

10. Reference 2, p. 86.
11. Nash discusses the Hoovers' activities in China and their legal fallout in great detail in *ibid.*, pp. 167-222.
12. *Ibid.*, pp. 496-502.
13. *Ibid.*, p. 292.
14. H. C. Hoover, *Principles of Mining: Value, Organization and Administration: Copper, Gold, Lead, Silver, Tin and Zinc*, McGraw-Hill, New York, NY, 1909.
15. *Ibid.*, p. 185.
16. This is a recurrent theme in *Principles of Mining*; see, for instance, *ibid.*, pp. 2-3, p. 52; p. 184 and p. 192.
17. *Ibid.*, p. 52.
18. *Ibid.*, pp. 192-3. The last chapter entitled "The Character, Training, and Obligation of the Mining Engineering Profession", (pp. 185-193) elaborates on this and related themes.
19. *Ibid.*, p. 193.
20. *Ibid.*, pp. 21-22 and p. 19.
21. Reference 2, pp. 475-495.
22. Reference 4, Vol. 1, pp. 118-119.
23. Hoover had no working knowledge of any language but English.
24. Reference 2, pp. 490-491.
25. Nash indicates that at times three or more hired translators may have been at work on *De re metallica* and its footnotes. *Ibid.*, pp. 491-492. Hoover in his *Memoirs* does not acknowledge the part played by these translators.
26. The standard life of Agricola is H. M. Wilsdorf, *Georg Agricola und seine Zeit*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1956. See the same author's article on Agricola in C. C. Gillispie, ed., *Dictionary of Scientific Biography*, Vol. 1, Scribner's, New York, NY, pp. 77-79. In what follows, I have made extensive use of H. Prescher, *Georgius Agricola, Persönlichkeit und Wirken für den Bergbau und das Hüttenwesen des 16. Jahrhunderts* [Kommentarband zum Faksimiledruck 'Vom Bergwerk XII B ücher Basel 1557], Acta humaniora der VCH Verlagsgesellschaft mbH, Weinheim, 1985.
27. For a good general account of the Reformation in Zwickau, see C. Karant-Nunn, *Zwickau in Transition, 1550-1574: The Reformation as an Agent of Change*, Ohio State, Columbus, OH, 1987.
28. G. Agricola, *Bermannus sive de re metallica*, Froben, Basel, 1530.
29. See Prescher, reference 26, pp. 60-76.
30. These works were published together with a second edition of the *Bermannus* as G. Agricola, *De ortu et causis subterraneorum Lib. V; De natura eorum quae effluent ex terra Lib. iii; De natura fossilium Lib. X; De veteribus & novis metallis Lib. II; Bermannus, sive De re metallica Dialogus, Interpretatio Germanica vocum vel metallicarum addito Indice foecundissimo*, Froben, Basel, 1546.
31. Reference 1, pp. xiii-xv.
32. *Ibid.*, p. xiv.
33. *Ibid.*, p. xv.
34. L. J. M. Columella, *On Agriculture*, (with a revision of the text and English translation), 3 Vols., Harvard University Press, Cam-

bridge, MA, 1941-1955.

35. Reference 1, pp. 5-8; 12-13; 20-22; 23-24.
36. *Ibid.*, p. 27.
37. J. Nef, *The Conquest of the Material World*, World Publishing, Cleveland, OH, 1967, pp. 42-52.
38. Agricola's description of drainage and ventilation machinery is contained in Book VI of *De re metallica* to which there are very few footnotes in the Hoover translation.
39. Reference 2, p. 527.

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## STEREOCHEMICAL MODELS OF BENZENE, 1869-1875

**The Conflicting Views of Kekulé, Koerner, Le Bel and van't Hoff**

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The stereochemical models of benzene proposed by Joseph Achille Le Bel and Jacobus Henricus van't Hoff in 1874-1875 were related to the well-known controversies on its constitution which began soon after the publication of August Kekulé's papers of 1865 and 1866. The models examined by van't Hoff in his booklet *La chimie dans l'espace* (1875) were based on a tetrahedral model for the carbon atom which Kekulé himself had described in 1867. However, the first to use Kekulé's model for a stereochemical treatment of the six-carbon benzene nucleus was Wilhelm Koerner in a paper published in 1869. The connections between these events have not received the attention they deserve.

The development of stereochemistry during its first decade was outlined by van't Hoff when he published the second edition of his booklet in 1887 (1). His historical introduction, however, was limited in scope: it reprinted both his and LeBel's 1874 papers, Johannes Wislicenus' preface to the 1877 German translation of *La chimie dans l'espace*, and the violent critique of Hermann Kolbe. After citing some more favorable notices by chemical authorities, van't Hoff concluded by quoting textbooks which presented his theory. At the end of Part IV of the work he devoted only one page of comment to aromatic compounds, opening with the statement that his theory (1):

... has nothing new to offer but a preference for Kekulé's hexagon as compared to the conceptions which assume three-dimensional arrangement of the six carbon atoms, as for example, the equilateral triangular prism.

The ring hypothesis for benzene and its derivatives was mentioned again at the very end of the book, referring to the strain theory that Adolf von Baeyer had recently proposed.

The role played by Kekulé's 1867 proposal of a tetrahedral carbon model was fully acknowledged in the first truly historical account of the development of stereochemistry which opened Carl Adam Bischoff's and Paul Walden's 1894 volume, *Handbuch der Stereochemie* (2). They discussed the stereochemical formulas for benzene suggested by Baeyer in 1888 and by Joseph Loschimdt in 1890, described structural models proposed from 1865 to 1892. However, they ignored the ideas of van't Hoff and Le Bel and failed to mention Koerner's work.

A survey of modern historiography regarding stereochemical models of benzene began with a paper by van Klooster who, on the occasion of the centenary of van't Hoff's birth, recalled (3):

... the fact that Kekulé, shortly after his appointment at Ghent in 1858, had already represented the carbon atom at the center of a tetrahedron and that Kekulé's assistant Koerner in 1869 had constructed a space model of benzene with these tetrahedra.

More recently, Koepfel discussed stereochemical benzene models but mentioned neither Koerner's model nor the interpretation of the benzene structure offered by Le Bel and van't Hoff (4). A discussion by Snelders compared the ideas of Le Bel and van't Hoff, but made no reference to their differences with regard to benzene structure (5). The distinction between the stereochemical approaches of Le Bel and van't Hoff has also been considered by Weyer, who carefully examined the earliest stereochemical literature, but without reference to benzene (6).

Ramsay has also studied these topics. Referring to the tetrahedral models for the carbon atom, he wrote (7):

There is no evidence that van't Hoff or Le Bel were aware of these models. Since it can be shown that a number of chemists were using tetrahedral carbon models before 1874, it is perhaps surprising that van't Hoff's proposal of the tetrahedral carbon atom was considered such a revolutionary idea by chemists.

Ramsay then quoted Koerner's model in these terms (7):

To explain the ortho/para substituent effect, he proposed in 1869 a "space-filling" structure of benzene [see figure 3].

We will discuss this model below, and therefore postpone our comments on its "space-filling" character. For the moment

we simply remark that the main purpose of Koerner's paper was to prove that the hydrogens of benzene were chemically equivalent. After explicitly rejecting Kekulé's representation, he proposed an alternative structure for the six-carbon benzene nucleus because it satisfied that condition.

Grossman has provided the most accurate distinction between the theoretical approaches chosen by van't Hoff and Le Bel in their 1874 papers, though without extending his analysis to the benzene case (8). He convincingly argued that they put forward "two very different theories", and suggested that van't Hoff extended his theory after reading the more general stereochemical formulation given by Le Bel. We shall show that this seems indeed to be the case.

The purpose of this article is, first, to outline the sequence of events mentioned above with respect to the early development of stereochemical models for benzene, and their different evaluation by Kekulé and Koerner. In his 1874 dissertation, van't Hoff developed his theory of molecular structure by using elements of Kekulé's tetrahedral carbon atom model of 1867. We shall then show that in writing the chapter on the constitution of benzene in his 1875 booklet, he recognized and eventually used the more general geometric approach taken by Le Bel in 1874. Finally, we shall argue that Le Bel's 1874 discussion of benzene reflects his inadequate understanding and incorrect formulation of the assumptions made by Kekulé in putting forward the theory of the constitution of aromatic compounds.

