A Nomenclature and Structural Representation System for Asymmetrical "I"-Shaped Hyperbranched Polymers

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A structural repeating unit (SRU) orientation and nomenclature system is described for registration of asymmetrical, "I"-shaped hyperbranched polymers in SCION, a DuPont proprietary database that operates by use of the Chemical Abstracts Service Registry System (CASRS) for registration and Messenger software for searching.

1. INTRODUCTION

SCION is a DuPont proprietary online database that uses the Chemical Abstracts Service Registry System (CASRS) for polymer registration.[1]

Registration of polymers is executed manually for DuPont by CAS keyboarding personnel. The orientation and nomenclature system described in this paper is to accompany manual encoding of polymers, but the principles behind it might be used for an automated polymer registration system.

A recent paper[2] discussed conversion of structural repeating unit (SRU) polymers with odd numbers of crossing bonds (see point 1) into symmetrical, hyperbranched, "I"-shaped SRUs with an even number of crossing bonds, so that they can be registered by the CASRS (see point 2).

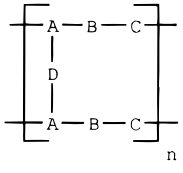
Point 1: A crossing bond is a bond that crosses limiting parentheses or brackets. Thus, in $-(-O-CH_2-)_n-$ the crossing bonds are represented by "−(−" and "−)−".

Point 2: The CASRS cannot register structural repeating unit (SRU) polymers with an odd number of crossing bonds.

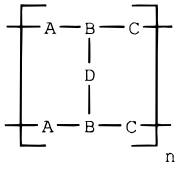
Typical symmetrical SRUs have structures such as those shown as examples 1.1 and 1.2.

Examples 1.1 and 1.2. (in which D is a vertical bridge comprising a bond or one or more moieties, and A, B, and C are "horizontal" moieties; those that are not junction units may be unitary divalent radicals or linear strings composed of unitary diradicals)

Example 1.1.



Example 1.2.

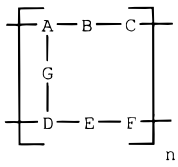


A new nomenclature system has been described for these new SRUs.[2] Their symmetry means that a comparatively simple nomenclature system is possible. Naming starts either with the vertical bridge (if it consists of a unitary moiety), or in the center of the bridge (for more complex cases), and proceeds simultaneously in both directions.

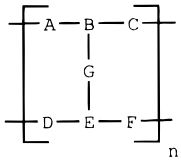
However, when "I"-shaped SRUs are asymmetrical, rules for the orientation and nomenclature of symmetrical SRUs are no longer adequate. This paper describes an orientation and nomenclature system for asymmetrical, "I"-shaped SRUs such as (but not limited to) those shown as examples 1.3, 1.4, 1.5, and 1.6.

Examples 1.3, 1.4, 1.5, and 1.6. (in which G is a vertical bridge comprising a bond or one or more moieties, and A, B, C, D, E, and F are "horizontal" moieties; those that are not junction units may be divalent radicals or linear strings composed of unitary diradicals)

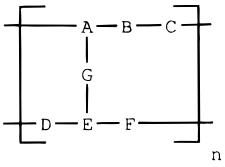
Example 1.3.



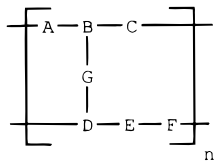
Example 1.4.



Example 1.5.



Example 1.6.



As for all polymers in SCION,[3] orientation of SRUs is completely independent of nomenclature, and nomenclature is ***never*** used as an aid to SRU orientation. The structures shown are hyperbranched, not ladder polymers; ideally, they should be represented by the structures shown as example 1.7, 1.8, 1.9, and 1.10, respectively, but CASRS limitations currently prohibit this.

Examples 1.7, 1.8, 1.9, and 1.10. Idealized representation of examples 1.3, 1.4, 1.5, and 1.6 as hyperbranched SRUs (A, B, C, D, E, and F are as described above in examples 1.3, 1.4, 1.5, and 1.6)

† Retired.

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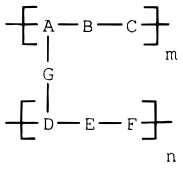
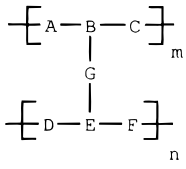
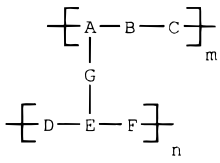
Example 1.7.



