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978-1-108-08029-3 - The Arrangement of Atoms in Space
Jacobus Henricus Van 't Hoff
Excerpt
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INTRODUCTION

EVERY time I write on stereochemistry a new name has to be added to complete the history of its development. In my 'Dix Années dans l'Histoire d'une Théorie' I mentioned Gaudin and his 'Architecture du Monde' (1873); then Meyerhoffer in his 'Stereochemie' added Paterno,¹ who in 1869 proposed to explain isomeric bromethylenes by a tetrahedral grouping round carbon; and Rosenstiehl,² who in the same year represented benzene by six tetrahedra; and now Eiloart, in his 'Guide to Stereochemistry,' goes back to Swedenborg's 'Prodromus Principiorum Rerum Naturalium sive Novorum Tentaminum Chymicam et Physicam Experimentalem geometrice explicandi.'³ Certainly, then, we were not over-hasty, Le Bel and I, when we published our ideas (November and September 1874) in the 'Bulletin de la Société Chimique' and in the 'Voorstel tot Uitbreiding der Structuur-Formules in de Ruimte' respectively. That shortly before this

¹ *Giorn. di Scienze Naturali ed Econ.* vol. v., Palermo; *Gazz Chim.* 1893, 35.

² *Bull. Soc. Chim.* 11, 393. ³ Jan Osterwyk, Amsterdam, 1721

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we had been working together in Wurtz's laboratory was purely fortuitous; we never exchanged a word about the tetrahedron there, though perhaps both of us already cherished the idea in secret. To me it had occurred the year before, in Utrecht, after reading Wislicenus' paper on lactic acid. 'The facts compel us to explain the difference between isomeric molecules possessing the same structural formulæ by the different arrangement of their atoms in space': this was the sentence which remained in my memory, and which I have since used as a motto; on trying to refer to it I could not find it again, and so cannot give the reference here.

On the whole, Le Bel's paper and mine are in accord; still, the conceptions are not quite the same. Historically the difference lies in this, that Le Bel's starting point was the researches of Pasteur, mine those of Kekulé.

The researches of Pasteur had made plain the connection between optical activity and crystal-form, and had led to the idea that the isomers of opposite rotatory power correspond to an asymmetric grouping and to its mirrored image. Indeed, the possibility of a tetrahedral grouping was suggested.¹ Le Bel closely follows Pasteur, then, when he sees this grouping in the four atoms or radicals—inactive bodies all different—united to carbon.

My conception is, as Baeyer pointed out at the Kekulé festival, a continuation of Kekulé's law of the quadrivalence of carbon, with the added hypothesis

¹ *Leçons sur la Dissymétrie Moléculaire.*

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that the four valences are directed towards the corners of a tetrahedron, at the centre of which is the carbon atom.

Practically our ideas, so far as they concern the asymmetric carbon, amount to the same thing—explanation of the two isomers by means of the tetrahedron and its image, disappearance of this isomerism when two groups become identical, through the resulting symmetry and identity of the two tetrahedra.

In the case of doubly linked carbon, however, there arises the possibility of a difference. Here, too, four groups are connected, and Le Bel considers that *à priori* only so much is known about their position, that of the two pairs one pair lies nearer to one carbon, the other pair to the other carbon. It may happen, then, that ethylene derivatives may have no symmetry in their molecules—they may be active. Carrying out my tetrahedral grouping I concluded that the four groups are in one plane with the carbon, this being accordingly the plane of symmetry of all ethylene derivatives; therefore no optical activity can occur. As regards this, Le Bel¹ at first altered his opinion in my favour, but later² altered it back again.

Of course, the facts must decide; as, however, Liebermann informs me, specially for this edition, that bromocinnamic acid from active cinnamic acid dibromide is inactive, and Walden states that fumaric acid from active bromosuccinic acid is inactive, it

¹ *Bull. Soc. Chim.* 37, 300.

² *Ibid.* [3], 7, 164, 1892.

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appears that, in accordance with facts previously known, the simple conception of the tetrahedral grouping and of the development of structural chemistry to stereochemistry on these lines is still permissible.

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CHAPTER I

THE ASYMMETRIC CARBON ATOM

I. STATEMENT OF THE FUNDAMENTAL CONCEPTION

The molecule a stable system of material points.—When we arrive at a system of atomic mechanics the molecule will appear as a stable system of material points; that is the fundamental idea which continually becomes clearer and clearer when one is treating of stereochemistry; for what we are dealing with here is nothing else than the spatial—*i.e.* the real—positions of these points, the atoms.

I choose this fundamental conception as the starting point for this reason, that there is already evident in the rough outlines of this future system of atom mechanics a very considerable simplification, which I will here discuss.

One might suppose that the arrangement of the atoms in the molecule would be something like that in a system of planets, equilibrium being maintained by attraction and motion, by equality between centripetal and centrifugal force. I will try to show

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that we must exclude this motion; and this as a necessary consequence of simple thermodynamic considerations.

As the partial decomposition of salts containing water of crystallisation shows, and, generally, as the formula $\frac{d.l.K}{d.T} = \frac{q}{2T}$ requires, the alteration of any dissociation phenomenon with the temperature is always of this nature, that while on cooling the decomposition gradually becomes less, yet it ceases only at absolute zero ($T=0$). But this is as much as to say that the internal stability of the molecule is attained only at absolute zero, *i.e.* in the absence of all internal motion. Otherwise interaction with another molecule is an essential condition of equilibrium.

This law is seen to be perfectly general when we consider that every compound would undergo visible dissociation at a sufficiently high temperature, thus fulfilling the above conditions.