I. The criteria adopted by Kekulé for representing the chemical properties of a substance through its molecular constitution are described in a note at the end of a paper where he proposed a constitutional formula for mesitylene which was intended to explain its synthesis from acetone (9). Kekulé first explained the advantages of representing multivalent (*mehrwertig*) atoms as aggregates of univalent (*einwertig*) atoms. These are the "sausage" symbols that he used from 1859 to 1866 in his textbook (figure 1). Ironically, Kekulé was offering this explanation at the very moment he chose to abandon his "sausages" and to follow different criteria, starting with a representation of mesitylene (figure 2C) which he also adopted for the benzene ring in the second volume of his textbook (10). Let us examine his line of reasoning through his own words (11):

Crum Brown, Frankland, Hofmann and others have used in drawings and models a representation of a different kind. Atoms are represented as circles or spheres, and affinities [valence bonds] as lines or bars coming out of them. It can easily be shown that this procedure, even if only as a drawing, is not as complete as the one I have used. Several ratios of combination cannot be represented unless the lines corresponding to the affinity units are arbitrarily stretched or bent as necessary. When applied to a model, the procedure has yet another disadvantage: it moves only apparently into space, while as a matter of fact all goes on in a plane. The model therefore does not provide

anything more than a drawing does. These faults can in some measure be avoided, both in the drawing and in the models ... by choosing the length of the lines expressing the affinities so as to make their endpoints equidistant, as shown in Fig. 2A, so to have  $ab = cd = ef$ . It is then possible to bond the atoms to each other either by one or by two affinity units [figure 2B]. This mode of representation, sufficient in the most frequently encountered cases, does not however allow bonding with three affinities of another carbon or nitrogen atom. But even this fault can be avoided, at least in the model, when the four affinities of carbon, instead of lying in a plane, are arranged so as to come out of the atomic sphere in the direction of tetrahedral planes. In this way the length of the metal wires corresponding to the affinity units are chosen so that their endpoints are always equidistant ... Such a model allows us to represent bonds with 1, 2, or 3 affinity units, and I believe it does all that a model should do.

It appears from these comments that Kekulé worked out his theory by thinking of atoms and molecules as three-dimensional objects. However, he refrained from using such models explicitly in his published papers and books for more than eight years. One explanation of this attitude could be that Kekulé wanted to protect himself against criticisms regarding the unnecessary assumption of atoms in space, a damning charge that would have hindered widespread acceptance and diffusion of his new ideas on the constitutions of organic compounds. However, the concreteness of atoms and molecules in Kekulé's mind (12) is clearly evident from the prescriptions for the models he gives in the sentences quoted above.

Kekulé's model is essentially the same as van't Hoff adopted in his stereochemical theory of molecular structure. The first application to benzene, however, was made by Koerner in 1869, and then by Kekulé himself in 1872. Let us review these circumstances, starting with Koerner's model.

This model is described in a paper Koerner wrote at the insistence of Stanislaio Cannizzaro to report on the work he was then doing in Palermo to demonstrate the equivalence of "the six hydrogen positions" and to work out a procedure for establishing the relative position of the substituents in the

### Acetamid.



Figure 1. Symbols introduced by Kekulé in the first volume of his *Lehrbuch* (reference 10, Vol. I, pp. 160-165) to represent molecular constitutions. They describe polyvalent atoms as representing "die Anzahl der chemischen Einheiten", i.e., the number of valences, through the union of univalent atoms. These choices are briefly explained in the footnote, p. 159-160.

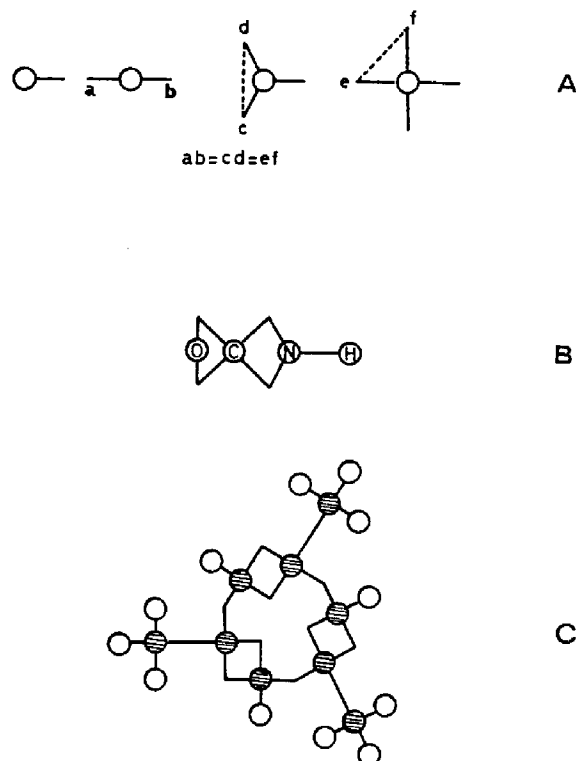


Figure 2. (A) Atomic models where "the length of the lines expressing the affinities is chosen so as to make their endpoints equidistant." (B) Their application to the case HNC O taken as a model for bonds established between atoms with 1, 3, 4, and 2 "affinity units". (C) The constitutional formula for mesitylene built according to the same prescription. (From reference 9)

benzene ring. The model, shown in figure 3, is described as follows (13):

This arrangement, as can be seen in the two images, assumes the twelve atoms to be in four parallel planes; the hydrogen atoms 1,3,5 and 2,4,6 respectively are situated in the two extreme planes; the carbon atoms a,c,e and b,d,f occupy the two intermediate planes. Such an arrangement has the greatest possible symmetry; it leads to six absolutely equal hydrogen positions and to three disubstituted isomers, but requires an additional assumption to explain the formation of addition products ...

This model, equivalent geometrically to a flattened octahedron with hydrogen atoms attached to each of the six vertices, was introduced by Koerner with an explicit rejection of Kekulé's assumption of alternating double bonds. After reviewing the literature for the previous four years, he concluded that this assumption (14):

... seems to me no longer justified ... and I prefer another which allows a simpler explanation of the facts so far known. This idea, which I conceived long ago, is shown in the figure, and is very close to that discussed by Claus and more recently by Ladenburg because each carbon atom is regarded as *directly connected with three other carbon atoms*, thus explaining the great stability of benzene and its derivatives [*italics in the original*].

The statement by Koerner that he had conceived such a model "long ago" most likely refers to the time he spent in Ghent as an assistant to Kekulé (1866-67), and it is the first evidence of disagreement with his former mentor. Koerner surely knew of Kekulé's 1867 paper discussed above, for it was published while he was in Ghent, but he does not quote it. However, Koerner's superior at Palermo, Cannizzaro, cited Kekulé's paper in his report (15) read on 13 June 1869 to the Council of the Istituto Tecnico (the governing board of the *Giornale*), where he explained why had asked Koerner to write the paper and recommended its publication (16).

In 1869 Kekulé published a review paper on benzene in which he examined the various structural theories that had been proposed. Intending to answer the criticisms aimed at his original proposal, he suggested guidelines for assessing the different models (figure 4), including his own, in general terms and on equal grounds (17):

Assumption [i.e. structure] No. 1 is what I have preferred; Claus has discussed assumptions No. 3 and 5, and has favored No. 3; No. 5 is still supported by Ladenburg; conversely, Wichelhaus recommends No. 4, as had been done earlier by Staedeler. The benzene formula proposed by Carius is close to scheme No. 5, while that proposed by

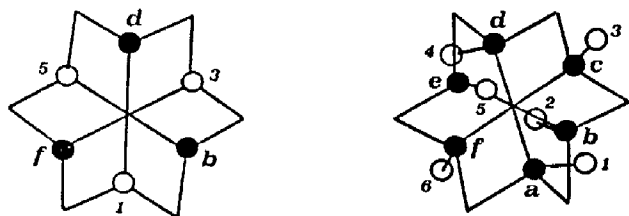


Figure 3. The stereochemical model of benzene proposed by Koerner in 1869, reference 13, p. 242. The carbon atoms are the black spheres identified by letters. In the first image the hydrogen atoms 1,3,5 are eclipsing the carbon atoms *a, c, e*, while the hydrogen atoms 2,4,6 are eclipsed by the carbon atoms *b, d, f*, as required by the tetrahedral model of carbon. The six carbon atoms are arranged as a flattened octahedron, and fill the space satisfying the condition that Kekulé characterized as "une forme plus condensée" in his 1865 paper, and referred to as "die Verdichtung...welche die aromatischen Verbindungen oder den ihnen gemeinsamen Kern charakterisiert" in his 1866 paper.

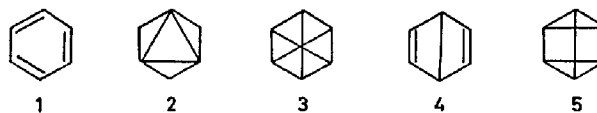


Figure 4. Representation of the bonding schemes used by Kekulé to discuss the constitution of benzene in 1869 and 1872. (References 17 and 21).

Kolbe is to No. 3, provided one leaves out the conception of chemical bonding between carbon atoms, which surely cannot be the case.

Before proceeding to explain why he had preferred, and still preferred, structure 1, Kekulé commented (18):

I admit that for a long time scheme No. 3 seemed to me particularly promising, and later on I found much of beauty in No. 5, although from a viewpoint different from that of Ladenburg.

Kekulé did not specify here what this viewpoint was. Indeed, his paper appears to be little more than an introduction to that immediately following, on the condensation products of aldehydes, where he makes explicit his future research program on benzene (19):

To establish definitively the structure of benzene by obtaining it synthetically in such a way that the nature of the synthesis shall leave no doubt about the type of bonding between the carbon atoms.

The crotonaldehyde condensation had been chosen as an exemplar reaction producing a carbon-carbon double bond (20).

