

Three Reference Systems for Chirality Specification. Application, Geometric Properties, and Mutual Relationships

TURE DAMHUS* and CLAUD E. SCHÄFFER

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In assigning *chirality descriptors* (*R*, *S*, Δ , Λ , etc.) to chiral molecular models, one makes use of *chiral reference systems*. Two main reference systems of this kind are in present use. In the first part of this paper we describe these by the use of examples, adding a new third system consisting of *chiral pairs of oriented lines*. In the second part the geometry and symmetry of the three reference systems are analyzed, and it is demonstrated how the use of skew lines may provide a certain quantitative measure of the chirality of a geometric system. The oriented-lines reference system as presented here, the geometrical description of the reference systems, and the conceptual analysis of the way they are used are believed to be new. Part of the material presented has been discussed in a IUPAC working party on stereochemical nomenclature. Here a general algorithm has been developed for ranking atoms in molecules. In this context, it is a perspective that the new reference system may be applicable in connection with atom priorities for obtaining in a simple and very general way chirality descriptors for a very large class of molecules such that they are almost always consistent with the Cahn-Ingold-Prelog rules in cases covered by the latter. Comments from the chemical community are called for as a background for the eventual development of new recommendations on chirality specification based upon the chiral reference systems described. We want to emphasize, however, that *the present paper itself does not attempt to make any nomenclature proposals*.

1. Introduction

A *chiral* (handed, or dissymmetric) object is an object that is not superimposable upon a mirror image of itself.

The importance of the concept of chirality in chemistry is well-known. For discussions in stereochemistry and for chemical nomenclature, it is necessary to have ways to specify, for a given chiral molecular model, whether one is speaking of the molecule itself or its mirror image. While there is unanimous agreement on whether a given *hand* should be called a left hand or a right hand, the history of chemistry tells that the assignment of the predicates "right" or "left" to the two mirror image forms of, e.g., the alanine molecule or the tris(ethylenediamine)cobalt(III) ion is considerably less obvious.

The approach currently used for handling that kind of problem may be described as follows.

First, one defines some standard collections of chiral *geometric* figures, which we shall call here *chiral reference systems*. It is understood that each figure is accompanied by its mirror image within such a collection. For a given reference system, a dichotomic (right/left-type) descriptor is assigned once and for all to each member of the system.

Then, when one has a chiral *chemical* model, one chooses a chiral reference system among the ones defined and compares the chemical model with each chiral figure within the chosen system. The chemical model is assigned the same descriptor as the one carried by the particular chiral figure that matches it the best.

The whole procedure can be illustrated by the determination of the handedness of a glove representing the chemical model. Let us say that you have defined two chiral reference systems, one comprising a right hand and a left hand and the other a right and a left foot. Obviously, the pair of hands is chosen in this case and the matching of one of the hands with the glove is no major problem.

The choice of a reference is, of course, in principle arbitrary, and the matching process is often less obvious than in the case of a hand and a glove; in some cases there may be different "natural" ways of carrying out the matching that may or not result in the same chirality descriptor. There are certainly cases of such a complication that any decision about a chirality descriptor will be felt as completely arbitrary and one then has to specify how the matching is accomplished, i.e., make a *convention* for the matching process.

Two main chiral reference systems serve chemistry at present (section 2A). The purpose of this paper is to introduce

a new, third, reference system, that of *chiral pairs of oriented lines* (section 2B), to discuss the geometric properties of and the mutual relationships between all three systems (sections 2C and 3C), and to illustrate the use of the reference systems, in particular the new one.

The present paper arose from work performed under the auspices of an IUPAC nomenclature commission (see Acknowledgment). In section 2B it is explained why the new reference system may have a significant role to play in future nomenclature. On the other hand, we must stress that *no specific recommendations concerning nomenclature are put forth here*. Our aim is to provide the chemical community with a convenient basis reference for applications of the three systems described. (Of course, for certain classes of molecules, conventions already have been fixed as to which reference system should be used and *how* it should be used: see references given in section 2A.)

We would appreciate communications from practicing chemists on all aspects of these chiral references, and we are particularly interested in experiences with the application of the new reference system. Such reactions from the community would be highly useful when possible IUPAC recommendations are considered for further classes of molecules.

2. Examples

A. The Two Established Chiral Reference Systems. Two main chiral reference systems are currently used:¹ the "steering-wheel" system and the *skew-lines* system.

The geometric figures in the steering-wheel system basically consist of an oriented plane (or just an oriented circle), together with an oriented normal to the plane; see Figure 1. This reference system is used in assigning the well-known *R,S*-descriptors² for configuration around asymmetric (carbon) atoms and the *C,A*-descriptors used in the CAS indexes for chiral mononuclear coordination compounds.³ Typical ap-

- (1) One might mention here a third type of reference system, namely, the helix (see: Reference 2c, Section 7.3. "The Blue Book",^{2b} p 489. Eliel, L. "Elements of Stereochemistry"; Wiley: New York, 1969; p 42). However, as is apparent from ref 4 and section 3 in the present paper, there is an intimate connection between helices and skew-line pairs.
- (2) (a) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem.* **1966**, *78*, 413-447 (*Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385). (b) IUPAC. "Nomenclature of Organic Chemistry" ("the Blue Book"); Pergamon Press: Oxford, 1979; Section E, Appendix 2. (c) Testa, B. "Principles of Organic Stereochemistry"; Marcel Dekker: New York, 1979; Section 5.4.
- (3) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273-1278; **1978**, *17*, 1563-1568. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1-36.

