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# Proposition for a New Definition of the Chiral Plane and Its Consequences for the Specification of Planar Chirality

Guy L. Lemière* and Frank C. Alderweireldt

*Laboratory of Organic Chemistry, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

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A new definition for the chiral plane is proposed to eliminate the existing confusion between chiral axes and chiral planes. The necessity of a new procedure for the specification of planar chirality is demonstrated. The new procedure is elaborated in analogy to the existing procedures for the specification of chiral centers and axes. Both the definition and the procedure are illustrated with examples from the literature.

Although the history of stereochemistry is more than 160 years old (Biot[1] (1813), Pasteur[2] (1860), van't Hoff[3] and le Bel[4] (1874)), the full specification of molecular chirality has been accomplished only 14 years ago by Cahn, Ingold, and Prelog[5] (1966). These authors used as steric elements the center, the axis, and the plane, and also the conformational helix, but without defining them. Two years later (1968) a group-theoretical description of the center, axis, and plane was given by Prelog.[6,7] Even the IUPAC rules, section E,[8] do not give any definition of the chiral elements but only use and exemplify them. Only 9 years ago (1971) precise definitions for the center and axis were presented by Hirschmann and Hanson.[9]

These authors first define the center of stereoisomerism (see 1) and futher they present a set of definitions (shown as in 2–11) for describing the center of stereoisomerism as achiral, chiral, pseudoasymmetric, proachiral, or prochiral. Then they define the axis of stereoisomerism (see 12) and present a set of five definitions (shown as in 13–17) applicable to axes and planes, analogous to those shown in 2–11. Hirshmann and Hanson, however, do not define the plane of stereoisomerism. They only give a description and they make no rigorous separation between the axis and the plane by stating: "These latter two concepts are not necessarily mutually exclusive as the same partial structure can often be viewed as either a chiral axis or a chiral plane" (ref 9, p 3302). This indistinct separation between axis and plane may lead to confusion when specifying the absolute configuration of a chiral element of stereoisomerism, since this element will get, for example, an *R* label when viewed as a chiral axis and an *S* label when viewed as a chiral plane (see further).

In this paper we want to support but also to amend the description of a plane of stereoisomerism as given by Hirschmann and Hanson. We think that the usefulness of their definition can be enhanced by transforming it into a more precise definition, which excludes any confusion between the plane and the axis of stereoisomerism. The introduction of this definition has some consequences for the Cahn–Ingold–Prelog procedure for the specification of planar chirality. Therefore we also propose a new procedure for the latter, which is more similar to the procedure for the chiral centers and axes than the existing Cahn–Ingold–Prelog procedure.

## Definition of Planes of Stereoisomerism

Definition (see Figure 1): A plane of stereoisomerism is defined by an atom $T_1$ and the proximal atoms A and B (specified in **13**) of the nearest improper center of stereoisomerism $T_2$.[10] $T_1$ is directly joined to (at least) three proximal atoms that lie outside the plane and that are limited in their orientations relative to it. Unshared orbitals are to be treated[11] as proximal atoms.

Intrinsic properties: $T_1$ and $T_2$ must be so interrelated that the same stereoisomer can be produced either by a rotation of the out-of-plane proximal atoms of $T_1$ from one side of the plane to the other or by an exchange at $T_2$ of differentiated proximal atoms. If both these changes are made simultaneously, the original structure is restored. The "terminal atoms" $T_1$ and $T_2$, the bond(s), and any other atoms that connect them by the shortest path form the "core", and, if there are two or more alternative paths of equal length, no distinction is made between them but all are included in the core.[12]

This definition of a plane of stereoisomerism resembles in many points the definition of an axis of stereoisomerism (Figure 2). In both elements of stereoisomerism a "core" and "terminal atoms" are presented. In both the "terminal atoms" are so interrelated that a change at either terminal atom produces the same stereoisomer and a change at both restores the original structure.

Nevertheless, no confusion is possible. In an axis both terminal atoms $T_1$ and $T_2$ have two proximal atoms by the definition, and the intersecting line of the planes defined by each terminal atom and its proximal atoms is the axis of stereoisomerism. In a plane, by the present definition, terminal atom $T_1$ has more than two proximal atoms which can not lie together with $T_1$ in one plane.

