The Origin of the Stereochemical Line and Wedge Symbolism

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Question

What is the origin of the line and wedge symbolism used in modern stereochemistry?

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Answer

This is a topic which, despite its pervasive impact on how we presently write chemical structures, probably has no clear cut origin but rather only gradually "seeped" into the chemical literature, while simultaneously undergoing numerous modifications. Standard histories of stereochemistry are silent on this subject (1, 2) and attempting to determine its first appearance in the research literature would be a momentous undertaking. However determining the approximate date at which it became sufficiently established to appear in the monograph and textbook literature is a more manageable task.

No trace of the line and wedge symbolism is to be found in the early monographs on stereochemistry by Bischoff (1894), Hantzsch (1904), Werner (1904) and Stewart (1919) (3-6). The three-dimensional orientation of bonds was instead initially represented by inclosing the topological formula of the molecule or complex ion within an appropriate polyhedron, such as a tetrahedron or an octahedron, and showing how these polyhedra interacted with one another via the sharing of their vertices, edges or faces in order to build up more complex chains or rings.

The first indications of our modern line and wedge symbolism are found in the 1930 monograph on stereochemistry by the German chemist, Georg Wittig (7), and involve the representation of ring systems in which the projecting edges of rings perpendicular to the plane of the paper were printed using thick lines in order to differentiate them from rings within the plane of the paper – a practice which may have first evolved in the literature dealing with carbohydrate chemistry.

Figure 1. Richard Kuhn (1900-1967).

Two years later, in a contribution to the 1932 collection on stereochemistry edited by Karl Freudenberg, the German biochemist, Richard Kuhn, used thick black lines to represent terminal bonds which projected from the plane of the paper and dotted lines to represent those receding from the plane of the paper (figure 2a) (8). The next year, the monograph by Stefan Goldschmidt on stereochemistry did the same, but replaced Kuhn's dotted lines for the receding bonds with thickened, but unblackened lines (figure 2b) (9).

Consistent use of wedges rather than thickened lines to represent bonds not lying within the plane of the paper seems to have first appeared in the literature

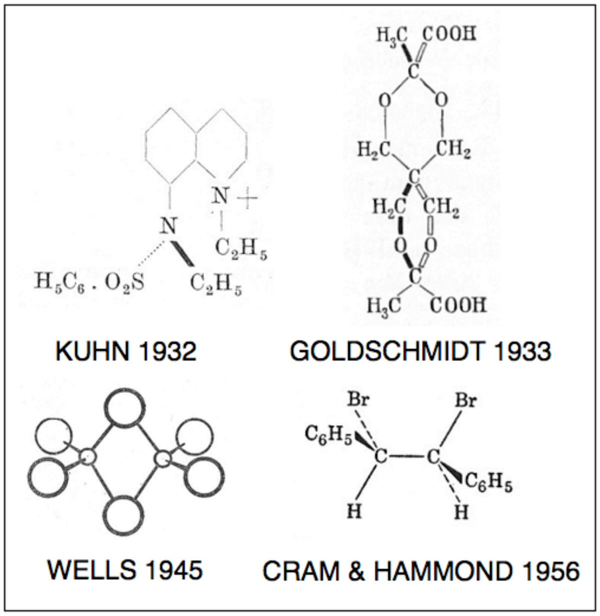

Figure 2. The development of stereochemical line and wedge symbolism.

dealing with inorganic crystal chemistry rather than with organic stereochemistry (7). Thus, A. F. Wells, in the 1945 edition of his classic monograph, *Structural Inorganic Chemistry*, used both projecting and receding wedges to represent the orientation of the bonds in many of his drawings of inorganic crystal structures (figure 2c) (10). The combination of thickened wedges for projecting bonds and dashed lines for receding bonds (figure 2d) finally makes an appearance in the papers contributed by Donald Cram and George Hammond to the 1956 collection on stereochemistry edited by Melvin Newman of Ohio State University (11).

Despite the appearance in stereochemical monographs dating from the 1930s of earlier precursors of the symbolism, it seems to have had no impact on the introductory organic textbook until the publication of the 1959 text by Cram and Hammond, which used the form employed earlier in their contributions to the monograph edited by Newman (12, 13). This important textbook was quite influential in molding a new approach to introductory organic chemistry in the 1960s and undoubtedly acted as a major vector for the spread of the line and wedge symbolism throughout the textbook literature during this decade.