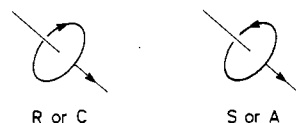


Figure 1. Steering-wheel chiral reference system with the universally adopted chirality descriptors^{2,3} *R* (rectus) or *C* (clockwise) and *S* (sinister) or *A* (anticlockwise).

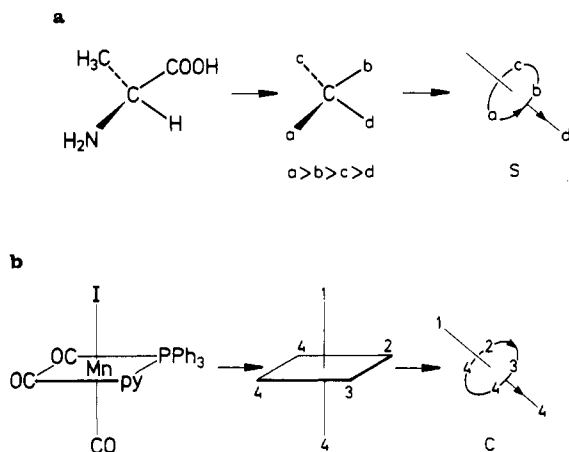


Figure 2. (a) Application of the Cahn-Ingold-Prelog (CIP) sequence rule² and, afterwards, the steering-wheel reference system for assigning a chirality descriptor to a particular enantiomer (catoptromer⁵) of the alanine molecule. (b) Application of the steering-wheel reference system for assigning a chirality descriptor to $[\text{MnI}(\text{PPh}_3)(\text{py})(\text{CO})_3]$ (PPh_3 = triphenylphosphine; py = pyridine) according to the rules employed by Chemical Abstracts Service.³

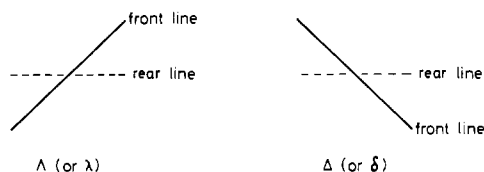


Figure 3. Two (mutually enantiomeric) members of the nonoriented-skew-lines reference system. The figure shows the convention for applying the chirality descriptors Δ (or δ)/ Λ (or λ) within the reference system.

lications are shown in Figure 2.

In the skew-lines reference system, as it has been used till now, the standard geometric objects are nonorthogonal skew pairs of lines; see Figure 3. The skew lines have—in agreement with IUPAC recommendations⁴—chiefly been used for the assignment of the chirality descriptors Δ and Λ to chiral configurations of chelate-bridged octahedron edges in bis- and tris(bidentate) complexes and the descriptors δ and λ to the chiral conformations of five- and six-membered chelate rings.⁴

B. The Oriented-Skew-Lines Reference System. The standard geometric figures are in this case skew pairs of oriented lines. For examples of members of this system, see Figure 4. The very apt symbols $\bar{\Delta}$ and $\bar{\Lambda}$ proposed as chirality descriptors in Figure 4, were suggested by K. Yamasaki (see the Acknowledgment).

The geometry of skew pairs of oriented lines will be discussed in detail in section 3. We point out here two properties

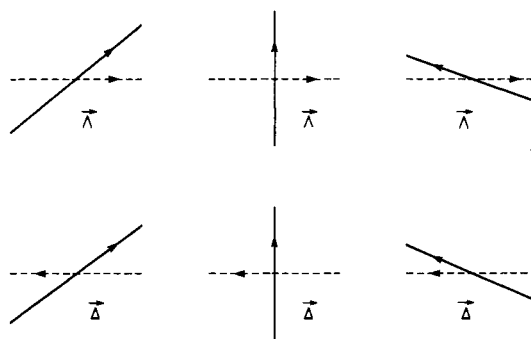


Figure 4. Six members of the oriented-skew-lines reference system. The figure shows the conventions proposed for using the descriptors $\bar{\Delta}$ / $\bar{\Lambda}$ within the reference system.

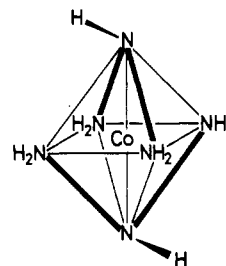


Figure 5. Simplified drawing of the chiral (+)-*mer*- $[\text{Co}(\text{dien})_2]^{3+}$ complex ion based on the structure reported in ref 7. The depicted enantiomer is $\bar{\Delta}$ if the oriented lines $\text{N} \rightarrow \text{H}$ are used for assigning the descriptor.

of such systems that are particularly important for their use in practice:

(i) A given chiral pair of oriented lines *changes* its descriptor (from $\bar{\Delta}$ to $\bar{\Lambda}$ or vice versa) if exactly one of the lines has its orientation reversed, whereas the descriptor remains the *same* if *both* lines switch to the opposite orientation.

(ii) The system is still chiral when the two lines are mutually orthogonal (this is not true if one removes the orientations).

Property i is useful because, if it is difficult to visualize what descriptor is appropriate for a given chiral pair of oriented lines associated with some molecular model, then it is almost always easier to see what is going on if the orientation of one of the lines is changed. (See the discussion of Figure 7 below.) We return to an important consequence of property ii in section 2C, but it is also of direct importance for the actual application of the reference system.