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[1] Biot, J. B. *Ann. Chim. Phys.* **1815** *4*, 90; *Mém. Acad. Sci.* 1817, *2*, 41.

[2] Pasteur, L., lectures delivered before the Société Chimique de Paris, January 20 and February 3, 1860.

[3] van't Hoff, J. H. "Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte struktuurformules in de ruimte; benevens een daarmee samenhangende opmerking omtrent het verband tusschen optisch aktief vermogen en chemische constitutie van organische verbindingen", J. Greven: Utrecht, 1874.

[4] Le Bel, J.-A. *Bull. Soc. Chim. Fr.* **1874**, 337.

[5] Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

[6] Prelog, V. *Chem. Br.* **1968**, *4*, 382; *Proc. K. Ned. Akad. Wet., Ser B: Palaeontol., Geol., Phys., Chem.* **1968**, *71*, 108.

[7] Prelog, V.; Helmchen, G. *Helv. Chim. Acta* **1972**, *55*, 2581.

[8] IUPAC Rules for the Nomenclature of Organic Chemistry, Section E: Stereochemistry", *Pure Appl. Chem.* **1976**, *45*, 11.

[9] Hirschmann, H.; Hanson, K. R. *J. Org. Chem.* **1971**, *36*, 3293.

[10] When $T_2$ has ideal $sp^2$ hybridization it also lies in the plane of stereoisomerism. When it does not, for example, as in strained paracyclophanes, it lies outside but very near to the plane.

[11] In Hirschmann's and Hanson's definition[9] of an axis of stereoisomerism (12) the sentence "an unused bonding orbital may be treated as a proximal atom" has to be changed into "an unused bonding orbital has to be treated as a proximal atom" to avoid further confusion between axes and planes.

[12] The present definition is limited to structures in which the out-of-plane groups are bonded to an identifiable terminal atom $T_1$. This restriction excludes the metal $\pi$ complexes.

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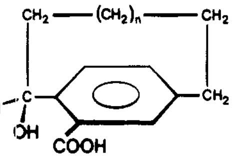
In some special cases, for example, in structure **1**, $T_1$ may be a terminal atom of a chiral plane of stereoisomerism and at the same time a chiral center of stereoisomerism. The configuration of the chiral carbon atom is independent of the chiral plane of the paracyclophane.



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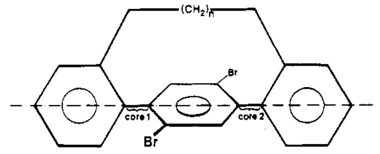
Most of the structures having a chiral plane according to the current idea have two or more chiral planes according to our new definition. This is illustrated by structure **2** in Figure 3. In this paracyclophane two cores with terminal atoms $T_1$ ($T_1'$) and $T_2$ ($T_2'$) can be found with A (A′) and B (B′) as differentiated proximal atoms to $T_2$ ($T_2'$) and C (C′) as an out-of-plane cf-group to $T_1$ ($T_1'$). The unshared electron pairs of the oxygen atoms $T_1$ and $T_1'$ are to be considered as proximal atoms. The plane containing A, B, and $T_1$ and the plane containing A′, B′, and $T_1'$ are two coinciding chiral planes of stereoisomerism.[13]

Until now in such structures the two planes are not distinguished, because both planes coincide and because the planes are so interrelated that the configuration of one plane can not be inverted without inverting the configuration of the other one. Nevertheless, in a number of analogous structures with coinciding chiral axes, the axes have to be distinguished (**3**) even when they can not be inverted independently (**4**). There is no reason to treat such structures otherwise than the many known structures, such as **5**, with chiral centers that can not be inverted independently but that are nevertheless distinguished and may not be considered as one single element of chirality.



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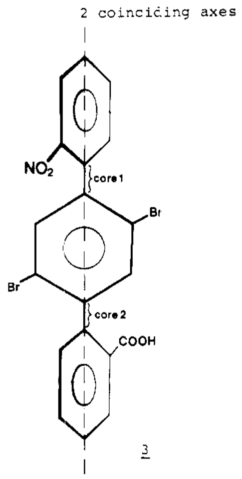

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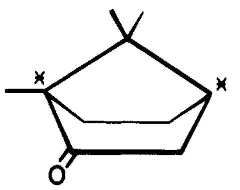

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Therefore it seems much more logical and quite in the spirit of Cahn, Ingold, and Prelog (see ref 5, p 400, 2.7) to distinguish the planes, and we think that this will become unavoidable, because in the literature more and more structures appear with one or more independently invertable chiral planes.