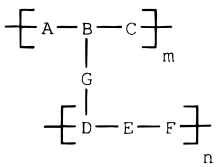
Example 1.8.



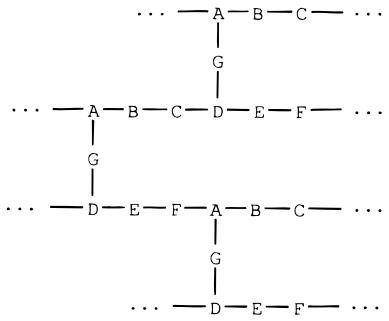
Example 1.9.



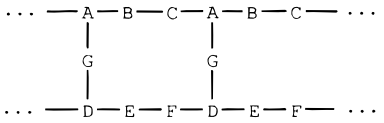
Example 1.10.



In hyperbranched SRUs, each SRU is joined to the previous one in an "offset" manner; thus, the hyperbranched polymer from the SRU of example 1.3 has the following structure:



The corresponding ladder polymer (which is not discussed in this paper) has the following structure:



The asymmetry of these SRUs necessitates complex nomenclature, and the system presented is a logical extension of that developed earlier for single-strand SRUs cross-linked to three-dimensional networks.[4]

Rules for orientation and nomenclature of either symmetrical or asymmetrical "I"-shaped SRUs have never been described by CAS or the International Union of Pure and Applied Chemistry (IUPAC). Section 2 of this paper describes orientation, section 3 describes nomenclature and shows how names are developed for four examples, and further examples are given in section 4. The examples shown are theoretical and may or may not have been reduced to practice.

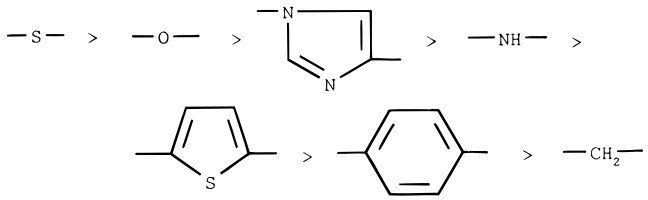
2. RULES FOR ORIENTATION OF ASYMMETRICAL "I"-SHAPED SRU POLYMERS

In SCION, orientation of single-strand SRUs proceeds by the following steps:

Step 1 (identifying the atom sequence of the SRU): at least two complete sequences of the SRU are drawn.

Step 2 (defining the "head" atom): An exhaustive set of rules,[5] the presentation of which is outside the scope of this paper, is used to determine SRU subunit seniority. Briefly, because (a) ring bonds cannot be broken in order to draw the SRU and (b) seniority is determined by the atomic numbers and environment of individual atoms, seniority usually works out as follows: (1) heterocyclic rings in which the heteroatom is also connected to at least one other backbone atom by an open-chain (nonring) bond; (2) heteroatoms in chains; (3) heterocyclic rings in which the heteroatom is not also connected to at least one other backbone atom by an open-chain (nonring) bond; (4) carbocyclic rings; (5) carbon chains (see point 3).

Point 3: SCION seniority examples (> means "is senior to").



For SRUs with two or more dissimilar heterocyclic rings, there are further rules for choosing the senior heterocyclic ring. For situations where a heteroatom in the chain is the SRU head atom, the heteroatom with the highest atomic number is chosen. Thus, the most senior atom is Bi, followed in order by Pb, Hg, Te, Sb, Sn, Se, As, Ge, S, P, Si, O, N, B, etc.

The "individual bond" rule is also important. It states that

- two individual single bonds are senior to a double bond
- three individual single bonds are senior to a double bond plus a single bond (aromatic ranks as double plus single)
- a double bond plus a single bond is senior to a triple bond
- four single bonds are senior to any combination of single and multiple bonds

Thus, true methylidyne (branch-point) is senior to "pseudo"-methylidyne in an aromatic ring.

Step 3 (SRU orientation): SCION rules are based on the principle: "start with the head atom (selected in step 1 above) and move in the direction of the heaviest/most crowded environment"; this means that the SRU citation direction is determined by, in order, atomic numbers of atoms (other than the head atom) and how many there are. This results in some SRUs having structures identical with those derived by CAS and IUPAC rules, but for different reasons, whereas other structures are different from CAS- or IUPAC-derived ones.