This can be understood from Figure 5, which is our first example of a possible application of oriented lines. The figure shows a particular enantiomer (catoptromer⁵) of the complex⁷ *mer*- $[\text{Co}(\text{dien})_2]^{3+}$, where $\text{dien} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{C}-\text{H}_2\text{NH}_2$. Disregarding conformations of the chelate rings, chirality of this molecule stems solely from the presence of the two coordinated secondary NH groups. It is thus natural to base the selection of a chiral reference system in some way or other on the two N-H line segments. These are mutually skew but also close to being orthogonal to each other. This means that referring to these skew lines as nonoriented would lead to an assignment of a chirality descriptor that might change from $\bar{\Delta}$ to $\bar{\Lambda}$ (or vice versa) upon small angle variations within the molecule, i.e., which was not stable to minor distortions away from the actual geometry.⁷ Further, it would

(4) (a) *Inorg. Chem.* **1970**, *9*, 1–5 (tentative rules). (b) IUPAC. "Nomenclature of Inorganic Chemistry" ("the Red Book"); Butterworths: London, 1970; Section 7.8 (or *Pure Appl. Chem.* **1971**, *28*, No. 1).

(5) The adjective "catoptropic" was used first in: Buckingham, D. A.; Maxwell, J. E.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1969**, 581–583. Its use was also advocated in ref 6.

(6) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, *6*, 219–277.

(7) Okiyama, K.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect.* **1979**, *B35*, 2389–2392. Note that these authors use the nonoriented N–N and H–H lines defined by the two NH groups under consideration, assigning the particular enantiomer in Figure 5 (which we call $\bar{\Delta}$) the descriptor "trans- λ -NH". Another possibility would have been to apply the helix-based descriptors *M* and *P* (cf. Note 1). Thus we here have an example of a molecular model that may easily be matched with members of several distinct reference systems.

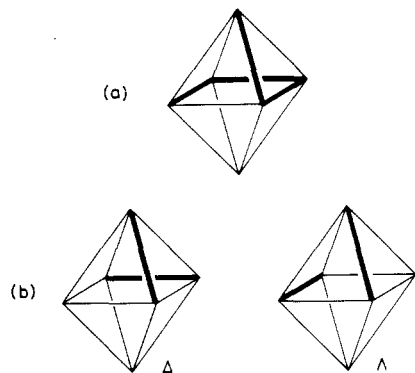


Figure 6. Configuration of edges on an octahedron that is chiral (a) but nevertheless contains exactly one Δ edge pair and one Λ pair (b).

be difficult to determine the descriptor immediately by inspection (and if the skew lines became orthogonal, no chirality descriptor could be obtained at all even though the system was still chiral). Here, the new reference system offers an easily visualized and geometry-stable assignment using the *oriented-line* segments $N \rightarrow H$ (or the two segments $H \rightarrow N$; these give the same descriptor, by property i above). Thus the particular enantiomer in Figure 5 is a $\bar{\Delta}$ form. It may be noted that $[\text{Co}(\text{dien})_2]^{3+}$ cannot at present be handled by the Chemical Abstracts System.⁸

Consider next the model complex of Figure 6a. Compounds corresponding to this model are at present under study by Yamatera and his co-workers⁹ ($[\text{Co}(\text{NH}_3)(\text{tetraen})]^{3+}$ with the unbranched amine tetraen = $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3\text{CH}_2\text{CH}_2\text{NH}_2$); see also ref 6. The example of Figure 6a was noted already in section 7.822 of the 1970 version⁴ of "the Red Book" as having the property of being chiral but exhibiting, nevertheless, an equal number of Δ and Λ pairs within the set of chelate-spanned octahedron edges, as shown in Figure 6b.

Thus, the molecule shown and its mirror image are both " $\Delta\Lambda$ ". To get a chirality descriptor, one clearly needs a further convention. An obvious one would be to agree that only *terminal* chelate rings are taken into account; then the particular specimen in Figure 6a would be called the Λ -enantiomer.

Having encountered this example, one may ask whether the configuration of all other chiral octahedral chelate complexes with an equal number of Δ 's and Λ 's may be treated similarly. A complete discussion of this has been given elsewhere,¹⁰ but we pick out one example for consideration here. Within the chiral configuration shown in Figure 7a, we again find one Δ pair and one Λ pair, as shown in Figure 7b. This time, however, it clearly does not help just to agree on using only terminal edges; and singling out one of the pairs in Figure 7b would require a rather artificial extra convention on top of the "terminal edges" convention. Using *oriented* terminal edges, however, solves the problem. The natural way to orient terminal edges in this system is either to orient all of them *outward* from the ligand, as is done in Figure 7c, or to orient them all oppositely, as is done in Figure 7d. Irrespective of which of these possibilities is chosen *and* irrespective of which pair of terminal edges is used, the same descriptor is obtained, as is seen from Figure 7c,d. (When looking at these figures, it may be helpful to use property i noted at the beginning of this section.)

As a third and rather different example, consider Figure 8a. This is an idealized model of a molecule synthesized

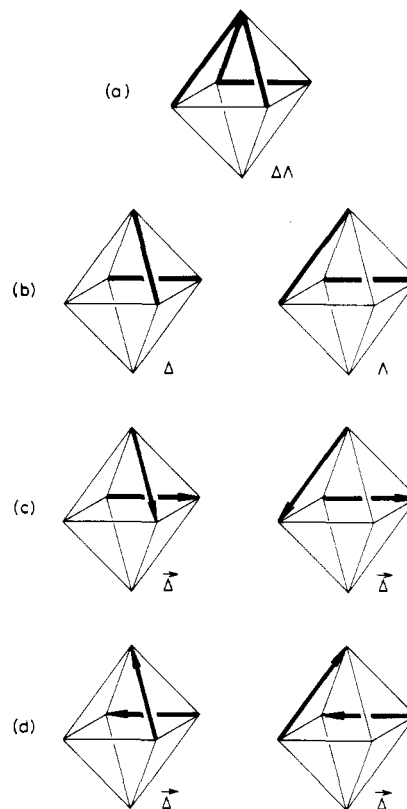


Figure 7. Again a chiral edge configuration with an equal number of Δ pairs and Λ pairs (a). (b) Shows that restricting attention to terminal edges still leaves us with one Δ and one Λ pair; (c) and (d) show assignments of chirality descriptors based on the oriented-lines reference system; in (c) terminal edges are oriented *outward* from the ligand, and in (d) they are oriented *inward*. In either case two $\bar{\Delta}$ pairs are observed.