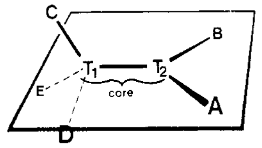


**Figure 1.** Schematic representation of a plane of stereoisomerism, where A, B, C, D, and E are differentiated proximal atoms and $T_1$ and $T_2$ are terminal atoms.

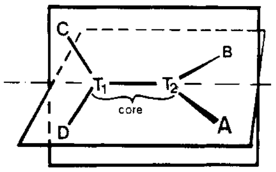


**Figure 2.** Schematic representation of an axis of stereoisomerism (– • –), where A, B, C, and D are differentiated proximal atoms and $T_1$ and $T_2$ are terminal atoms.

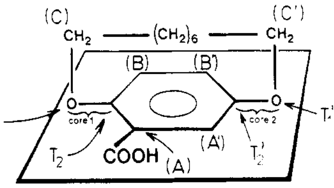
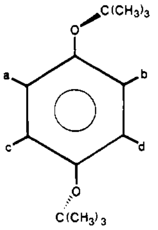


**Figure 3.** Factorization of structure **2** into two chiral planes of stereoisomerism.

In structure **6**, suggested by Hirschmann and Hanson,[9] a, b, c, and d are bulky enough to prevent the $OC(CH_3)_3$ groups from rotating around the O–phenyl bonds. This structure has two not interrelated chiral planes that can be inverted separately, giving rise to four stereoisomers (two *dl* pairs). Product **7**[14] is very similar to **6**, but it has only one chiral plane. This product exists in two enantiomeric forms: the benzylic protons show a diastereotopic AB quadruplet in the $^1H$ NMR spectrum. Product **8**[15] has three chiral planes. The three neopentyl groups may be reorientated independently to the other side of the plane, giving rise to eight stereoisomers (four *dl* pairs). Product **9** is a special case of a paracyclophane. It does not have two planes but a chiral biphenyl-type axis and a chiral plane. Product **10**[16] has three noncoinciding and independently invertable chiral planes. A chiral plane coincides with the plane of each phenyl ring. The cores of the three chiral planes have their terminal atom $T_1$, atom Z, in common. The other terminal atoms of the cores are the carbon atoms of the phenyl rings directly bound to Z. In this product Z is a chiral center of stereoisomerism, but as mentioned before the configuration is independent of the configuration of the chiral planes. When one chiral center Z and three chiral planes are present, one can expect $2^4 = 16$ stereoisomers. There are, however, 32 stereoisomers because each of the just calculated number of



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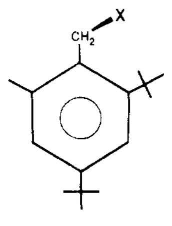

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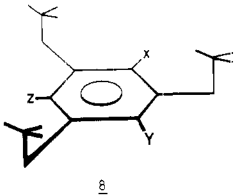
[13] Hirschmann and Hanson came to an analogous conclusion when stating that the individual cores and their proximal atoms are the elements of stereoisomerism rather than the larger entity that would result from the combination of two or more of such cores.[9]

[14] Cupas, C. A.; Bollinger, J. M.; Haslanger, M. *J. Am. Chem. Soc.* **1968**, *90*, 5502.

[15] Nillson, B.; Martinson, P.; Olsson, K.; Laster, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 3190.

[16] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535.



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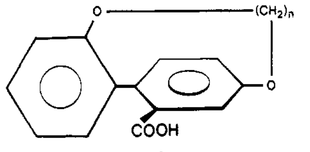

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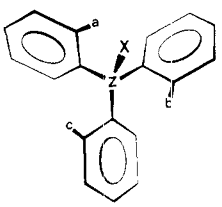

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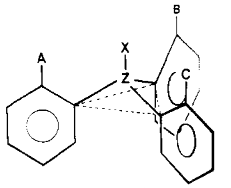

10b

structures can exist in two propeller forms.