The reason why Kekulé had "found much of beauty" in the Ladenburg model is stated in the 1872 paper where he proposed the assumption of oscillating valence bonds (21). This paper opens with an introductory section in which benzene models were discussed along the same lines as in the 1869 paper (sometimes with the same wording), but with the addition of bibliographic references and models proposed by Paul Havrez and by James Dewar. Here are the relevant points (22):

It has to be accepted that the atoms of a polyatomic molecule are arranged in space so as to best obey all possible attractive forces. The planar arrangement of several atoms shall not be excluded even if it may appear unlikely. Indeed one could be induced to confer a larger probability to conceptions of the constitution of benzene which lead to a regular spatial arrangement of the six carbon atoms.

At this point Kekulé referred to the space modeling procedure (described in the 1867 paper) "... recommended long ago for visualizing our representations of atomic linkages ..." (23), and gave his views on the proposals of Claus and Ladenburg (24):

Schemes [i.e., structures] No. 3 and 5 can be transformed into models in two ways: one form of scheme No. 5 is a triangular prism with the six carbon atoms as its vertices; the most beautiful form of scheme No. 3 resembles a somewhat flattened octahedron lying on a triangular face.

Of course, Kekulé discarded these models, and gave his preference to the constitutional formula as a representation of chemical properties, because scheme No. 1 is in better agreement with the formation of benzene from acetylene and with the synthesis of mesitylene from acetone; it correlates more clearly with the chemical properties of naphthalene and anthracene; and it offers a simpler explanation of addition reactions. To overcome the objections against the assumption of alternating double bonds he now put forward the idea of an oscillation of valence bonds, having given up hope for demonstrating the constitution of benzene synthetically by means of aldehyde condensation. Nevertheless, there can be little doubt that Kekulé had a definite view of spatial modeling of atoms and molecules, and that this view had a suggestive influence on those who first considered a flattened octahedron (Koerner) or, as we shall see, a prism (van't Hoff) as possible spatial forms for the benzene nucleus (25).

II. The 1874 paper by Le Bel sought to identify two general principles which determine "... the relationship between the atomic formulas of organic substances and the rotatory power of their solutions". He adopted a geometrical criterion for examining molecules having the formula  $MA_4$ , where M is "... a simple or a complex radical combined to four monoatomic

(univalent) atoms A" (26).

Le Bel's first principle is that when a solution of such a substance shows rotatory power, its molecular constitution corresponds to a substitution of three atoms A by univalent atoms or groups R, R' and R'' so that (27):

... the set of the radicals R, R', R'' and A, reduced to material points differing among themselves, forms in itself an edifice not superimposable on its (mirror) image, so that the residue M cannot re-establish its symmetry.

The second general principle states that when one, two or three substitutions in  $MA_4$  give "only one and the same chemical isomer", and its disubstituted derivatives do not have rotatory power, then (28):

... we are forced to assume that the four atoms A occupy the vertices of a regular tetrahedron whose symmetry planes are the same as those of the total molecule  $MA_4$ .



August Kekulé (1829-1896) posing (front row center) with a group of students, circa 1865.  
Wilhelm (Guglielmo) Koerner (1839-1925) is second from the left in the back row.

When these principles are applied to benzene (29):

... the geometric assumptions which account for isomers in the aromatic series ... consist in placing the six hydrogen atoms either on the six equivalent vertices of a rhombohedron (*rhomboèdre*) or on those of a vertical pyramid (*pyramide droite*) with an equilateral triangle as a basis. A very easy geometric discussion shows that, in each case, two different substitutions will give one asymmetric and two symmetric isomers.

These geometric references are anomalous and require interpretation. Le Bel does not give any reference to the

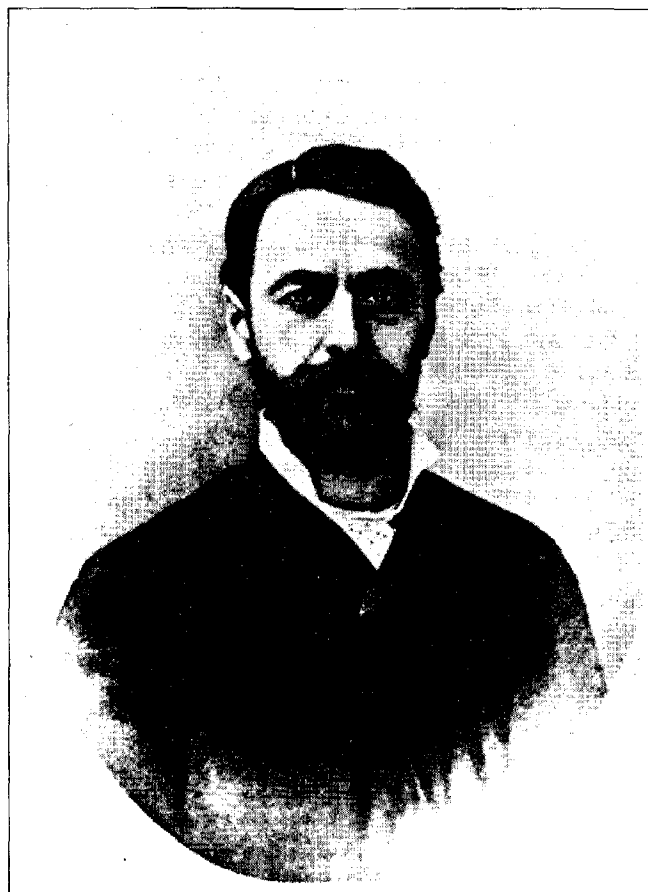
rhombohedral and pyramidal "hypothèses géométriques", merely commenting that these had "already been discussed elsewhere (*ailleurs*)". This seems to imply he is referring to a recent source familiar to all French readers. However, we have been unable to find in French chemical journals of the years 1869-1874 any discussion or paper on a geometric interpretation of isomerism in the aromatic series where terms such as rhombohedron or pyramid were used (30).

Considering that in 1874 Le Bel was working in the laboratory directed by Adolphe Wurtz at the *École de Médecine*, we have checked some entries in the *Dictionnaire de chimie pure et appliquée* then being published under Wurtz's direction. The entry "Série aromatique", written by Alfred Naquet for volume 1 (1869), fails to stress the essential difference between substitution and addition reactions (31). The entries "Hydrocarbures" and "Isomérisie", written by Wurtz himself for volume 2 (1873), never use the terms chosen by Le Bel in the sections treating aromatic compounds. The constitution of benzene preferred by Wurtz is one of those based on "the inequality of the atomicities" (i.e. either No. 2 or No. 4 as shown in figure 4), while he qualifies the hexagon, which he uses only as a matter of convenience, as (32):

... the graphic representation of Mr. Kekulé, who has numbered in a certain way the attacking points of the elements or groups which can substitute the hydrogens of the benzene nucleus.

Le Bel no doubt attached this same meaning to "l'hexagone de M. Kekulé", which he cited and illustrated on the same page of his paper, while discussing the optical activity of *p*-cymene derivatives, a point we shall come back to later. Finally, the last part of Le Bel's statement referring to the asymmetric, optically active isomers derived from benzene by disubstitution, shows that he applied the terms *rhomboèdre* and *pyramide* to three-dimensional geometric forms meant to show the constitution of the  $C_6$  nucleus. Indeed, he had followed the same line in his discussion of the possible optical isomers derived by substitution from ethylene, assuming that its four hydrogen atoms were situated at the base corners of a square pyramid. Moreover a *triangular pyramid* has only four vertices, not six, and therefore Le Bel must have meant something else; it was either a slip of the pen or a geometrical blunder. These considerations suggest that Le Bel actually intended the *triangular pyramid* mentioned in the case of benzene to be a *triangular prism*, where the six hydrogen atoms can take equivalent positions. This is the Ladenburg formula.

Le Bel's reference to a rhombohedron is a more difficult case. There is in the French literature of that period an example where the expression *hexagone rhomboédrique* and the term *rhomboèdre* were used to describe the constitution of benzene as a hexagon having three shorter sides alternating with three longer sides, as shown in figure 5 (33). This however cannot be the case with Le Bel, because such a planar disubstituted



Joseph Achille Le Bel (1847-1930)

geometric arrangement would never give asymmetric, optically active isomers. It seems therefore that he really meant to discuss benzene in terms of the six-rhombus faced parallelepiped shown in figure 6. Its eight vertices have different symmetry properties with respect to the trigonal rotation axis, falling into different sets: two are apical and six peripheral to the

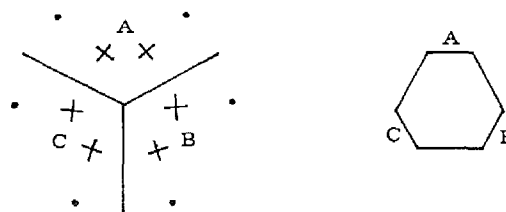


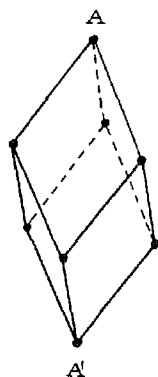
Figure 5. The *rhombohedral* "graphic formula of benzene" proposed by G. D. Hinrichs in 1875, reference 33, p. 49. Here the dots represent "the monovalent hydrogen" and the plus signs "the quadrivalent carbon" atoms. A, B, and C correspond to the shorter bonds, originating from three acetylene molecules and "representing the Berthelot synthesis" of benzene.

trigonal axis. It seems most likely that Le Bel meant to refer to the six equivalent vertices and to neglect the other two (34), as he had done with the apex of the square pyramid in the case of ethylene. He did not discuss the various binding schemes critiqued by Kekulé and shown in figure 4. We conclude therefore that in his 1874 paper Le Bel either exhibited an inaccurate knowledge of the binding schemes proposed for the aromatic  $C_6$  nucleus, or intended to avoid taking a definite stand in the debate on the molecular constitution of organic compounds (35).