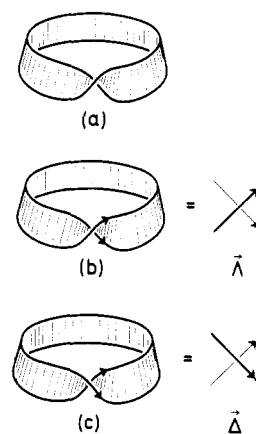


Figure 8. (a) A particular realization of a Möbius strip and thus a model of the molecule recently synthesized and described in ref 11. (b, c) Assignments of chirality descriptors to two enantiomeric Möbius strips using the oriented-lines chiral reference system.

recently¹¹ and having the topology of a *Möbius strip*. The molecule is chiral, but none of the established reference systems are applicable in any obvious way to give chirality descriptors for the molecule and its mirror image. (Note¹¹ that the Möbius strip enjoys what might be called "topological chirality": it remains chiral irrespective of how it is stretched or twisted; i.e., even if it were made of rubber, it could not be deformed into an achiral configuration.) On the other hand, as is evidenced by Figure 8b,c, the oriented-lines system works well

(8) Sloan, T. E., personal communication.

(9) Yamatera, H., personal communication.

(10) Brorson, M.; Damhus, T.; Schäffer, C. E. *Inorg. Chem.* **1983**, *22*, 1569-1573.

(11) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 3219-3221.

here. Property i again ensures that we obtain the same descriptor irrespective of how the edge curve of the Möbius strip is oriented.

Apart from being useful for easy assignment of chirality descriptors to certain complicated molecules in inorganic as well as organic chemistry, the oriented-lines reference has a potential for a much more general application in connection with algorithms like the so-called CANON algorithm.¹² This is, in principle, a completely general algorithm for numbering the atoms in a molecule in such a way that the atoms around any asymmetric atom in the molecule are ranked in the same order¹⁵ as they would have been by the CIP rules.^{2,3} The algorithm has been developed under the auspices of the IUPAC working party on stereochemical nomenclature mentioned in the Acknowledgment, and several preliminary versions of it have already been assessed by that working party. Once such a numbering algorithm becomes sufficiently widely adopted,¹⁶ one might envisage having an equally general procedure for assigning chirality descriptors based on oriented lines by connecting appropriately chosen numbered atoms, orienting the connecting lines, e.g., from atoms with lower numbers to atoms with higher numbers. An appropriate context could be the *permutational nomenclature*¹⁷ already described in the literature. The details of such an approach remain to be investigated, however; among other things one should ensure consistency with established descriptors in cases covered by the existing rules.^{2,3} The remark made about asymmetric carbon atoms in section 2C gives some hope that such consistency would be attainable.

C. Comparison of the Three Reference Systems: Additional Remarks. As mentioned earlier, we shall discuss the geometry of the chiral reference systems in detail in section 3. We want to note here, however, that the three reference systems can be shown¹⁸ to be equivalent in the following sense:

Simple conventions *may be made* by which any geometric figure within a particular type of reference system is assigned a geometric figure within each of the other types of reference systems such that corresponding geometric figures always are subject to the chirality descriptor relations

$$R \text{ or } C \leftrightarrow \Delta \leftrightarrow \bar{\Delta} \quad S \text{ or } A \leftrightarrow \Lambda \leftrightarrow \bar{\Lambda}$$

From a fundamental point of view, then, one could do with just one of these reference systems and any one of them would be as good as any other. In practice, however, what counts is, of course, which reference systems match most obviously with the chiral object under examination and which ones yield, after matching, different descriptors for the object and for its mirror image. (Figure 7 gave an example of a case where the nonoriented lines as well as the oriented ones easily could be made to match with the chiral model, but only the latter yielded chirality descriptors in a natural way.) We therefore find that the most reasonable attitude is to have all three

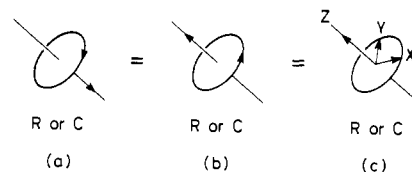


Figure 9. Alternative views on the steering-wheel reference system.

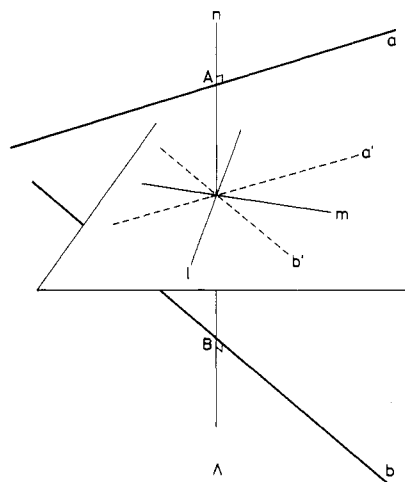


Figure 10. Illustration for the detailed discussion of the geometry of a pair of nonoriented lines a and b. The figure shows a Λ chiral configuration. The line n is the common normal of lines a and b. The axes m and l lie in a plane parallel to both lines a and b, and in this plane they bisect the angles between the projections a' and b' of lines a and b onto the plane.

reference systems in chemistry.