## Proposition for a New Procedure for Specifying Planar Chirality

As indicated above our definition for a plane of stereoisomerism is very analogous to the definition of an axis of stereoisomerism. This analogy will now be used to make a new procedure for specifying planar chirality.

Paracyclophane **2** has two chiral planes according to the new definition. These two planes are interrelated in such a way that it is impossible to invert the configuration of one of them without inverting that of the other one. Therefore it could eventually be sufficient to assign an absolute configuration label to only one of them. According to the Cahn–Ingold–Prelog procedure, only one of the two planes is picked out by the choice of a pilot atom (see $p_{CH_2}$ in Figure 4A) and is given a label *R* or *S*. Nevertheless, since it is more logical to distinguish the two elements of stereoisomerism for the reasons discussed before, it is also more logical to give an absolute configuration label to both. Consequently it is no longer necessary to look for a pilot atom.

Standard subrule 0[5] says: *The nearer end of an axis precedes the further end.* This rule can be translated in terms of Hirschmann and Hanson as follows: *The differentiated proximal atoms at terminal atom $T_2$ precede the differentiated proximal atoms at terminal atom $T_1$.* For chiral axes it never matters which terminal atom is taken as $T_1$ and which as $T_2$ provided that the choice, once made, is adhered to. This new version of subrule 0 can also be applied to the new definition of a chiral plane, but here the assignment of $T_1$ and $T_2$ is fixed by the definition of the chiral plane.

Figure 5 shows a chiral center, **11**, a chiral axis, **12**, and a chiral plane, **13**, in a schematic way. According to the chirality rule, the chiral center **11** and the chiral axis **12** are to be observed from the preferred side. In this example, the path from high to low precedence of the differentiated proximal atoms, $A > B > C$, turns clockwise, and an absolute configuration label *R* is to be assigned to both the center and the axis. By analogy with the previous procedures, the chiral plane **13** is observed from the preferred side indicated by the "fiducial" out-of-plane group C. The path of high to low precedence of the differentiated proximal atoms, $A > B > C$, equally turns to the right in **13**, and here too an absolute configuration label *R* is to be assigned to the plane. However, this plane would get a label *S* by the standard Cahn–Ingold–Prelog procedure as can be seen from **14**, where C is the "pilot" atom. The use of the new procedure would have the far-reaching consequence that all planes, specified up to now in the literature, will have to be reversed.[17] Since sooner or later new rules will have to be elaborated and accepted by the IUPAC commission, in order to eliminate some ambiguities of the existing rules, a unified procedure for all kinds of chiral elements is to be preferred. In Figure 4B our new procedure is applied to paracyclophane **2**.

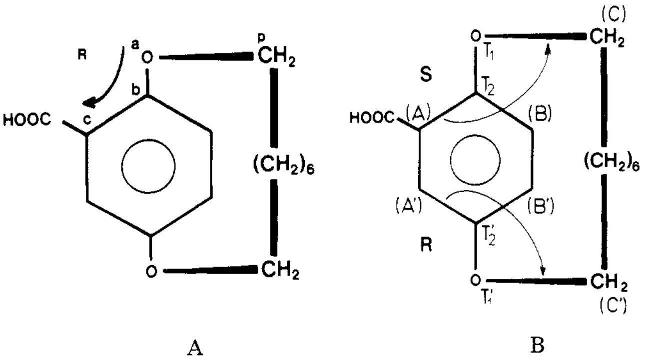

**Figure 4.** Comparison of the specification of planar chirality in product **2** by (A) the Cahn–Ingold–Prelog procedure and by (B) our new procedure.

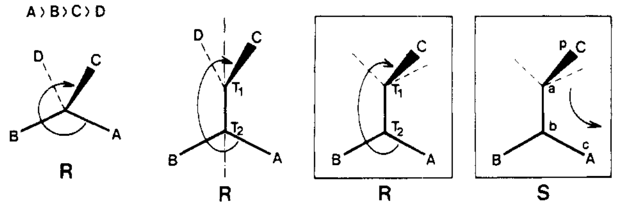

**Figure 5.** Comparison of the procedures for the specification of central (**11**), axial (**12**), and planar (**13** and **14**) chirality.