We have argued that Le Bel also failed to appreciate the distinction between substitution and addition reactions, a crucial point in Kekulé's arguments for the constitution of aromatic compounds. This is clearly apparent in Le Bel's discussion of the optical activity of camphor and turpentine. Camphor (figure 7) is described as a benzene *substitution* derivative, with the substituents given as  $CH_3$ ,  $(C_3H_7, H)''$ ,  $O''$ ,  $H_2$ , and  $H_2$ . *Para*-cymene is optically inactive because "the methyl and propyl radicals are in the positions 1 and 4 of the Kekulé hexagon, i.e. in a symmetry plane of benzene" (36). Turpentine oil derives from *para*-cymene by *substitution* of two hydrogen atoms of the aromatic nucleus by "two  $H_2$  groups", and the resulting product will be optically inactive or active, depending on whether the *substitution* has occurred in positions which are or are not "symmetric with respect to the plane passing through 1 and 4" (37). There is indeed a confusion in the meaning of the term *substitution* as used here by Le Bel with respect to the meaning given to it by Kekulé, who meant the replacement of each hydrogen atom by another univalent atom or group. Aromatic substitution, as defined by Kekulé, implies that reaction products have the  $C_6$  benzene nucleus with six unchanged affinities, while on the contrary their number increases in addition reaction products. In Le Bel's interpretation of the constitutions of turpentine oil and camphor, the atoms or groups on the  $C_6$  ring saturate respectively eight and ten affinities (38).

III. In September 1874 van't Hoff published the outline of a general theory for interpreting "the chemistry of carbon compounds" and correctly predicting the number of their isomers

Figure 6. The rhombohedron as a six-rhombus faced polyhedron. The A and A' vertices are on the trigonal axis; the other six vertices are geometrically equivalent with respect to any  $2\pi/3$  rotation or any  $2\pi/6$  rotation-reflection ( $S_6$  operation), and can represent the homotopic carbon atoms of the benzene nucleus.



Jacobus Henricus van't Hoff (1852-1911)

by expanding "structural formulas into space". His fundamental assumption consisted (39):

... in imagining the four affinities of the carbon atom directed towards the vertices of a tetrahedron having the carbon atom at its centre.

The most relevant consequence of this assumption was explained thus (40):

In the case in which the four affinities of a carbon atom are saturated by four univalent groups differing among themselves, it is possible to obtain two, and only two, different tetrahedra which are mirror images of each other, but which can never be thought of as being brought into coincidence; i.e. one obtains two isomeric structural formulas in space.

In this, and in his subsequent paper, van't Hoff thus unveiled his "asymmetric carbon atom". The difference between Le Bel's and van't Hoff's approaches has been already pointed out in the introduction. We can summarize it here by saying that Le Bel related the optical activity of dissolved substances to an intrinsic asymmetry of their molecules, which caused

optical isomers to exist in the form of non-superimposable images; van't Hoff, on the other hand, outlined a theory of molecular structure of the same substances, and in 1874 related their optical activity *only* to the presence of an asymmetric carbon atom in their molecules. We also drew attention to Grossman's suggestion that van't Hoff extended his theory *after* reading the more general formulation given by Le Bel (41). We shall now argue that this was indeed the case by analyzing how the two men differed in dealing with the structure of benzene and aromatic compounds, and we will see that it is even possible to establish approximately when van't Hoff incorporated Le Bel's more general approach into his theory.

In his 1874 paper van't Hoff cited in Part 1, Section a (carbon compounds that contain at least one asymmetric carbon atom) camphor, borneol, camphoric acid, turpentine oil and menthol, specifying structural formulas based on those proposed by Kekulé (42). This list also contains the optically active substances discussed by Le Bel under the heading "série aromatique" and assumed for them the same constitution as that in figure 7. The difference is that van't Hoff cited them all together as "corps aromatiques" in the opening of Part 2 (compounds with double-bonded carbon atoms), but he did not discuss them again, nor did he introduce the aromatic series as such, because Part 2 focussed on the isomerism of maleic and fumaric acids and their analogues.

Van't Hoff sent a subsequent condensed version of the 1874 French paper, written after reading Le Bel's article, to Arthur Henninger, an acquaintance of both men (43). This was published after the 5 March 1875 meeting of the *Société Chimique de Paris* (44). As we learn from the *Procès-Verbaux* of the Society, the manuscript was discussed on 19 March 1875, and criticized by Marcelin Berthelot, chairman of that meeting (45). The definition of the asymmetric atom now had wording slightly different from that of the 1874 Dutch and French versions, and the paper lacked figures. With respect to our present discussion there are two points of interest: first, the list of the six-membered ring compounds has disappeared, all being now reduced to the mention of "cymène inactif dérivé du camphre actif" in Part 1; second, in the closing passage, after referring to the paper by Le Bel, van't Hoff makes the following comments (46):

In this fine work the author treats the matter that I have outlined in the first part of the present paper from a somewhat different viewpoint, nevertheless, I wanted to present it all because it forms a whole. It is evident that *concerning aromatic compounds, Mr. Le Bel has discussed the asymmetry problem in the most general terms (dans toute sa généralité), whereas I only treated a special case* [italics added].

The difference in the approach taken by Le Bel was therefore soon clear to van't Hoff. But it is hard to believe that he had not noticed at least some of Le Bel's misunderstandings of

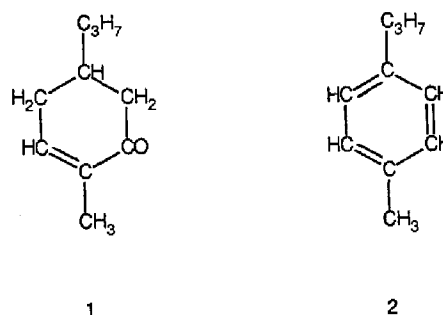


Figure 7. The relationship between the constitution of camphor 1, and *p*-cymene 2, as referred to in the 1874 papers by Le Bel (reference 26, p. 345) and van't Hoff (reference 39, p. 447). Both considered camphor to have the constitution proposed by Kekulé in reference 42, which is not the modern one.

Kekulé's benzene theory pointed out in our previous discussion of Le Bel's paper. The statement above is also untrue, because van't Hoff had not discussed a special case of aromatic compounds, but only mentioned, in a rather different context, the same substances that Le Bel considered as belonging to the "série aromatique". The simplest way of explaining van't Hoff's curious comments is to suppose that he intended to avoid a marginal polemic with respect to a topic which at that time was very controversial and which divided the chemical scientific community. As a 22 year-old graduate he was looking for approbation by the same community and seeking a position. He was also surely attempting to provide chemists with concepts that were easily understood and could help to solve the problem of correctly predicting the number of isomers of carbon compounds.

It is therefore reasonable to assume that, stimulated by what he referred to as the generality of Le Bel's treatment, van't Hoff felt that he should not, and could not, avoid a full discussion on the structure of benzene and aromatic compounds. During this attempt he must have perceived the essential value of the principles given by Le Bel for discriminating between the hexagonal and the prismatic models of the  $C_6$  nucleus. This is why van't Hoff soon acknowledged the generality (i.e. perceived the greater value) of Le Bel's viewpoint on aromatic compounds, and went on to test his claim of "a very simple geometric discussion" for disubstituted benzene derivatives. Moreover, van't Hoff must have seen how useless it would have been to argue against the *rhomboèdre* or the *pyramide droite à base de triangle équilatéral*, the geometric forms Le Bel had chosen to exemplify the application of his principles to aromatic isomers. Indeed, he avoided doing so both in his short paper sent to the Paris Chemical Society in March 1875, and in the longer discussion on benzene he was preparing with the use of his tetrahedral carbon models. Some feelings of indebtedness to Le Bel must have remained in van't Hoff's mind



for a long time, because he knew that in his original formulation of the structural theory he had failed to grasp that the root of optical activity was in molecular asymmetry. This could be the reason (among others) why the 1887 (second) edition of the *La chimie dans l'espace* bears the dedication "à M. J. A. LE BEL. En témoignage de ma respectueuse affection" (47).

It seems therefore most likely that while, or after, writing to Henninger in March 1875, van't Hoff was already working on aromatic compounds for the booklet to be published, at his own expense, in Rotterdam with the date of May 1875, and to be sent soon after to the most eminent chemists of his time (48). Here his discussion of benzene is very different, and it is quite surprising with respect to what he had said in his 1874 papers and in the short communication sent two months before to the Paris Chemical Society. Let us examine it.