We may add, as a necessary consequence, that the state of things at absolute zero is to be explained solely by atomic mechanics, thermodynamics having nothing to do with this explanation, because thermodynamics comes into play only when, at a temperature above zero, dissociation begins; and we may add further that, to render equilibrium possible, instead of the centrifugal force which ordinarily acts, there must be a repulsion, for the action of matter (atoms) alone appears insufficient, and there must be something else, perhaps electricity.

For stereochemistry the above considerations are important as showing that motion of the atoms may for the present be neglected, the state of things being tacitly assumed to be as it would be at absolute zero. Indeed, the phenomena of isomerism are in a certain sense opposed to motion; they are certainly not a consequence thereof; for when the temperature rises they ultimately disappear, and become constantly more marked as it falls. He who chooses to assume motion, however, may conceive the motionless systems here to be described as the expression of the position of certain points about which the motion, doubtless a periodical motion, takes place.

Insufficiency of structural chemistry. The asymmetric carbon atom.—Everyone is now familiar with the fact, only occasionally observed in 1874, that the simple structural formulæ are insufficient to explain the existing cases of isomerism; and that, to consider first carbon-compounds of the type $C(R_1R_2R_3R_4)$ —*i.e.* compounds in which four separate groups or atoms are combined with the carbon—an extra isomerism occurs when these four groups are different, and disappears if but two of them become the same. Assuming a fixed position of the groups round the carbon atom, only a tetrahedral grouping brings us to the same conclusion, as figs. 3 and 4 show: these become identical when R_3 and R_4 become the same; while this leaves the isomerism unaffected if we represent the formula in one plane (figs. 1 and 2).

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To illustrate the matter with models we may use the cardboard tetrahedra, the different groups being represented by attaching caps made of coloured paper : *e.g.* R_1 white ; R_2 yellow ; R_3 black ; R_4 red ; to make the two tetrahedra alike an extra pair, say a pair of black caps, may be used, and may be placed on R_4 , for instance. The Kekulé models, improved by v. Baeyer, and sold by Sendtner (Schillerstrasse 22, München), may be used for the same purpose.

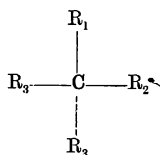


Fig. 1.

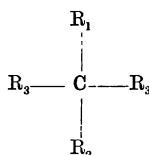


Fig. 2.

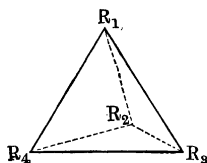


Fig. 3.

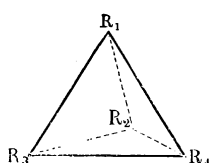


Fig. 4.

A word as to the shape of the tetrahedra. If we wish to represent only the two possible formulæ given above, their peculiar lack of symmetry, their object-and-image relation, and the way they may be rendered identical, the regular tetrahedron with variously coloured corners quite suffices. But if the mechanics of the atoms is to be taken into account, we must admit, without making any hypothesis as to the nature of the forces acting, that in general

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these forces will be different between different groups, and the same between similar groups; and then the difference between fig. 3 and fig. 4 must be expressed in the dimensions also. The edges $R_1 R_4$, $R_1 R_3$, &c., will then be different in the two figures, but the corresponding dimensions in each, $R_1 R_4$ in fig. 3, $R_1 R_4$ in fig. 4, &c., will be equal. The two tetrahedra then express by their shape their object-and-image relation (so-called enantiomorphism), and at the same time a mechanical necessity is satisfied. It is now superfluous to vary the colours of the corners; but the way in which identity arises can now be shown only by two more models in which, in accordance with the fundamental requirement of mechanics, R_4 and R_3 take corresponding positions which are equally distant from the plane of symmetry now called into existence, and passing through $R_1 R_2$; for we now have

$$R_4 R_1 = R_3 R_1 \text{ and } R_4 R_2 = R_3 R_2.$$

II. EXPERIMENTAL CONFIRMATION OF THE
 FUNDAMENTAL CONCEPTION

A. CHARACTER OF THE ISOMERISM DUE TO THE
 ASYMMETRIC CARBON

Optical activity.—The isomerism expressed by the difference between the two enantiomorphous forms is characterised in the first place by this, that it is to be expected when the carbon is united to four different groups, and only then.

But in the second place all the molecular dimen-

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sions being equal in the two forms, we must expect a kind of isomerism distinguished by a near approach to identity. This state of things fully coincides with the facts, and may be summed up as follows.

All physical properties depending on molecular dimensions and attractions (mathematically speaking, on the quantities a and b of Van der Waals' theory) are identical in the two isomers; thus, *sp. gr.*, *crit. temp.*, maximal tension, boiling point, melting point, latent heat of fusion and vaporisation, &c. The same holds for the physical properties which manifest themselves as the expression of these fundamental quantities, on contact with other bodies, *e.g.* solubility.

As regards chemical properties we must expect exactly equal stability, the same speed of formation and of conversion in given reactions, equilibrium when equal quantities of each are present together, no heat of transformation when one is converted into the other, and accordingly equal heat of formation in both cases.

Finally, the only difference is due to the lack of symmetry, and this is manifested physically in the opposite optical activity, the so-called right- and left-handed rotation, shown by the isomers in the dissolved state—in the state, that is, when the rotation must arise from molecular, not from crystalline structure. It is important to note that a corresponding enantiomorphous structure causes the opposite activity in other cases also, as may be deduced empirically from active crystals, *e.g.* quartz,