The new procedure is now concisely repeated. The planar chirality is factorized into chiral planes according to the new definition (in most cases more chiral planes than in the old procedure). For each chiral plane a fiducial out-of-plane group is selected according to the conformational selection rules.[18] This is necessary since $T_1$ ($T_1'$) has three out-of-plane groups. The groups on the terminal atom $T_2$ and the fiducial out-of-plane group are arranged in sequence according to the standard subrules (see our new formulation of standard subrule 0). The fiducial out-of-plane group indicates the side of the plane from which the arranged groups of $T_1$ and $T_2$ are observed. An absolute configuration label is then given according to the chirality rule.

The great analogy between the procedure for specifying axial chirality and our new procedure for specifying planar chirality has an other advantage: a chiral axis which is treated erroneously as a chiral plane will get the same absolute configuration label as when it is treated correctly, and vice versa (see Figure 5, **12** and **13**). However, with

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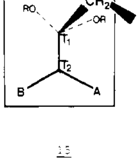
[17] For some structures with planar chirality the Cahn–Ingold–Prelog procedure does not work because one can not find one single pilot atom as required. For example, in structure **15** one can not find a pilot atom because the oxygen atoms can not be distinguished by the standard subrules.[5] When the Cahn–Ingold–Prelog procedure is interpreted broadly by accepting both oxygen atoms as pilot atoms and by viewing the plane from the side of these atoms, only in this case is the absolute configuration label assigned by the Cahn–Ingold–Prelog procedure not reversed by ours.



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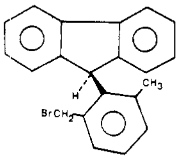
[18] Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.

the old procedure for specifying planar chirality, application of the wrong procedure results in the opposite absolute configuration label (see Figure 5, **12** and **14**). This is important since in the literature one can indeed find examples of such a confusion between chiral axes and chiral planes (see further).

The helicity rule[5] may be applied to the structures discussed in this paper as well, since torsional isomers are concerned. However, as a consequence of the reversal of the absolute configuration labels, the symbols *R* and *S* now correspond to *M* and *P*, respectively, just like in the biaryl series. The parallelism between chiral planes and axes is thus complete.

The molecules discussed in this paper and having planar chirality are torsional isomers. In most cases, when rotating the out-of-plane groups over 360°, two potential-energy hollows are encountered, one at either side of the plane. In these cases the two molecular forms corresponding to the two energy hollows can be sufficiently specified by *R* and *S* or *P* and *M*. However, there are also structures with more than one potential-energy hollow at either side of the plane. In these cases the different molecular forms can be specified by *R* and *S* or *M* and *P* supplemented by the symbols sp (syn-periplanar), sc (syn-clinal), ac (anti-clinal), and ap (anti-periplanar).[5,18] For example, product **16**[19,20] has one chiral plane (not a chiral center as mentioned by the authors)[20] coinciding with the plane of the 2-(bromomethyl)-6-methylphenyl ring. Terminal atom $T_2$ is $C_1$ of the substituted phenyl ring and $T_1$ is $C_9$ of fluorene. The fiducial out-of-plane group is the proton of $C_9$ of fluorene. In this case there are two potential-energy hollows at either side of the chiral plane. The energy barrier between the ap and sp rotamers is very high and the separate isomers can be isolated at room temperature.[19] The energy barrier between the *R* and *S* rotamers is very low and the presence of the latter can only be detected by $^1$H NMR at low temperature by the tendency of the bromomethyl proton signal to split into an AB quadruplet.[20] Also product **10**, discussed before, has two energy hollows at either side of the three chiral planes.



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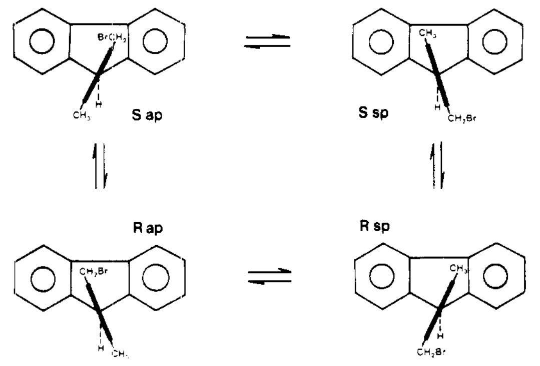
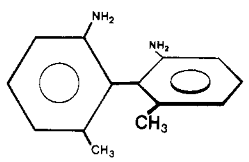