Chapter IV, the last of *La chimie dans l'espace*, consists of four pages devoted to aromatic compounds, and two pages devoted to some concluding remarks. We shall analyze now the part concerning the "série aromatique", which opens with the following proviso (49):

The application of my assumption to aromatic compounds faces a difficulty because current theory has not yet decided on the constitution of benzene, the fundamental substance of the series. Therefore I shall limit myself to the following points:

1. Examination of the number of substitution derivatives predictable by the hexagon proposed by Mr. Kekulé and the prism proposed by Mr. Ladenburg.
2. My viewpoint, applied to the two symbols (*aux deux symboles*), does not allow predicting a difference in the number of the substitution products.
3. For addition products my viewpoint allows isomers not predicted by the present symbols (*par les symboles actuels*).

These introductory points show first of all that van't Hoff, dealing separately with the substitution and the addition products of benzene, had a full understanding of the theory of aromatic compounds and knew the current state of the controversies regarding their constitution; secondly, that he chose to evaluate only two of the proposed structures in terms of spatial arrangement of molecules built with tetrahedral carbon atoms, and avoided taking a stand by explaining the reasons for his choice. His results are collected in figure 8.

The consequences van't Hoff drew from the hexagonal benzene formula are the same as those of Kekulé. The predictable isomers are "only one for the compounds  $C_6R_6$  and  $C_6R_5X$ ; three for  $C_6R_4X_2$  and  $C_6R_3X_3$ " (50). Moreover he added that since a strict application of the "symbole de M. Kekulé" requires, as noted by Ladenburg, the substitution in (1,2) to be distinguished from that in (1,6), in this instance the isomers predictable for  $C_6R_4X_2$  become four.

The consequences drawn for the prismatic spatial model are different from those of Ladenburg (who based them on his

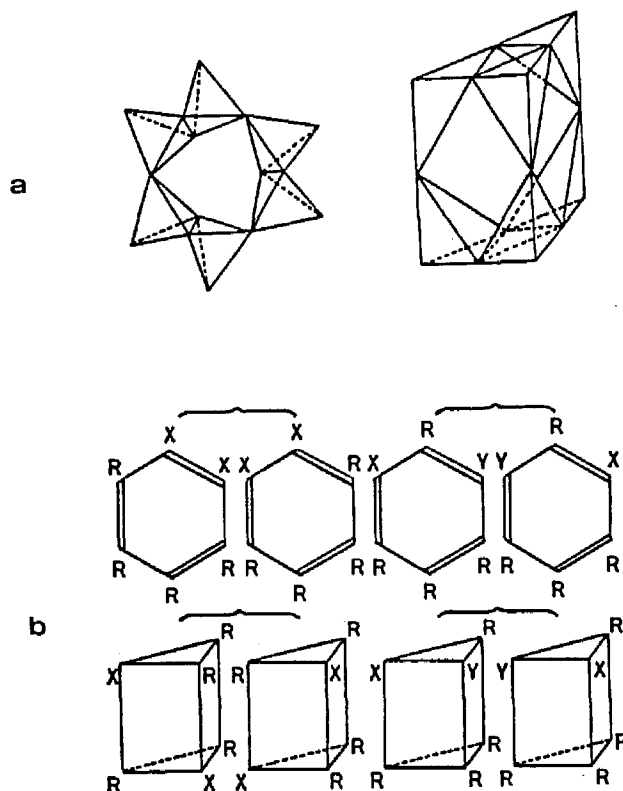


Figure 8. The molecular structures used by van't Hoff to discuss aromatic compounds: (A) the models of Kekulé and Ladenburg; (B) the counting of the  $C_6R_4X_2$  and  $CR_4XY$  isomers (48).

representation), because now one case of  $C_6R_4X_2$  gives two non-superimposable mirror images, and therefore four isomers altogether. Van't Hoff's isomer counting was apparently based only on his 1874 tetrahedral carbon structural theory, because he did not state in this same context that two of these four isomers are expected to be optically active. We shall return to this point after considering the other case of disubstitution.

Van't Hoff's discussion of the  $C_6R_4XY$  case follows the same lines. Kekulé's hexagon, strictly considered, predicts five isomers; and the same number is found for the Ladenburg prism because non-superimposable mirror images are now produced in two cases. In the next step van't Hoff took into account that (51):

... answering the criticism by Mr. Ladenburg, Mr. Kekulé has introduced in his hexagon a mode of motion that cancels the increase of the isomer number consequent to the fixed double-bond position.

In this instance the hexagon and prism space models lead to different predictions, because the isomers of the Kekulé bond-

ing scheme are now reduced to three for any disubstituted benzene derivative, while those of the Ladenburg bonding scheme remain unchanged. Finally, van't Hoff compared his deductions with the known results regarding the isomers of nitrobenzoic and nitrotoluic acids, and concluded that the available experimental evidence did not yet allow a choice between the hexagon and the prism models to be made.

The first comment of van't Hoff on the possibility of optical isomers among benzene substitution products comes in at the end of this long discussion on point 1 of the list made at the beginning of the chapter (52):

I shall *add* that an isomerism such as the one due to the difference shown in the Fig. 8, could (*pourrait*) produce optical activity according to what was said on pp. 20-22 (of Chapter II, ref. 49): the active cymene is perhaps its realization, and this is for me the *third case* of optical activity" [italics added].

This is a rather ambiguous statement because Chapter II of reference 48 concerns the optical activity of compounds containing asymmetric carbon atoms. In the pages referred to above we find stated as "the first cause of optical activity: the compound contains asymmetric carbon atoms". The possibility of other cases of optical activity is seen then as depending on the link between molecular constitution and optical activity as explained in the section titled "Physical interpretation of the rotatory polarization of dissolved active substances". The thesis put forward by van't Hoff is an extension to active molecules of the interpretation of the rotatory polarization of crystals given by Karl F. Rammelsberg (53) and is thus reported (54):

I was suddenly (*au premier abord*) struck by the relation between Mr. Rammelsberg's views on active crystals and my own observation on active molecules. According to this scientist the rotatory polarization in solids coincides with the existence of two crystalline forms ... *one of which is the mirror image of the other.* [italics added]

The crucial point of its extension by van't Hoff is that (55):

... the arrangement of the molecules in the active crystal (is) fully analogous to the arrangement of the atomic groups as I have assumed in the active molecule.

Rammelsberg's assumption of an arrangement of molecules along "positive and negative helices ... recalling the comparison made by Mr. Pasteur", as a possible explanation of the mirror hemihedral forms found in active crystals, is adopted also by van't Hoff. In fact, he goes on to show that the atomic groups arranged around the tetrahedron of an asymmetric carbon atom are always located along a helical path.

It is surely correct to discuss the optical activity of the prismatic models of disubstituted and trisubstituted benzene

isomers in such terms, i.e. by distinguishing between right and left helical arrangements now introduced as an elaboration of ideas previously expressed by Rammelsberg, Pasteur and John Herschel. In fact, these authors were already quoted by van't Hoff at the end of his 1874 paper (39), and were mentioned again in his shorter communication to the Paris Chemical Society (44), because the extension of their assumptions was meant to link the asymmetric carbon atom to the "physical interpretation of the rotatory polarization of dissolved active substances". But now van't Hoff uses this quotation to emphasize the *third case* as a consequence of the tetrahedral spatial arrangement which generates the asymmetric carbon atom, or to stress the general and unifying value of this key concept of his new structural theory, proposed for correctly counting isomers numbers. To show that his own theory was self-contained, sufficient in itself to deal with the cases of optical activity known or predictable for saturated (the first case), ethylenic (the second case), and aromatic compounds (the third case), seemed perhaps to van't Hoff the best way either to prevent any possible future claim of having used somebody else's ideas, or to hide the modifications arising from his reading of Le Bel's paper.

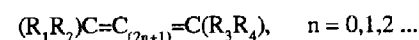
More decisive evidence that something had changed in van't Hoff's mind after reading Le Bel's paper can be found in the conclusion of Chapter IV. Its last part opens with a correction of the "règle générale" that van't Hoff had given at the start of Chapter II, where the "règle" reads (56):

Any carbon compound whose solution causes a deviation of the polarization plane, contains an asymmetric carbon atom.

The reason for the correction is thus explained (57):

... during this work we have come to predict the possibility of optical activity in *two more cases*; and these cases refer to *unsaturated (carbon) compounds* ... In order for my observation to keep all its value the sentence "any carbon compound" has to be replaced by "any *saturated* carbon compound" [italics added].

Of the "two more cases" of possible optical isomers mentioned above among the "combinaisons non-saturées" of carbon, one is obviously that of the aromatic compounds, in their prismatic form, characterized before as "the third case" (52). The other is that of the allenes, where the optically active cases are given in terms of the general formula:



and qualified as "the second case" at the beginning of the Chapter III. The prediction of their optical activity is done in these terms (58):

The four groups will form the vertices of an asymmetric tetrahedron;

therefore according to the reasoning done at pp. 20-22 [of Chapter II, reference 48] it is possible to predict optical activity ... This I shall call the *second case* ...  $R_1$  has to be different from  $R_2$ , and  $R_3$  different from  $R_4$ , without requiring  $R_1$  and  $R_3$  or  $R_4$  to be different [italics added].