For the particular case of the asymmetric (carbon) atom one can easily prescribe, thanks to property ii in section 2B, an explicit convention enabling one to inspect always a skew pair of oriented lines directly related to the molecule instead of a steering wheel, if one prefers that, and to obtain a $\bar{\Delta}$ for every R configuration and a $\bar{\Lambda}$ for every S configuration. Referring to Figure 2a, if one agrees to use the oriented line segments $a \rightarrow b$ and $c \rightarrow d$, one gets the descriptor $\bar{\Lambda}$.

A further aspect of the choice of chiral reference system is the interplay between chirality description and description of *diastereoisomerism*. A collection of examples illustrating some problems of this sort will be presented elsewhere.¹⁹

As a final remark, we note that it might be tempting to speak of the *oriented line segments* in molecules leading one to use the oriented-lines reference system as "vectors". However, this is an instance where the distinction between the *affine* concept (the concept in the ordinary "point" space we live in, namely, the oriented line segments) and the *linear* concept (the concept in the linear space (Euclidean 3-space) accompanying the point space, i.e., the vectors) is highly relevant: two *vectors* span at the most a two-dimensional subspace of Euclidean 3-space and therefore do not in any reasonable sense form a chiral system. We therefore strongly discourage any use of "vector" in this connection (if "oriented line segment" becomes tiresome, one could use a short and neutral ad hoc term like, e.g., "arrow"). We should mention, though, that we do present in section 3 a relationship between the $\Delta/\bar{\Delta}$ -descriptors and certain products of *three* vectors.

3. Geometry of the Three Reference Systems. The Quantitative Nature of the Skew-Lines Systems

A. The Steering Wheel. The geometric properties of this reference system are rather evident, so we restrict ourselves to a couple of minor comments: The name steering wheel²⁰

(12) The CANON algorithm¹³ has been developed by Dr. W. Schubert from Prof. Ugi's group (see the Acknowledgment). Other algorithms of this kind exist (see, e.g., ref 14); the present authors are not competent to assess the variety of such work, however. What is relevant to us is just the fact that in the near future the assignment of priority numbers to atoms in arbitrary molecules will be a routine matter with the aid of small computers.

(13) Schubert, W.; Ugi, I. *J. Am. Chem. Soc.* **1978**, *100*, 37-41.

(14) Meyer, E. F., Jr. *J. Chem. Educ.* **1978**, *55*, 780-781; *J. Comput. Chem.* **1980**, *1*, 229-232.

(15) Only in certain rare cases, where CIP used imaginary atoms to resolve multiple bonds, a different order may result (Schubert, W., private communication).

(16) In fact, the CANON algorithm is now operational at Chemical Abstracts Service (Schubert, W., private communication in late 1982).

(17) Ugi, I.; et al. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 703-730. Gasteiger, J.; et al. *Top. Curr. Chem.* **1974**, *48*, 1-37.

(18) The detailed proofs are elementary but a little lengthy. A full discussion may be obtained from the authors on request.

(19) Damhus, T.; Schäffer, C. E., in preparation for *Comments Inorg. Chem.*

is very well chosen in the sense that, if we look at Figure 1, imagining that the arrow on the oriented line shows that we are looking *down* the steering column in a car, then *R* corresponds to turning the car to the right and *S* corresponds to turning the car to the left (thanks to the way cars are constructed, which is, of course, *in principle* only a technical convention!). However, if one does not find this association appealing, Figure 9 offers a couple of alternatives. Just turning Figure 1 around gives Figure 9b, which is easily seen to be in harmony with the "right-hand-rule" of electromagnetism. The association with a usual orthogonal coordinate system shown in Figure 9c is rather obvious (*x* and *y* axes are chosen so that the orientation of the *xy* plane given by Figure 9b is the one usually called positive in mathematics when this plane is viewed from the positive *z* axis) and is seen to lead to a right-handed coordinate system for *R* configuration.

B. Nonoriented Lines. For the detailed discussion to be given here, Figure 4 is not sufficient; instead, we shall use Figure 10. A nonorthogonal skew pair of nonoriented lines *a* and *b* as shown there forms a chiral system of point-group symmetry D_2 . One of the 2-fold axes—let us call it the primary one—is the common normal *n* of lines *a* and *b*. The remaining two 2-fold axes, which we shall call the secondary and tertiary axes, respectively, are perpendicular to the primary axis and intersect it halfway between its intersections *A* and *B* with the skew lines. These axes (*m* and *l* on Figure 10) determine a plane and bisect the angles between the projections of lines *a* and *b* on this plane, the secondary axis *m* bisecting the acute angle and the tertiary axis *l* the obtuse angle.

A chiral skew pair of nonoriented lines can be associated with a *screw* (or *helix*) by taking one of the lines as a tangent and the other one as the axis of the screw (see Figure 2 in section 7.8 of "the Red Book"⁴). Thanks to the existence of the 2-fold symmetry about the secondary and the tertiary axis, one obtains for a given chiral skew pair (e.g., lines *a* and *b* in Figure 10) *either* a right screw *or* a left screw, irrespective of which line (*a* or *b*) is chosen as a tangent and which one as the axis. Thus, the chirality of a skew pair is "absolute" in the same way as the chirality of a hand; i.e., a given skew pair is unambiguously assigned either "right" (Δ) or "left" (Λ) by a human being if it is associated with a screw in the fashion mentioned. (We are, of course, here assuming that it is just as evident to humans which screws are right and which are left as is the classification of hands.)

The skew pair {*a*, *b*} in Figure 10 is a Λ pair.

When lines *a* and *b* in Figure 10 are rotated relative to one another about their common normal, they will have two positions in which they form an achiral system: (1) when they are parallel (point-group symmetry D_{2h}) and (2) when they are orthogonal to one another (point-group symmetry D_{2d}).

