.$$

Symmetry elements of $\gamma\gamma$ and $\vartheta\vartheta$: (I′) S (S is the plane bisecting the angle between 3 and 3′; see fig. 12); thus the classification is: Domatic.

The $\gamma\vartheta$ formation has no elements of symmetry, belongs thus to the asymmetrical class.

For peculiarities of particular formations see table III.

We get a special case if one of the rings occurs in the fixed form. Then $\varphi_1 = \varphi_2 = \varphi_3 = arc.\ cos\ {}^1/_3 \sqrt{6} = \pm 35^\circ$ holds true.

From form. (8) it then follows: $\beta = 60^\circ$.

Ring II can now likewise occur in the fixed form; in projection we get then fig. 22; so $\varphi_4 = \varphi_5 = \varphi_6 = \pm 35^\circ$.

Ring II, however, can also have the mobile configuration, thus the formation in which $\varphi_4 = +35^\circ$, $\varphi_5 = -74^\circ$, $\varphi_6 = +35^\circ$ and $\varphi_4 = -35^\circ$, $\varphi_5 = +35^\circ$, $\varphi_6 = -74^\circ$.

We have ascertained all the possibilities presenting themselves in the case of two six-rings which have been coupled in *cis-position*. We shall now try to find what possibilities present themselves in the case of two six-rings being coupled in trans-position.

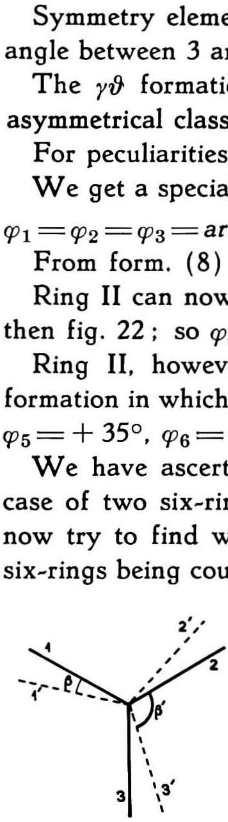


Fig. 16.

If we project in the same way as in fig. 11, we get fig. 16.

We must now build ring I on 1 and 1′ and ring II on 2 and 3′. If we call the projection of the angle between 2 and 3′: β', then $\beta' = 120^\circ - \beta$ holds true.

Now, it follows from formula (8) that β and β' may not become greater than 70° (so for $\varphi_1 = 0$). If $\beta = 50^\circ$ then $\beta' = 70^\circ$ and vice versa. Consequently, β and β' can only move between the limits 50° and 70°. Hence, we can never build a ring on 2′ and 3, unless β is negative (if the angle β which is drawn is taken as positive); but in this case a ring on 2 and 3′ is impossible.

In analogy to the discussions about the six-rings with cis-coupling, in this case we have the following possibilities:

$$\gamma_1\gamma_2,\ \gamma_1\vartheta_2,\ \vartheta_1\gamma_2,\ \vartheta_2\vartheta_2.$$

In the case of cis-coupling of two rings with mobile configuration, both rings have, each considered on its own, the same formation. This does not hold in the case of trans-coupling, therefore we designate the various positions of ring I with γ_1, and ϑ_1, and the various positions of ring II with γ_2 and ϑ_2; while in the case of cis-coupling we did not use indices.

In the last-mentioned case $\gamma_1\vartheta_2$ is *not* identical with $\gamma_2\vartheta_1$; for they cannot be obtained from one another by reflection. All formations in the case of trans-coupling of two rings with mobile configurations have no elements of symmetry, they are thus *asymmetrical.*

We get a special case if one of the rings occurs in the fixed configuration. Then $\beta = 60^\circ$, hence $\beta' = 60^\circ$. Ring II can now either occur in the fixed configuration or in a particular formation of the mobile configuration (the formation for which: $\varphi_4 = +35^\circ$, $\varphi_5 = +35^\circ$, $\varphi_6 = -74^\circ$.