Their prediction as mirror images had been made in Chapter I and their cardboard models (numbered XX and XXI for the case  $R_1 = R_3$ ,  $R_2 = R_4$ ) prepared, and distributed, for counting them as isomers. At the beginning of Chapter III they became the first example of unsaturated optically active molecules, labeled as the second case (59). If we leave aside the reference to Chapter II of reference 48, whose meaning has been discussed above, it is evident that this case strictly adheres to the first principle stated by Le Bel and quoted earlier (27):

... the set  $R_1, R_2, R_3$ , and  $R_4$ , reduced to material points, forms in itself an edifice not superimposable to its mirror image, while the residue M cannot re-establish its symmetry.

It is hard to imagine that this rather obvious connection had escaped the attention of van't Hoff. His theory of atomic bonding in space in fact put him in the position of being able to predict when the structure of the group M allowed or forbade molecular symmetry; and of appreciating the different consequences of having M as C=C, or as C=C=C, etc. Therefore it is no surprise that he made these predictions explicit, adding the two cases based on unsaturated bonding to the prediction of optical activity based on the saturated asymmetric carbon atom.

It seems probable that the correction of the rule given in Chapter II was inserted in the concluding part of Chapter IV when van't Hoff could no longer revise the galley-proofs of the preceding text. This last chapter, devoted to aromatic compounds, must have been started at about the time he sent Henninger the communication to be read before the Paris Chemical Society. It must have been more time-consuming than he had foreseen, because 19 figures out of the total 55 (17 in the last plate) refer to the discussion of aromatic compounds.

It is more difficult to conjecture whether the application of the principles stated by Le Bel was first made to the sequence of ethylenic bonds which corresponds to the allenes, and then extended to aromatic compounds. The remark made before in footnote 59, and the order of the chapters in the book would suggest that this was the case. But the expository sequence of the book does not have to be the same as the sequence of van't Hoff's thoughts. Reading Le Bel's paper must have stimulated a complex interplay of thinking, model making, and writing which could make an interesting historical investigation (60). At any rate, we hope we have helped to establish the role that the discussion of stereochemical models of benzene played in the development of van't Hoff's ideas and in his relationship with Le Bel during the years 1874-75.

How did Le Bel feel about all this? He lived in a cultural

context where the connections between crystal morphology, molecular structure and optical activity had an established tradition. This link became evident in succeeding years. Le Bel's attempts to test the optical activity expected with the disubstituted derivatives of the prismatic structure of benzene are first reported in the *Procès-verbaux* of the meeting of the Paris Chemical Society on 23 June 1882: the mould cultivation of a dilute solution of toluidine (1-methyl, 2-aminobenzene) hydrochloride failed to show optical activity (61).

Le Bel never published an explicit revision of his "pyramidal" or "rhombohedral" geometric assumptions, while he consistently maintained that "the regular tetrahedral form of  $CR_4$  molecules is not among the necessary and sufficient conditions for justifying the rotatory power" (62). He explained in 1890 what in 1874 had given to his "demonstrations une forme particulière et en apparence moins simple", causing him to reject the idea that the four affinities, or valencies, of carbon were directed along the four trigonal axes of a tetrahedron. The reason given is based on the assumed congruence between molecular form and crystal form, one of the axioms on which Bravais had worked out his theorems: "because the assumption of the regular tetrahedron requires the  $CR_4$  substances to be cubic and the  $CR_3R'$  substances to be rhombohedral" (63). While this prediction is verified by  $Cl_4$  and  $Cl_3H$ , it is not by  $CBr_4$ . Le Bel prepared this, and found that its crystals were birefringent to parallel polarized light, and therefore could not belong to the cubic system, in agreement with his theory. Then, in the conclusion he added the following comment (64):

... benzene and its derivative  $C_6Cl_6$  could even fail to crystallize in the hexagonal system (they actually make hexagonal crystals) and allow nevertheless understanding the correctness of the rules derivable from the Kekulé hexagon.

A year later Le Bel made a new "examen analytique" of the "relations between rotatory power and molecular structure". He adopted the name "stéréochimie" for defining what van't Hoff had called "la chimie dans l'espace", spoke of "théorie du carbone asymétrique", and proposed an axiomatic formulation to show that the tetrahedral model was not needed for explaining the optical activity of saturated carbon compounds. In the section discussing "corps aromatiques" he accounted for the failure of all attempts to obtain optically active isomers in terms of "une vérification nouvelle de l'hypothèse de Kekulé". How this was to be understood he made clear in a footnote (65):

... the results on benzene and its derivatives agree with the structural assumption of either a rigid regular hexagon or "a closed chain having a certain mobility".

This referred once more to the rejection of the single and double bond alternation in the benzene ring as interpreted by

van't Hoff in figure 8.

These ideas and feelings about the role of the unsaturated carbon compounds in the early events of stereochemistry seem to have remained in Le Bel's mind until near the end of his long life. He referred to them again on 22 December 1924, on the occasion of the 50th anniversary of the birth of stereochemistry, an international gathering convened in Paris by the French Chemical Society for the joint celebration of "notre illustre collègue J. A. Le Bel et la mémoire de J. H. van't Hoff" (66). In the closing speech of the ceremony Le Bel said (67):

Van't Hoff proposed a very interesting theory of ethylene which seemed to justify the existence of four poles: two carbon atoms, figured as two tetrahedrons, would become bound through two poles by their polar attraction, which stabilize the molecule while the four hydrogens form a rigid rectangle, explaining the maleic-fumaric isomerism and some other facts. On the other hand, the four poles are in absolute contradiction with the results derived from the hexagon theory of Kekulé, where the two ortho compounds (1,2) and (1,6) are identical, while according to van't Hoff the compound having a double bond in (1,2) has to differ from that which has a single bond in (1,6) (sic: to read (1,2)). In spite of this contradiction the majority adopted the tetrahedron [italics added].

A very representative group of that majority was in fact present in the audience, and he chose to take this occasion to distinguish again his own theory from that of van't Hoff. These feelings surely must have been very deep in his mind and heart. At the roots of these feelings is the treatment of the optical activity given by van't Hoff for unsaturated compounds and the stereochemical models of benzene.

#### References and Notes

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1. J. H. van't Hoff, *Dix années dans l'histoire d'une théorie*. P. M. Bazendijk, Rotterdam, 1887.
2. C. A. Bischoff and P. Walden, *Handbuch der Stereochemie*, V. H. Bechold, Frankfurt, 1894, pp. 5-140. They discuss in historical terms the formulas of benzene on pp. 84-86 and 112; the models proposed for the  $C_6$  nucleus are shown on pp. 645-649.
3. H. S. van Klooster, "Van't Hoff (1852-1911) in Retrospect". *Proceedings of the International Symposium on the Reactivity of Solids, Gotheburg 1952*. Elander, Goetborg, 1953, pp. 1095-1100, quote on p. 1099.
4. T. A. Koeppe, "Significance and Limitations of Stereochemical Benzene Models", in O. B. Ramsay ed., *Van't Hoff-Le Bel Centennial*, American Chemical Society, Washington, D.C., 1975, pp. 97-113.
5. H. A. M. Snelders, "J. A. Le Bel's Stereochemical Ideas Compared with Those of J. H. van't Hoff (1874)", *ibid.*, pp. 66-73.
6. J. Weyer, "A Hundred Years of Stereochemistry. The Principal Development Phases in Retrospect", *Angew. Chem., Inter. Edit. Engl.*, 1974, 13, 591-598.
7. O. B. Ramsay, *Stereochemistry*, Heyden, London 1981, pp. 62-68, quotations from p. 65. See also O. B. Ramsay, "Molecular Models in the Early Development of Stereochemistry: I. The van't Hoff Model. II. The Kekulé Models and the Baeyer Strain Theory" in O. B. Ramsay ed., *Van't Hoff-Le Bel Centennial*, American Chemical Society, Washington, D.C., 1975, pp. 74-96. The purpose of Koerner's paper has been stressed also in a paper by J. M. McBride, "Completion of Koerner's Proof that the Hydrogens of Benzene are Homotopic. An Application of Group Theory", *J. Am. Chem. Soc.*, 1980, 102, 4134-4137. Ramsay also states, p. 65, that Koerner, after being a student in Kekulé's laboratory in Ghent, "returned" to Palermo. This is not accurate, because he moved to Palermo for the first time in December 1867, as recorded by R. Anschütz in his memorial paper, *Berichte*, 1926, 59, A, 75-111, see p. 87. Comments on Koerner's structure of benzene can be found on p. 91. Other comments and additional biographical information have been published recently by H. W. Schütt, "Guglielmo Koerner (1839-1925) und sein Beitrag zur Chemie isomerer Benzolderivate", *Physis*, 1975, 17, 113-125.
8. R. B. Grossman, "Van't Hoff, Le Bel, and the Development of Stereochemistry: A Reassessment", *J. Chem. Educ.*, 1989, 66, 30-33.
9. A. Kekulé, "Ueber die Constitution des Mesitylens", *Zeit. Chem.*, N.F., 1867, 3, 214-218.
10. A. Kekulé, *Lehrbuch der organischen Chemie*, Encke, Erlangen, 1861-1866, Vol. II, p. 246.
11. Reference 9, p. 217.
12. Reference 10, Vol. I, p. 157-158.
13. W. Koerner, "Fatti per servire alla determinazione del luogo chimico nelle sostanze aromatiche", *Giornale di scienze naturali ed economiche*, 1869, 5, 212-256, quote on p. 242.
14. *Ibid.*, p. 241.
15. S. Cannizzaro, "Rapporto del Prof. Cannizzaro detto nella seduta del 13 giugno 1869", *Giornale di scienze naturali ed economiche*, 1869, 5, 208-211, see p. 210.
16. Perhaps Palermo in 1869 was one place where spatial representations of carbon compounds were considered acceptable in a publication. Cannizzaro and Koerner are to be praised for this. A few months previously Emanuele Paternó, then a chemistry student and also working in Koerner's laboratory, had published some models using the tetrahedral carbon atom for discussing the possible isomers of  $C_2H_4Br_2$ , in *Giornale di scienze naturali ed economiche*, 1869, 5, 117-122. This paper later became a case for arguments on priorities for such an idea, and Paternó in 1913 published a personal letter by Adolf Lieben, dated 25th June 1869 from Turin, trying to discourage

both Cannizzaro and Paternó from publishing "... speculations about the true position of atoms in space ..."; the facsimile is reproduced in the *Gazzetta*, 1913, 43, 501-503. Some other details on the 1869 work by Paternó are given in the book by Ramsay quoted in reference 7.