Of course, minor modifications continue to appear, the most common being the use of either horizontally hatched wedges or thickened horizontally hatched lines to represent receding bonds. Of these, the use of the hatched wedge is the most objectionable and has apparently led to considerable confusion. Since both the use of hatching and the wedge direction were intended to indicate the presence of receding bonds, this symbol contains an unnecessary redundancy, which is further compounded by the fact that the wedge aspect of the symbol is often incorrectly applied by pointing – in direct opposition to the laws of perspective – the thick end at the atom furthest from the viewer rather than at the atom closest to the viewer (14). It is geometrically impossible to correctly represent a tetrahedral arrangement of bonds using only wedges if the narrow ends of all four wedges are connected to the central atom, an arrangement which actually corresponds to a square-based pyramid.

In the examples shown in figure 2 the line and wedge symbolism has been used in formulas in which the atomic centers are explicitly indicated using either their letter symbols or spheres. However, the line and wedge may also be used in conjunction with the highly abbreviated framework formulas increasingly popular among biochemists and organic chemists (15). In these formulas the symbols for C and H are suppressed unless they are part of a functional group, as are all C–H bonds. This latter practice, however, creates a problem when it comes to representing the absolute configuration around a chiral center in which one of the four attached atoms is a terminal H. Though this is really an issue related to the conventions for drawing minimalist framework formulas and should be independent of the issue of which particular symbolism is used to represent projecting versus receding bonds, the two seem to have become entangled in recent debates over the problem of how to unambiguously represent absolute configurations in connection with the development of self-consistent computerized data banks for molecular structure.

Speaking as an inorganic chemist, and solely to the issue of a self-consistent stereo symbolism, rather than to the issue of suppressed bonds in framework formulas, I would conclude that a symbolism based on either thickened bold and hatched straight lines or one based on bold wedges applied using the laws of perspective, as per Wells' original suggestion and as used in the representation of simple crystal structures and VSEPR geometries, is infinitely preferable to one using hatched wedges with reversed perspective.

Literature Cited

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2. P. Ramberg, *Chemical Structure, Spatial Arrangement: The Early History of Stereochemistry*, Ashgate: Aldershot, Hampshire, 2003.

3. C. A. Bischoff, *Handbuch der Stereochemie*, Bechhold: Frankfurt, 1894.

4. A. Hantzsch, *Grundriss der Stereochemie*, 2nd ed., Barth: Leipzig, 1904.

5. A. Werner, *Lehrbuch der Stereochemie*, Fischer: Jena, 1904.

6. A. W. Stewart, *Stereochemistry*, 2nd ed., Longmans, Green & Co: London, 1919.

7. G. Wittig, *Stereochemie*, Akademische Verlagsgesellschaft: Leipzig, 1930. Wittig also uses thick bond lines to represent bonds lying above the plane of a ring irrespective of whether they are projecting or receding from the plane of the paper and in three structures actually uses a wedge, but fails to generalize this symbolism.

8. R. Kuhn, "Molekulare Asymmetrie" in K. Freudenberg, Ed., *Stereochemie*, Deuticke: Leipzig, 1932, pp. 803-824.

9. S. Goldschmidt, *Stereochemie*, Akademische Verlagsgesellschaft: Leipzig, 1933.

10. A. F. Wells, *Structural Inorganic Chemistry*, Clarendon: Oxford, 1945.

11. M. S.. Newman, Ed., *Steric Effects in Organic Chemistry*, Wiley: New York, NY, 1956. A glance at Cram's research publications shows that he began using variants of this notation as early as the late 1940s.

12. D. J. Cram, G. S. Hammond, *Organic Chemistry*, McGraw-Hill: New York, NY, 1959.

13. This lack of impact is also present in midcentury monographs on stereochemistry. Thus the volume E. de Berry Barnett, *Stereochemistry*, Pitman: London, 1950 contains no trace of the proposals of Kuhn, Goldschmidt or Wells but relies instead on the use of explicit polyhedra as in the early monographs by Stewart et al..

14. For examples of the inverted wedge symbolism see T. W. G. Solomons, C. B. Fryhle, *Organic Chemistry*, 9th ed., Wiley: Hoboken, NJ, 2008.

15. For the early history of this symbolism, see W. B. Jensen, "Denison-Hackh Structure Symbols: A Forgotten Episode in the Teaching of Organic Chemistry," *Bull. Hist. Chem.*, **2011**, *35(1)*, 43-50.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu