THE SIGNS OF CHIRAL PROPERTIES: SUGGESTED TERMS "CONSIGNATE" AND "DISSIGNATE"

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We have felt for some time the need for a term to indicate whether or not the sign of a chiral property follows the signs appropriate to a region in space around an origin (usually a chromophore). The terms "octant" (or "pro-octant") and "anti-octant" (or "reverse-octant") are widely used at present,[1] often with quotation marks to apologise for their colloquial nature.

Confusion can arise in dealing with Quadrant and Octant Rules at the same time, and even more when different schools use different reference frames for their octants (e.g. Scott's left-handed coordinate frame for olefins[2]).

We propose that right-handed Cartesian coordinates should be standard, set up as in (I) for three dimensions and in (II) for two dimensions; the +x direction is always on the observer's right-hand side, and the +z direction, in a three-dimensional system, is towards the observer. The coordinate frame (I) gives signs for octants coinciding with those of the original Harvard Rule[3] for the carbonyl group, which has been far more widely used than any other Rule of this kind.[4]*

A pair of terms is needed to indicate whether the contribution to the value of a chiral property (e.g. $\Delta\varepsilon$ in c.d., amplitude $\underline{a}$ in o.r.d.) associated with any point $\underline{P}$ in space agrees or disagrees in sign with the product of the point's coordinates (III).

We propose that a chiral property whose sign agrees with the sign of the product of the coordinates should be called "consignate" (IV or VI); a property whose sign disagrees with the product of coordinates would then be called "dissignate" (V or VII). These terms have been developed on the analogy of

*The "Harvard" axes are in fact a left-handed set, but many subsequent workers (e.g. Weigang[4]) have chosen a right-handed set as proposed above, which gives the same results as the original "Harvard" Rule.
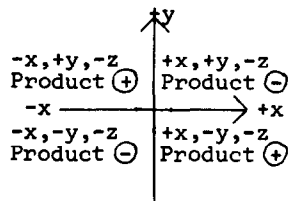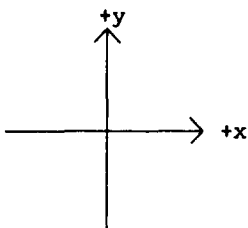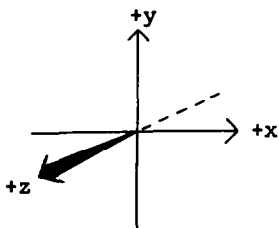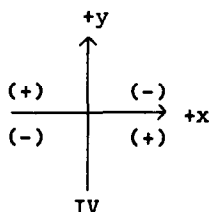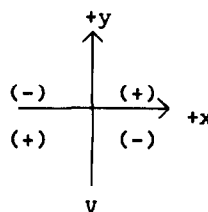
I: Three dimensions   II: Two dimensions
    Right-handed Cartesian coordinates;
        preferred orientations.

-x,+y,-z   +x,+y,-z
Product ⊕   Product ⊖
-x ─────────────→ +x
-x,-y,-z   +x,-y,-z
Product ⊖   Product ⊕

III

Projection of I onto xy plane;
+z is above paper.
Coordinate signs are given for
points in Rear Octants.
Products of signs are shown as
⊕ or ⊖

IV

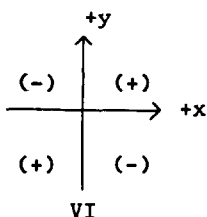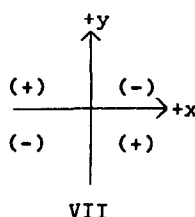(+)   (-)
(-)   (+)

Consignate

V

(-)   (+)
(+)   (-)

Dissignate

Designation of Chiral Properties in Rear Octants (z, -ve)

VI

(-)   (+)
(+)   (-)

Consignate

VII

(+)   (-)
(-)   (+)

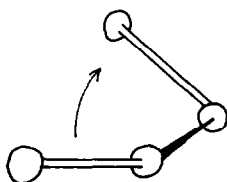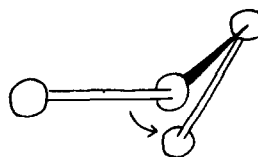Dissignate

Designation of Chiral Properties :-
    (A) in Front Octants (where z is +ve)
or (B) in Quadrants (where the sign of z is not relevant)

VIII

Helix: cisoid, (+) or P
Property (+); consignate
Property (-); dissignate

IX

Helix: cisoid (-) or M
Property (-); consignate
Property (+); dissignate

"conrotatory" and "disrotatory", which have proved so useful in the treatment of Orbital Symmetry.[5]

When it is necessary to distinguish between Octant, Quadrant, or other regional "rules", the appropriate word may be included as a prefix: e.g. "octant-consignate", "octant-dissignate", "quadrant-consignate". The prefix may be omitted when the nature of the rule under discussion is unambiguous. (No simple designation of this kind will deal with curved[6] or conical surfaces[4] for sectors, but the proposed terms are very useful in most of the situations encountered by organic chemists).

Octant Rules. The effects of perturbing groups on the chiroptical properties of chromophores obeying an Octant Rule are very conveniently described. Examples include:

(i)   Carbonyl groups (n→π* transition, 290 nm).[3]

     α-Axial or β-equatorial alkyl, Cl, Br, or I in cyclohexanones:

        consignate (or octant-consignate).

     α-Axial or β-axial F,[7] OH, OAc:[8] usually dissignate.

     β-Axial Me: often dissignate,[9] but sometimes consignate.[9,10]

(ii) Olefins (longest-wavelength transition).

     Allylic alkyl groups: usually dissignate (octant-dissignate),[2,11]

     Allylic OH, OAc, Cl: usually consignate.[2]

The new terms are far more convenient in the last mentioned examples than anti-"reverse-octant" or equivalent expressions.

Quadrant Rules. The signs corresponding to quadrant-consignate (VIB) and quadrant-dissignate (VIIB) behaviour are the same as those found in front octants when an Octant rule applies, because of the way in which the coordinate system is set up. Obedience to a quadrant rule implies that the sign (but not necessarily the magnitude) of a chiroptical property is independent of the z coordinate of the perturbing group. The carbonyl n→σ* transition (190 nm) provides an example effects of α- or β-axial alkyl groups are thought to be quadrant-dissignate (VIIB).[12]

Helical Structures. Although Cartesian coordinates are inappropriate, the value of a chiral physical property for a helical structure may be described as consignate when its sign is the same as that of the helix, i.e., a positive property for a right-

handed helix, or a negative property for a left-handed helix. Values are <u>dissignate</u> when they are of opposite sign to that of the helix. Examples for <u>cisoid</u> conjugated dienes[13] are shown in VIII and IX. Torsional effects in mono-olefins[14] can be discussed in similar terms.

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