17. A. Kekulé, *Berichte*, "Ueber die Constitution des Benzols", 1869, 2, 362-365, quote on p. 364.

18. Reference 17, p. 364.

19. A. Kekulé, "Condensationsprodukte des Aldehyds; Crotonaldehyd", *Berichte*, 1869, 2, 365-368, quote on p. 365.

20. The interpretation of the synthesis of mesitylene proposed in 1867, reference 9, was itself an assumption, and not yet a demonstrated synthetic pathway.

21. A. Kekulé, "Ueber einige Condensationsprodukte des Aldehyds", *Ann. Chem.*, 1872, 162, 77-124. This paper was an implicit admission of failure to establish the nature of the benzene carbon-carbon bond unambiguously, as announced in 1869, reference 19.

22. *Ibid.*, p. 82.

23. *Ibid.*, p. 82.

24. *Ibid.*, p. 83.

25. Although it is not possible to know if Koerner ever discussed his model with Kekulé during his stay in Ghent, there can be little doubt that the model derives from the tetrahedral arrangement of the carbon atom affinities put forward by Kekulé in 1867, reference 11. Moreover, it has to be pointed out that van't Hoff in 1872 studied under Kekulé in Bonn, and in 1873 was in Wurtz's laboratory before returning in Holland for his Ph.D. in Utrecht under E. Mulder.

26. J. A. Le Bel, "Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolutions", *Bull. Soc. Chim. (Paris)*, 1874, 22, 337-347.

27. *Ibid.*, p. 338.

28. *Ibid.*, p. 339.

29. *Ibid.*, p. 345.

30. The 1869 papers of Kekulé discussed above, reference 17 and 19, were summarized by A. Wurtz in the *Bull. Soc. Chim. (Paris)* 1869, 12, 465-467, and in *Ann. Chim. Phys.* 1871, 23, 324-328. These summaries do not report Kekulé's discussion of the different constitutional formulas proposed for benzene. The 1872 paper, reference 21, apparently was never summarized in French journals. (We have particularly sought a French source because Le Bel was above all reporting to the French chemical community, although, being Alsatian, i.e., German speaking, it cannot be excluded that he simply referred to Kekulé, reference 21).

31. This same failure is also to be found in the discussion by Le Bel, as we shall see. A. Naquet made such a distinction quite clearly only in the third edition of his book: *Principes de chimie fondée sur les théories modernes*, Vol. 2, Savy, Paris, 1875, pp. 496-504. Its first edition had been published in 1865, and the second in 1867, too early for Kekulé's theory to be reported in his textbook.

32. A. Wurtz, *Dictionnaire de chimie pure et appliquée*, Vol. 2, Hachette, Paris, 1873, pp. 142-152, quote on p. 150.

33. G. D. Hinrichs, "Sur la structure des molécules de la benzine et du térébène", *Compt. Rend.*, 1875, 80, 47-51. Gustav D. Hinrichs

(1836-1923) interpreted the molar heat of benzene vapor assuming that the absorbed or lost heat goes into molecular rotational motion. By comparing the value of the inertial momentum calculated under such an assumption with the value corresponding to the distribution of the C and H atomic masses on a rhombohedral hexagon, Hinrichs concluded that the *forme générale* of benzene is a *rhomboèdre*. His paper was communicated by M. Berthelot at the meeting of the *Académie des Sciences* held on 4 January 1875, i.e. about three months after the publication of Le Bel's paper, reference 26. In their historical review of stereochemistry C. A. Bischoff and P. Walden (reference 2, p. 15) refer to Hinrichs, Professor of Physics, Chemistry and Mineralogy at the State University of Iowa, as a precursor of research on atoms in space, quoting a 1867 lithographed paper titled *Atommechanik oder die Chemie, eine Mechanik der Panatome*. Hinrichs quotes the book *The Principles of Chemistry and Molecular Mechanics*, Davenport, Iowa 1874, which however is not mentioned in his obituary note published by Charles Keyes in *The American Mineralogist*, 1924, 9, 5-8. A copy of Hinrich's book can be found in the Smith Collection at the University of Pennsylvania.

34. However, this constitutional scheme contradicts the second part of the statement by Le Bel concerning the *hypothèses géométriques* on benzene, reference 26, because its unequal disubstitution leads to one symmetric (para) and two asymmetric (ortho and meta) isomers.

35. The two alternatives are really not mutually exclusive: Le Bel stresses his intention to keep his analysis within a geometrical frame, and probably considers the debate on constitution devoid of real value in terms of an understanding of molecular reality. In a footnote on the first page of reference 26, he quotes A. Bravais' *Etudes Cristallographiques*, Gauthier-Villars, Paris, 1866, pp. 194-236, where crystals are also discussed as assemblages of polyatomic molecules. Le Bel's predilection for Bravais' crystallographic approach suggests that he was much more confident in Bravais' geometric considerations extended through rotatory power, which constitutes the core of his paper, than in the perspective of the structural bonding debates. This is in line with the fact that he paid more attention to molecular symmetry than to molecular structure, and with his choice of geometric forms for discussing the possible optical activity of ethylene and benzene derivatives.

36. Reference 26, p. 345. This statement remains true both for the hexagon as Kekulé's representation, and for the six equivalent vertices of the rhombohedron as the geometric form chosen by Le Bel.

37. *Ibid.*, p. 346.

38. The discussion of their optical activity by Le Bel remains quite ambiguous, because the carbon atoms of the benzene ring after what he calls *substitution* belong to the MA<sub>4</sub> type, but are not examined in terms of his first principle. At the same time the symmetry plane through the positions 1 and 4 of the hexagon coincides with the plane passing through the para positions of the rhombohedron as discussed above, note 36.

39. J. H. van't Hoff, "Sur les formules de structure dans l'espace", *Archives Néerlandaises des Sciences Exactes et Naturelles*, 1874, 9, 445-454. This text is the French translation of a pamphlet in Dutch

summarizing van't Hoff's dissertation. A similar French text was published again in 1887 as part of the historical introduction in reference 1, pp. 13-17. For other details on the Dutch text and on his doctoral dissertation see the articles by H. S. van Klooster, reference 3, H.A.M. Snelders, reference 5, and J. Weyer, reference 6.

40. *Ibid.*, p. 446.

41. A comment on the paper by R. B. Grossman, reference 8, is in a letter which I have sent to the Editor of *J. Chem. Educ.*, 1991, 68, 797-798.

42. A. Kekulé, "Ueber einige Körper der Camphergruppe. Constitution des Camphers", *Berichte*, 1873, 6, 929-934. The quotation of Le Bel is not from this original paper, but from its summary published in the *Bull. Soc. Chim.*, (Paris), 1873, 20, 558-559. Van't Hoff's comment does not have a bibliographic reference. Obviously the formulas both referred to differ from the correct modern formulas of these substances, while turpentine oil owes its optical activity mainly to  $\alpha$ -pinene.

43. Arthur Henninger (1850-1884) was then a student at the Ecole de Médecine directed by Wurtz, which van't Hoff had visited in the middle of 1873. A joint communication by Henninger and Le Bel (assistant to Wurtz), published in *Compt. Rend.*, 1874, 79, 480, reports on the building of a distillation apparatus.

44. J. H. van't Hoff, "Sur les formules de structure dans l'espace", *Bull. Soc. Chim.* (Paris), 1875, 23, 295-301.

45. M. Berthelot, "Extrait des procès-verbaux. Séance du 19 mars 1875", *Bull. Soc. Chim.* (Paris), 1875, 23, 338-340. This is the heart of the criticism by Berthelot: "Without denying in general the interest of formulas of this type, more rational than the usual planar formulas, it must nevertheless be considered that a satisfactory representation of chemical compounds cannot be achieved without introducing into them the notion of the rotational and vibrational motions of each single atom and group of atoms within the molecule", quote on p. 338.