16a 16b 16c 16d

## Nomenclature. Specification of Axial and Planar Chirality in Names

According to the IUPAC rule E-5.9,[8] names of chiral compounds whose absolute configuration is known are differentiated by prefixes *R*, *S*, etc. assigned by the sequence rule procedure, preceded when necessary by the appropriate locants. Some examples are given for compounds having chiral centers: (*R*)-glyceraldehyde, (6*S*,12*S*,5′*R*)-rotenone. No examples are given for products with axial or planar chirality.

In accordance with the IUPAC rule and with a suggestion of Cahn, Ingold, and Prelog,[5] we propose to specify chiral axes and planes in names by the locants of the terminal atoms $T_2$ and $T_1$, followed by the absolute configuration label *R* or *S*, eventually further followed by the symbols sp, sc, ac, or ap. However, the suggestion of Cahn, Ingold, and Prelog to let the labels *R* and *S* be preceded by "*a*" for a chiral axis or "*p*" for a chiral plane is not necessary in our opinion since the chiral elements are sufficiently specified by the other symbols, even when an axis is taken erroneously for a plane or a plane for an axis. For example the names of products **17**,[21,22] **18**,[23] and **16a** are, respectively, (1,1′*R*)-2,2′-diamino-6,6′-dimethylbiphenyl, (1,8*S*,2,3*S*)-*trans*-cyclooctene, and (1′,9*S*ap)-9-[2-(bromomethyl)-6-methylphenyl]fluorene.



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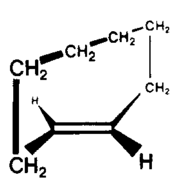

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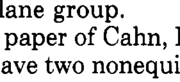
## Some Examples from the Literature

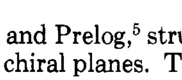
Some examples will now demonstrate the use or misuse of chiral axes and chiral planes in the literature.

Mislow and co-workers,[16] in a study on products of the type $Ar_3ZX$ (**10**), call the plane going through the three aryl carbon atoms bonded to Z a chiral plane and call the axis going through XZ a chiral axis. These concepts do not correspond to the chiral axis and plane as used by Cahn, Ingold, and Prelog nor as defined by Hirschmann and Hanson and by us.

Raban and co-workers,[24,25] in a study on sulfenamides **19**, call the nitrogen–sulfur bond a chiral axis. According to our definition, however, the chiral element in these products is a chiral plane containing the sulfur atom and the groups $R_2$ and $R_3$. The nitrogen–sulfur bond is the core, the nitrogen atom is the terminal atom $T_2$, and the sulfur atom is the terminal atom $T_1$, with $R_1$ as the fiducial out-of-plane group.



19a



19b

In the paper of Cahn, Ingold, and Prelog,[5] structures **20** and **21** have two nonequivalent chiral planes. The moiety of the acid **20** with respect to the plane of the unbrominated phenyl ring is in the *R* form, and the moiety with respect to that of the brominated ring is in the *S* form. In the anhydride **21** the labels become reversed because the pilot atom in the former is a methylene carbon atom, whereas in the latter it is an anhydride oxygen atom. This

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[19] Nakamura, M.; Oki, M. *Tetrahedron Lett.* **1974**, 505.

[20] Oki, M. *Angew. Chem., Int. Ed. Eng.* **1976**, *15*, 87.

[21] McGinn, F. C.; Lazarus, A. K.; Siegel, M.; Ricci, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 476.

[22] Pignolet, L. H.; Taylor, R. P.; Horrocks, W. DeW., Jr. *Chem. Commun.* **1968**, 1443.

[23] Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 1268.

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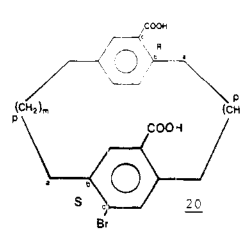
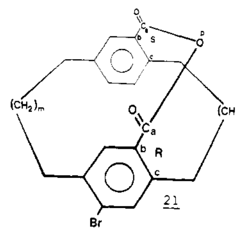
[25] Raban, M.; Carlson, E. M. *Isr. J. Chem.* **1976/1977**, *15*, 106.