Let us now consider this relative rotation a little more closely, looking at the lines from outside and along the common normal *n* in such a way that the line closest to our eye is moving anticlockwise. We note that the chirality after passage of a parallel position becomes that of a left-handed screw and remains left-handed until the lines become mutually orthogonal, giving an achiral situation. Continuing, the system becomes right-handed, remaining so until the lines are again parallel. It is seen that the system changes right-left character every 90° .

Note in Figure 10 that either line *a* or *b*, each taken together with *m*, gives a system with the same chirality descriptor as do lines *a* and *b* taken together, while either line *a* or *b* taken together with *l* gives the opposite descriptor. These observations illustrate a situation one frequently meets, namely, that a given chiral system through suitable, more or less equally

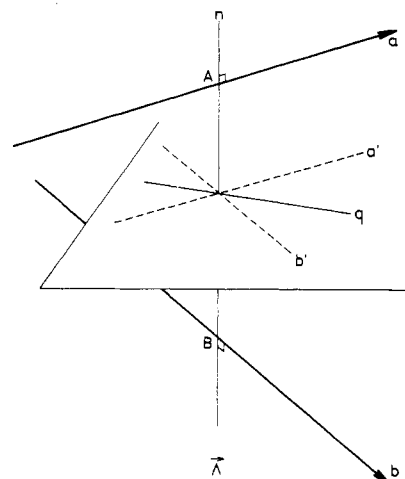


Figure 11. Diagram of a pair of oriented lines *a* and *b* forming a $\bar{\Lambda}$ chiral configuration. Again, line *n* is perpendicular to both lines *a* and *b*, and the plane shown is perpendicular to line *n*. The line *q* is the unique 2-fold symmetry axis of the system.

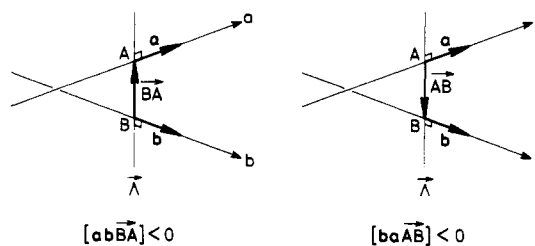


Figure 12. Correlation of the oriented-lines chirality descriptors with scalar triple products of vectors defined by the system. The points *A* and *B* are the intersection points between lines *a* and *b*, respectively, and their common normal (cf. Figure 11).

acceptable, conventions can be classified as *either* "right" *or* "left".

C. Oriented Lines. A pair of nonintersecting oriented lines, *a* and *b* (see Figure 11), is always a chiral system (symmetry C_2), except when the lines are parallel (C_{2v}) or antiparallel (C_{2h}). Note that such a system always has exactly *one* 2-fold symmetry axis (*q* in Figure 11). Starting from the parallel position and rotating the top line anticlockwise as before, one first generates a left-handed screw. This is the situation on Figure 11, and the pair {*a*, *b*} is thus a $\bar{\Lambda}$ pair. However, in contrast to the nonoriented-lines case, the system is still chiral when the angle α of rotation has become 90° , and the system continues to be chiral until the lines become antiparallel. For reasons of continuity, we then *define* the chirality descriptor to be the same in the entire open interval $0^\circ < \alpha < 180^\circ$ —in casu $\bar{\Lambda}$ —even though the immediate possibility of referring to a screw disappears when $90^\circ \leq \alpha < 180^\circ$. The correspondence with a screw (and thus the "absoluteness" of chirality; cf. section 3B) can, however, be maintained throughout the entire range $0^\circ < \alpha < 180^\circ$, giving the chirality descriptor just defined, if the 2-fold axis is taken together with either one of the skew lines (neglecting its orientation) to determine the screw as in section 3B.

The reversal of the orientation of one of the lines in a chiral pair of oriented lines results in a change of chirality descriptor. This may, for example, be understood by referring to the remarks at the end of section 3B and noting that reversal of the orientation of one of the oriented lines results in the unique 2-fold axis switching from being the acute angle bisector to being the obtuse angle bisector or vice versa.

One may alternatively use the following observation (for which we are indebted to E. Larsen), which may help in general in dealing with oriented lines. Consider Figure 12.

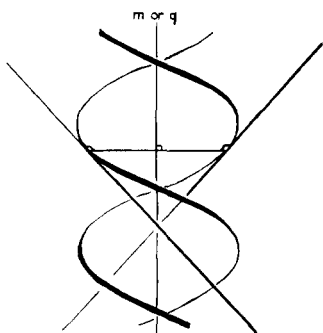


Figure 13. A chiral line pair defining a double helix by the prescriptions discussed in the text. The common axis of the two helical strands is the secondary 2-fold axis in the nonoriented-lines case (cf. Figure 10) and the unique 2-fold axis in the oriented-lines case (cf. Figure 11). Owing to the 2-fold symmetry, the two strands are phase-shifted relative to each other by precisely 180°.

A chiral pair $\{a, b\}$ of oriented lines is given. If we choose first a unit vector \mathbf{a} parallel to line a , then a unit vector \mathbf{b} parallel to line b and, last, the vector BA , we get for a $\bar{\Delta}$ configuration a negative scalar triple product, i.e., $[\mathbf{ab}(BA)] = (\mathbf{a} \times \mathbf{b}) \cdot BA < 0$. If we start with a vector \mathbf{b} on line b , then take a vector \mathbf{a} on line a , and, consequently, take as the last one the vector AB (note the direction!), we also get a negative scalar triple product for the $\bar{\Delta}$ case, so the result is independent of the naming of the two oriented lines. Thus, we have a prescription for obtaining the chirality descriptor for a chiral pair of oriented lines, as defined previously, by judging the sign of a scalar triple product of vectors. Since

$$[(-\mathbf{a})\mathbf{b}(BA)] = [\mathbf{a}(-\mathbf{b})(BA)] = -[\mathbf{ab}(BA)]$$

and

$$[(-\mathbf{a})(-\mathbf{b})(BA)] = [\mathbf{ab}(BA)]$$

we see again that switching one orientation changes the chirality descriptor, whereas switching two orientations leaves one with the same chirality descriptor.