If both rings occur in the fixed configuration, we get in projection fig. 23. Elements of symmetry: *m* II (I′ I′) *S*. Classification: prismatic.

If we plot φ_1 against φ_4 (see fig. 11) we get the diagrammatical representation of fig. 17*a* in the case of two six-rings with cis-coupling. Two lines making angles of 45° with the φ_1, and the φ_4 axis represent the geometrical place of all possible values of φ_1 and φ_4 which belong together.

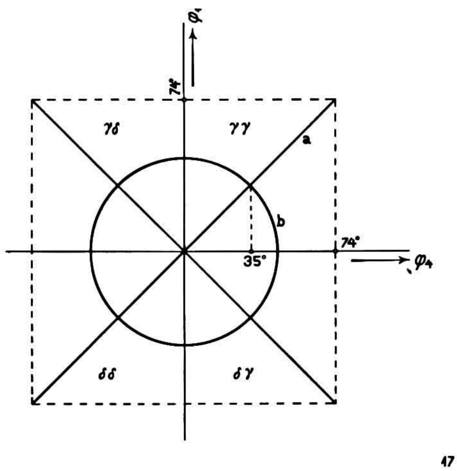


Fig. 17.

For two six-rings in trans-coupling we get the condition of fig. 17*b*.

By expressing β in terms of φ_1, and $\beta' = (120 - \beta)$ in terms of φ_4 through form. (8) and then eliminating β, we obtain the relation between φ_1 and φ_4, of which the diagrammatical representation has been drawn in fig. 17*b*.

This relation is as follows:

$$3(\cos^2\varphi_1 + \cos^2\varphi_4) - 5\sqrt{6}(\cos\varphi_1 + \cos\varphi_4) + 3\cos\varphi_1\cos\varphi_4 + 14 = 0.$$

From the diagrammatical representation it is obvious that the mobility of two six-rings in trans-coupling is much slighter than of two six-rings in cis-coupling.

In table III we give a summary of the configurations and formations of the double six-rings deducted here.

TABLE III.
The double six-ring.

coupling	configuration ring I	configuration ring II	configuration I + II	Formations	elements of symmetry	classification
cis	mobile	mobile	very mobile	irregular $\gamma\gamma$, $\gamma\vartheta$, $\vartheta\vartheta$	none	asymmetrical
				bed-bed $\gamma\gamma$	II^p (I′ I′) S S	rhombic pyramidal
				bed-bed $\gamma\vartheta$	S	domatic
				bed-bed $\vartheta\vartheta$	II^p (I′ I′) S S	rhombic pyramidal
				crossed-crossed	m II (I′ I′) S	prismatic
	fixed	mobile	fixed	bed-chair	none	asymmetrical
	fixed	fixed	fixed	chair-chair	II^p	sfenoidic
trans	mobile	mobile	slightly mobile	irregular $\gamma_1\gamma_1$, $\gamma_1\vartheta_2$, $\vartheta_1\gamma_2$, $\vartheta_1\vartheta_2$	none . . .	asymmetrical
	fixed	mobile	fixed	bed-chair	none	asymmetrical
	fixed	fixed	fixed	chair-chair	m II (I′ I′) S	prismatic

In order to make a correct survey possible, we shall draw the symmetrical formations together.

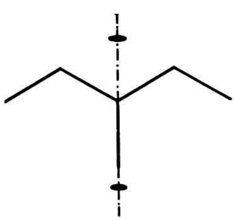

cis-bed-bed $\gamma\gamma$
18

Fig. 18.
II^p (I′ I′) S S
rhombic pyramidal
(rhombic)

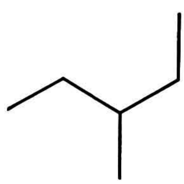

cis-bed-bed $\delta\gamma$
19

Fig. 19.
S
domatic (monoklin)

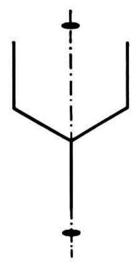

cis-bed-bed $\delta\delta$
20

Fig. 20.
II^p (I′ I′) S S
rhombic pyramidal
(rhombic)