Cahn-Ingold-Prelog procedure



20



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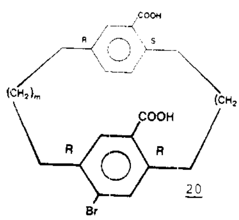
Our procedure



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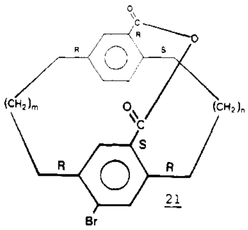

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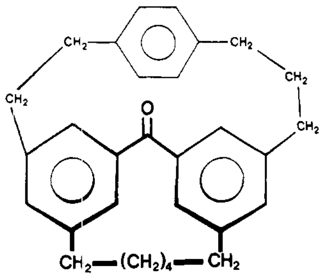
inversion of the label is the result of the Cahn-Ingold-Prelog procedure and of two chiral axes which are viewed as chiral planes (**21**). Indeed, according to our definition the acid **20** has two chiral planes in each phenyl ring. In the anhydride **21** these same chiral planes can be found and they have the same absolute configuration label as in the acid **20**. The carboxylate groups which are free to rotate in the acid can not rotate in the anhydride, which results in two new chiral elements, which are chiral axes (see definition of Hirschmann and Hanson) and not chiral planes. As can be seen the axes have the inverse label with respect to the same chiral elements viewed as chiral planes in the original paper.

Also structure **22** can be found in the paper of Cahn, Ingold, and Prelog. The phenyl-CO bonds can not rotate and this gives rise to two chiral axes and not to chiral planes as mentioned by the authors. Application of the procedure for specifying chiral axes results in the opposite absolute configuration labels with respect to the labels assigned by the authors according to their procedure for chiral planes.



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## Concluding Remarks

We hope to have brought some convincing arguments for the necessity of a new definition for the plane of stereoisomerism and a new procedure for the specification of planar chirality. Although we are aware of the practical problems created by the eventual inversion of the absolute configuration labels assigned to chiral planes, we think that something has to be done about this. In the near future the confusion about the ambiguity of the now generally used rules will be greater than the transient confusion caused by the use of new rules. We all overcame the transition from D and L into *R* and *S*. The present problem is a minor one, compared to that. By the use of the new procedure most structures with planar chirality will get two configuration labels, whereas they get only one label by the Cahn-Ingold-Prelog procedure. Therefore, there usually will be an outward sign to indicate which nomenclature is followed.

We already mentioned the great resemblance between the definitions of the axis and the plane of stereoisomerism. The distinction between both elements of stereoisomerism is more or less artificial. In both cases we are concerned with an assembly of differentiated atoms around a linear core $T_1$-$T_2$. Therefore it would be better to join both types of elements of stereoisomerism in one group of "lines of stereoisomerism". Since our new procedure for the specification of planar chirality is almost the same as the Cahn-Ingold-Prelog procedure for the specification of axial chirality, this junction does not cause any problems. We would gladly cooperate with any efforts in this direction.

**Acknowledgment.** We are very indebted to Professor Dr. Hans Hirschmann for the constructive comments he made during the preparation of our manuscript and for his comprehension of our viewpoints. Without the patient and profound discussions with him we should not have come to the present version of our paper.

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# Heterogeneous Ethylation of Phenylacetonitrile

Roberto Solaro, Salvatore D'Antone, and Emo Chiellini*

*Istituti di Chimica Organica e Chimica Organica Industriale, Centro CNR Macromolecole Stereordinate Otticamente Attive, Università di Pisa, 56100 Pisa, Italy*

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Data are reported relevant to the ethylation of phenylacetonitrile (PAN) in aqueous-organic medium under the standard conditions adopted for "phase-transfer reactions" in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB). The kinetic profile of the reaction has been investigated as a function of variables such as stirring rate, temperature, and concentration of the components of the reaction mixture. The experimental observations are consistent with an interfacial-type process where the quaternary ammonium salt functions as a transfer agent which resides primarily in the organic phase.

In the course of our previous studies[1-4] on the activity of macromolecular amines and ammonium salts as catalysts in reactions, such as alkylation of phenylacetonitrile (PAN) and dichlorocarbenation of styrene and benz-