We shall discuss scalar triple products related to skew-line pairs further in section 3E.

D. Double Helices. As a further observation (which in our experience is very helpful to some people but confusing to others) we may note that a unified approach to the nonoriented-lines case and the oriented-lines case is suggested by the above analyses based on the 2-fold axes perpendicular to the common normal of the skew lines: instead of referring to a screw (helix), one may refer to a *double helix* having each of the skew lines as a tangent (one line being a tangent to one strand of the double helix and the other a tangent to the other strand). See Figure 13, where the axis labels m and q have their usual meaning. The double helix is placed so that its axis (i.e., the common axis of its two constituent single helices) is the secondary axis in the case of nonoriented lines and is the unique 2-fold axis in the case of oriented lines. In this way a right double helix corresponds to Δ and $\bar{\Delta}$ and a left double helix to $\bar{\Delta}$ and Δ .

This viewpoint makes the chirality of a chiral pair of oriented lines "absolute" in the sense discussed in section 3B. In the nonoriented-lines case, however, the chirality is more "absolute" when the screw or single helix is used since the use of a double helix requires a convention as to whether the secondary axis or the tertiary axis is to serve as the double-helix axis.

E. The Possibility of Chirality Quantification Using Skew Lines. Consider once again Figure 12 and recall the discussion of the scalar triple product in section 3C. Observe that, by definition, this product varies as the *sine* of the angle $\angle(\mathbf{a}, \mathbf{b})$ from \mathbf{a} to \mathbf{b} (as viewed down the common normal from line a to line b , i.e., along AB), taking on its numerically maximal

value in the orthogonal positions:

$$[\mathbf{ab}(BA)] = (\mathbf{a} \times \mathbf{b}) \cdot BA = |BA| \sin(\angle(\mathbf{a}, \mathbf{b}))$$

This observation suggests taking the scalar triplet product as a kind of quantitative measure of the chirality of the system under consideration. As a matter of fact, experiments can be imagined that would, in principle, allow correlation of this chirality measure with observable quantities (for an example where the observable is the rotatory strength of an electronic transition in a chiral molecule, see ref 21). However, in such experiments it is more likely that one would consider the chirality to *decrease* in some way as a function of the distance $|BA|$. To be able to discuss this effect by itself, it might thus be desirable to separate off the dependence on the distance between lines a and b and consider instead

$$\chi(\{a, b\}) = [\mathbf{ab}(\mathbf{e}(BA))]$$

where $\mathbf{e}(BA)$ is the unit vector $BA/|BA|$. One may consider the function χ thus defined as a quantitative measure of the geometric part of the chirality of this system (or, rather, we may *define* the geometric part of the chirality to be precisely the contribution expressed by χ). Alternatively, in the words of Mislow and Bickart,²² the function χ provides a "fuzzification" of the otherwise very "black or white" concept of chirality.

For a pair $\{a, b\}$ of oriented lines, the "chirality measure" $\chi(\{a, b\})$ has the following properties:

- (i) $\chi(\{a, b\}) = 0$ if and only if the pair is achiral
- (ii) $\chi(\{a, b\}) > 0$ if and only if the pair is a $\bar{\Delta}$ pair
- (iii) $|\chi(\{a, b\})|$ takes its maximum value 1 when the pair is orthogonal

Through a suitable convention, a given pair of *nonoriented* lines may be put in correspondence with a certain pair of *oriented* lines. With reference to the geometry discussion in sections 3B and 3C, the convention we have in mind may be formulated: orient the two lines so that the unique 2-fold axis is the bisector of the acute angle, and open up this angle to double its magnitude (by turning the now oriented lines around their common normal in such a way that they do not pass through an achiral position). If we use χ for this new pair as a measure of the chirality of the given pair, we get zero when the two given lines form an achiral system, a positive number precisely if they are Δ , and a maximum for the numerical value when they are at an angle of 45° to each other. This is just the way one would want a chirality measure for *nonoriented* lines to work.

We now illustrate this by two examples. The first one is that of tris(bidentate) complexes with symmetry D_3 . When the angle between the 3-fold axis and (any) one of the lines connecting the ligating atoms within a chelate ring is 0°, we have the trigonal-prism coordination and the system is achiral with symmetry D_{3h} . Similarly, when the angle mentioned is 90°, we have a planar molecule, again achiral with symmetry D_{3h} . It is satisfactory to attribute "maximum chirality" to the situation in which the angle is halfway between 0 and 90°, i.e., 45°.

The second example is the four-bladed propeller occurring in tetrakis(pyridine) complexes of symmetry D_4 , e.g., $[\text{Pd}(\text{py})_4]^{2+}$. When the angle between the 4-fold axis and the line connecting the 2- and 6-carbon atoms of one of the pyridine molecules is 0 or 90°, the molecule is achiral with symmetry D_{4h} , and when the angle is 45°, we have intuitively the maximum propeller effect and, therefore, quite naturally, the "maximum chirality".

A quantification corresponding to the above one is of course not possible for the steering wheel, which comprises essentially

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only one geometric situation (and its mirror image) compared to the continua of situations exhibited by the skew-lines systems.