46. Reference 44, p. 300-301.

47. Reference 1, p. 3 (printed as shown).

48. J. H. van't Hoff, *La chimie dans l'espace*. P. M. Bazendijk, Rotterdam, 1875. The preface of this book looks like a letter to the chemical community outside of the Netherlands, regretting that Dutch colleagues had not discussed his theory, but instead "just inserted its French translation in the *Archives Néerlandaises*", see here reference 39. In Chapter I, a footnote on p. 7 has a list of nine "savants étrangers" to whom van't Hoff sent a copy of the book and a set of cardboard models, asking them to express "un jugement". According to H. S. van Klooster, the same complaint lies behind two of the 32 Statements put by van't Hoff in his Dissertation, and to be defended publicly during its discussion. Statement No. 7 reads: "There should be a committee appointed to act on matters of a chemical nature". See reference 3, p. 1096.

49. *Ibid.*, p. 38. The discussion of the structural assumptions made by van't Hoff regarding addition products clearly distinguishes between the two proposals: the Ladenburg prism can give molecules which contain a three-membered ring, whereas the Kekulé hexagon allows for molecules containing the six-membered ring. The discus-

sion of their structure leads van't Hoff to predict isomers which today we would characterize as conformational. A discussion of this is beyond the scope of the present paper.

50. *Ibid.*, p. 38.

51. *Ibid.*, p. 39. The Kekulé paper referred to is reference 21.

52. *Ibid.*, p. 40.

53. K. F. Rammelsberg, "Ueber die Beziehungen zwischen der Circularpolarisation, der Krystallform und der Molecularconstruction der Körper", *Berichte*, 1869, 2, 21-37.

54. Reference 48, p. 20.

55. *Ibid.*, p. 21. Almost the same words were used by van't Hoff in the summary reference to Rammelsberg's work (53) made at the end of the 1874 paper, p. 454 of reference 39, and of its March 1875 reduced text, p. 300 of reference 44.

56. *Ibid.*, p. 18. Here van't Hoff put camphor, borneol and camphoric acid as concluding examples of this rule, and then quoted Le Bel's paper of reference 26 as "having just made the same observation and proving its correctness", p. 19.

57. *Ibid.*, p. 42.

58. *Ibid.*, pp. 29-30.

59. *Ibid.*, pp. 13-14. This circumstance suggests that van't Hoff changed his mind between the writing of Chapters I and III. A reference to the mirror image isomers  $(R_1R_2)C=C(R_1R_2)$  is made in the last footnote of Chapter I, reference 48, p. 16, footnote appended to this peculiar sentence: "but I do not want to annoy my readers by considering matters which *I shall absolutely not need in the continuation*" [italics added]. At the time of writing this chapter he probably had not yet decided to discuss benzene and aromatic compounds. It is worth noting that attempts to test the predicted optical activity of substituted allenes, started in 1903, all failed until 1935 when a successful separation of optical isomers was first reported by Peter Maitland and William H. Mills, "Resolution of an Allene Hydrocarbon into Optical Antipodes by Asymmetric Catalysis", *J. Chem. Soc.*, 1936, 987-998.

60. The use of cardboard models "pour faciliter la représentation" during the elaboration of the theory, was reported by van't Hoff in a footnote of Chapter I, *ibid.*, p. 7.

61. "Extrait des procès-verbaux. Séance du 23 Juin 1882", *Bull. Soc. Chim.* (Paris), 1882, 38, 98. This report is also quoted by van't Hoff in the page devoted to aromatic compounds in the 1887 edition of his booklet, reference 1, p. 81. The "dédoublément" procedure had been worked out by Pasteur. The failure of these repeated attempts later led Le Bel to favor the hexagonal structure of benzene. He never wrote a paper on these experiments, but only mentioned them on the occasion of discussions at the meetings of the Paris Chemical Society, e.g., see the *Procès-verbaux* of 28 November 1890. They are quoted again in a lecture given on November 1891 to the Paris Chemical Society, see p. 615 of reference 65 below.

62. J. A. Le Bel, "Sur les conditions d'équilibre des composés saturés du carbone", *Bull. Soc. Chim.* (Paris), 1890, 3, 788-796.

63. *Ibid.*, p. 790. See the comment made in footnote 35 and Bravais' papers there quoted.

64. *Ibid.*, p. 796.

65. J. A. Le Bel, "Les relations du pouvoir rotatoire avec la structure moléculaire", *Revue scientifique*, 1891, 48, 609-617. Aromatic compounds are discussed on p. 615. This paper, very relevant for understanding the distinction Le Bel meant to stress between his own theory and the structural theory of van't Hoff, again gives evidence for those aspects of Le Bel's ideas mentioned in footnote 35, still persisting in 1891.

66. "Le cinquantenaire de la théorie du carbone asymétrique", *Bull. Soc. Chim. (Paris)*, 1925, 37, 341-356.

67. *Ibid.*, pp. 353-4. The relevant part of the original text reads: "... les deux corps ortho-1.2 et 1.6 sont identiques tandis que d'après van't Hoff le corps 1.2 où il y a double liaison entre les carbones doit différer du corps 1.6 où il y a la liaison simple." (I am very grateful to Prof. J. Michael McBride for pointing me out the logical incongruence originating from the misprint: the last 1.6 must read 1.2).

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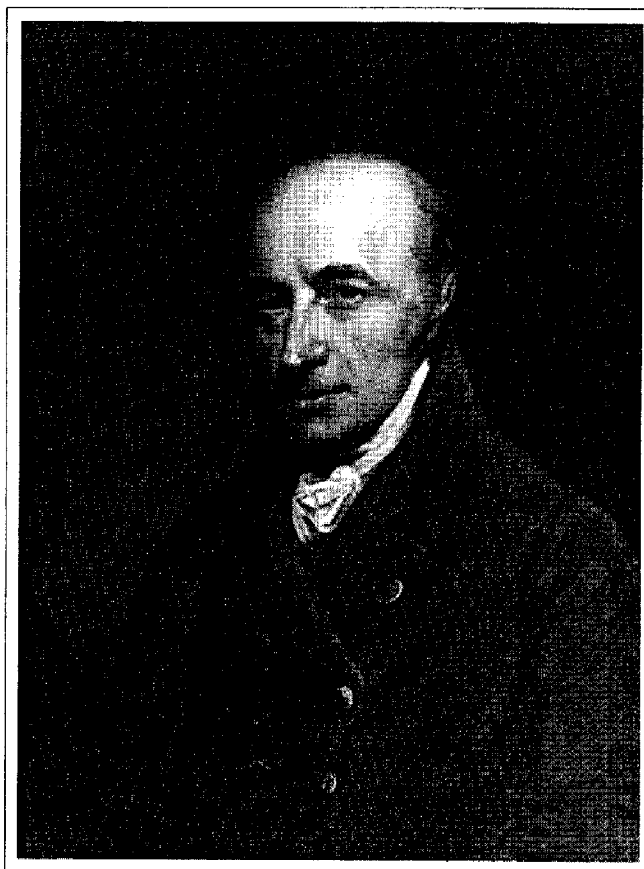
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## SOME EARLY CHEMICAL SLIDE RULES

*William D. Williams, Harding University*

An article by George Bodner in the Winter 1990 issue of the *Bulletin* described a rare chemical slide rule designed by Lewis C. Beck and Joseph Henry - their little-known "Improved Scale of Chemical Equivalents" (1). The reader is urged to review that description. The present paper attempts to place this slide rule in context by describing its origins, as well as some of its predecessors and successors.

The concept of "A Synoptic Scale of Chemical Equivalents" was first presented in 1814 by the English chemist, William Hyde Wollaston (2). Chemical substances were arranged on a scale with distances proportional to the logarithm of their equivalent or combining weights, much as the value of  $\pi$  was marked on the scales of the more conventional slide rules of recent memory. A logarithmic slider, numbered from 10 to 320, allowed quick calculation, via the method of direct and inverse proportions, of the weights of substances reacting with one another, the quantity of products, or the relative proportions of elements in a compound. Wollaston's original design, measuring 12 by 2.5 inches, was marketed in



William Hyde Wollaston (1766-1828)

London that same year. A contemporary called it "an instrument which has contributed more to facilitate the general study and practice of chemistry than any other invention of man" (3). It accelerated the acceptance of Dalton's atomic theory and promoted chemistry as a mathematical science.

Only a few of these original slide rules are still in existence. Some are in European museums (4). Only two are known to have survived in the United States and both are located at Harvard University. They are described as (5):

Pine; paper labels. L of each 12 in. Inscr. on face: Chemical Equivalents; lists of elements and compounds; Published by W. Carey, 182 Strand, Jan. 1, 1814. On slider: graduated, numbered scale. On back: By Special Appointment / [arms] / Thomas Jones, / (Pupil of Ramsden.) / ASTRONOMICAL / and / philosophical / INSTRUMENT MAKER / To His Royal Highness / The Duke of Clarence / 62 Charing Cross, / LONDON.

Drawings and discussions of the Wollaston slide rule appeared in several early American chemistry texts (6). Wollaston used oxygen = 10 as his equivalent (atomic) weight standard, but his choice was not accepted by all of his contemporaries. Thomas Thomson observed that Dalton, Philips,