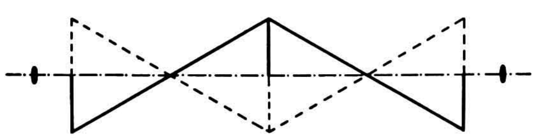
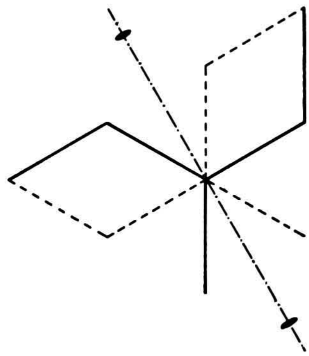

cis-crossed-crossed
21

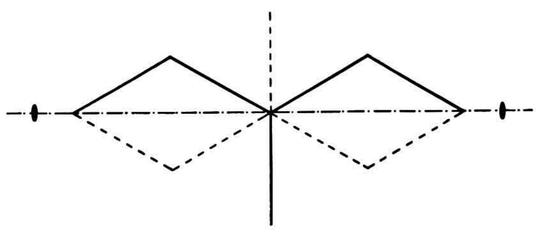
Fig. 21.
m II (I′ I′) S prismatic (monoklin)



cis-chair-chair

22

Fig. 22.
II^P sfenoidic (monoklin)



trans-chair-chair

23

Fig. 23.
m II (I′ I′) S prismatic (monoklin)

Summary.

In the foregoing we have systematically investigated all the possibilities which present themselves in the single and double carbon six-rings.

The only forces which we allowed to carry weight with our investigation were the "forces of affinity" and the "directing forces". We have assumed the directing forces to be great enough to prevent somewhat important changes of valence angles and on this basis we have founded our investigation.

On this basis we deduced on strictly mathematical grounds that two configurations are possible for the carbon six-rings. One of these configurations shows an infinite number of formations continuously passing into one another, with the other only one formation is possible; hence the names "mobile configuration" and "fixed configuration". We have indicated in what way the characterizing magnitudes for each formation are to be computed and have indicated the symmetry elements for the formations which receive consideration.

Quite analogically, we have extended the discussions on the single six-ring to the double six-ring.

We have, however, entirely neglected the steric forces and the dipole forces. If we could consider these, we should be able to point out which of the configurations and formations found here are the most probable ones. Next time we hope to come back on this question.

Anticipating the facts which we shall have to state then, we only wish to point out that the spatial formation which is always being given for the cis-dekalin, the cis-bed-bed $\gamma\gamma$ formation (see fig. 18) is certainly not the most probable one; we shall rather have to choose the cis-chair-chair configuration (see fig. 22).

We equally want to point to the fact that perhaps some of the isomerism cases of the six-rings, which are being recorded as cis-trans-isomerism, must be reduced to the configuration isomerisms which we have traced here; for there is still too little attention being paid to the latter isomerism possibilities.

In connection with these problems of isomerism, we want to draw attention to a systematical classification of isomerism given by Ir. F. TELLEGEN in Part IV of his dissertation. Delft 1934 (yet to appear).

Lastly I want to express my thanks to Prof. BÖESEKEN, Prof. ZWIKKER and Ir. TELLEGEN for the discussions which I might have with them about the questions treated in this paper.

Delft, April 1934.

Physical Laboratory of the Technical High School Delft.

Botany. — *On the pea test method for auxin, the plant growth hormone.* By F. W. WENT. (From the WILLIAM G. KERCKHOFF Laboratories of the Biological Sciences, California Institute of Technology, Pasadena, California).

(Communicated at the meeting of September 29, 1934).

Introduction.

For experiments on auxin the test method which has been used almost exclusively is the *Avena* method, described by me (1928) and modified by VAN DER WEY (1931). This test is quantitative and relatively easy, but it requires a constant and high humidity and constant temperature, while all operations have to be carried out in red or orange light. To