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are indebted to this working party for help in various ways; in particular, we thank K. Yamasaki for suggesting the symbols Δ and Λ (cf. Figure 4). The material has also been briefly presented to the Commission itself at its 1980 annual meeting; the Commission decided that it would not attempt to use it to make any new recommendations regarding chirality descriptors at that time but suggested that we meanwhile publish the basic ideas for assessment by the community. T.D. acknowledges support from the Danish Natural Science Research Council (Grant No. 11-0608).

Contribution from BFGoodrich Research and Development Laboratory, Brecksville, Ohio 44141, and the Chemistry Department, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106

Structure and Bonding of Melaminium β -Octamolybdate

WILLIAM J. KROENKE,*† JOHN P. FACKLER, JR.,† and ANTHONY M. MAZANY†

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Only a few of the known organoammonium isopolymolybdates have been subjected to an X-ray crystal structure analysis. The only organoammonium or amine β -octamolybdate to have its crystal structure determined is 3-ethylpyridinium β -octamolybdate.¹ The other structure determinations of β - $\text{Mo}_8\text{O}_{26}^{4-}$ have been made on the hydrated ammonium β -octamolybdate.²⁻⁵ The structure of melaminium β -octamolybdate reported here is the first octamolybdate structure containing a multifunctional complex cation. It also represents the first melaminium isopolymolybdate to be reported in the open literature. Melaminium β -octamolybdate crystallizes in the triclinic system with space group $P\bar{1}$ and $Z = 1$ ($R = 0.028$). The unit cell dimensions are $a = 10.286 \text{ \AA}$, $b = 10.706 \text{ \AA}$, $c = 10.209 \text{ \AA}$, $\alpha = 115.75^\circ$, $\beta = 85.58^\circ$, and $\gamma = 93.11^\circ$. The β - $\text{Mo}_8\text{O}_{26}^{4-}$ anions in the melaminium, pyridinium,¹ and ammonium⁴ molybdates, while similar, show significant differences in several bond lengths and angles. These differences appear to be related to major differences in the cation-molybdate interactions. This structure, the first reported for the melaminium cation, contains ring-protonated melamine rings, similar to the ring-protonated cyclotriphosphazanium rings in a cyclophosphazanium hexamolybdate.⁶ This confirms the prediction from an early UV spectroscopic study⁷ that the endocyclic ring nitrogen atoms in melamine are more basic than the exocyclic nitrogen atoms. The distinguishing feature of the melaminium β -octamolybdate structure is its extensive hydrogen bonding. All 12 nitrogens of the two non-symmetry-related melaminium rings are positioned to be able to form hydrogen bonds with either molybdate oxygen atoms or nitrogen atoms on adjacent rings. The closest approach distances associated with 11 of these potential hydrogen bonds vary from 2.73 to 3.12 \AA . The proposed strong hydrogen-bonding interactions appear to stabilize the structure and explain its high thermal stability.

Introduction

Melaminium octamolybdate, $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$, is the first amine isopolymolybdate based on a multifunctional cation to have its crystal structure determined. Because each melaminium cation contains six nitrogen atoms, it seemed likely that the crystalline structure will be characterized by very extensive hydrogen bonding between melaminium nitrogen atoms and molybdate oxygen atoms, as well as between adjacent melaminium cations. In fact, hydrogen-bond formation has been shown to exist in the two octamolybdates based on monofunctional cations (ammonium⁴ and 3-ethylpyridinium¹) with known structures.

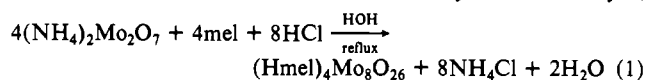
Besides studying the hydrogen-bonding interactions between the melaminium cations and the molybdate anions, this structure determination was made to unambiguously identify the structure of the octamolybdate anion. For example, the IR spectrum of $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ ⁸ in the Mo-O absorption regions is significantly different from the published IR spectra of known molybdates containing either the β - or α - $\text{Mo}_8\text{O}_{26}^{4-}$ anions.

Another important goal of this structural study was to determine the structure of the melaminium cations. No crystal structures of melaminium salts are published. Specifically, the identification of the protonation site of the melaminium cation should unambiguously determine whether the ring nitrogen atoms are more basic than the exocyclic nitrogen atoms.

$(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ was first isolated from an aqueous solution study of the formation of melaminium isopolymolybdates.⁸ It is a white crystalline solid with exceptional thermal and chemical stabilities compared to the other known melaminium isopolymolybdates. $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ is insoluble in all common polar and nonpolar solvents. It will dissolve, with decomposition, in cold caustic soda and in a hot mixture of sulfuric and nitric acids. It is stable in air up to $\sim 260^\circ\text{C}$. Above 260°C it slowly discolors and evolves ammonia.

Experimental Section

Synthesis of $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$. Melaminium β -octamolybdate is prepared by the reaction of either ammonium dimolybdate or ammonium paramolybdate and melamine in aqueous HCl solution as described in reaction 1.⁸ It was characterized by elemental analysis,



IR spectroscopy, and powder XRD.⁸ The subsequent X-ray structure determination confirmed it to be formulated as $(\text{C}_3\text{H}_6\text{N}_7)_4\beta\text{-Mo}_8\text{O}_{26}$ or $(\text{Hmel})_4\beta\text{-Mo}_8\text{O}_{26}$, where Hmel represents the melaminium(1+) cation. The $(\text{Hmel})_4\text{Mo}_8\text{O}_{26}$ is insoluble in water and organic solvents.

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*BFGoodrich Research and Development Laboratory.

†Case Western Reserve University.