In addition, the following rules are applied to asymmetrical, hyperbranched SRU polymers in ***descending*** order of precedence:

- *Rule 2.1:* The head atom must be placed in the ***top, left***most position of the SRU.
- *Rule 2.2:* The bridge must be ***vertical***.
- *Rule 2.3:* The bridge must be as ***short*** as possible.
- *Rule 2.4:* If rule 2.3 leaves a choice, the bridge must be placed as ***early*** (i.e., as far to the left) as possible with respect to both the upper and lower horizontal atom sequences.
- *Rule 2.5:* The total size of the bridge must be as ***small*** as possible; thus, an unsubstituted bridge is senior to a substituted bridge of equal length.

• *Rule 2.6:* Each horizontal atom sequence is drawn with its head atom on the ***left***.

Note on rule 2.6: this may move the bridge to the right after its initial position, with respect to either or both horizontal sequences, has been determined according to rule 2.4.

• *Rule 2.7:* Substitution in a horizontal atom sequence must be as far to the ***left*** as possible.

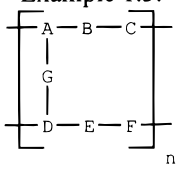
3. RULES FOR NOMENCLATURE OF ASYMMETRICAL "I"-SHAPED SRU POLYMERS

There is an inherent difficulty in creating a nomenclature system for asymmetrical "I"-shaped SRUs such as those contained in the polymers shown as examples 1.3, 1.4, 1.5, and 1.6—namely, how to deal with the junction moiety or unit, whether it is a ring or a single atom. Whether the complete name of the SRU begins with a linear moiety or atom sequence that connects to the central junction unit (as in examples 1.4 and 1.6), or with the central junction unit itself (as in examples 1.3 and 1.5), merely naming the remaining moieties that emanate from the central junction unit is insufficient to indicate in which direction they go. Therefore nomenclature must include indications of directions.

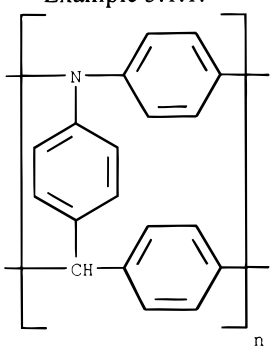
Nomenclature of these SRUs is based upon the following rules. A glossary of new symbols, introduced specifically for nomenclature of hyperconnected SRU polymers, is appended.

3.1. Rules for the SRU of Example 1.3

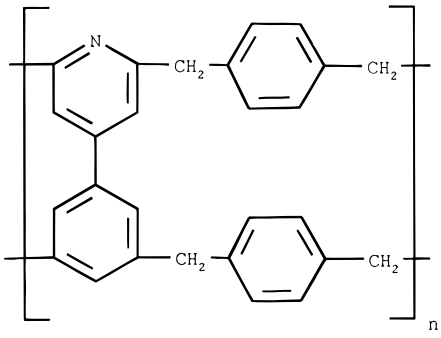
Example 1.3.



Example 3.1.1.



Example 3.1.2.



• *Rule 3.1.1:* Name the junction unit A, which is either the head atom or a ring containing the head atom. If the vertical sequence AGD has a unitary name, it ***must*** be used. Examples:

• NITRILO (see example 3.1.1 above)

• 2,6,4-PYRIDINETRIYL (see example 3.1.2 above) (see point 4)

Point 4: For rings, point of entry is named first; for reasons that will become apparent as the name of the SRU is developed, the first (horizontal) linear string named after the ring has been exited is attached to position 6, and the second (vertical) linear string named after the ring has been exited is attached to position 4.

• *Rule 3.1.2:* Preface the name generated by rule 3.1.1 with the parenthesized symbol (←L) to indicate that a crossing bond originates from the left-limiting bracket of the SRU and is connected to the left of the first moiety.

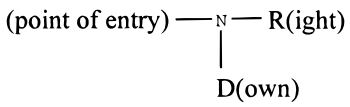
Examples:

• (←L)NITRILO

• (←L)2,6,4-PYRIDINETRIYL

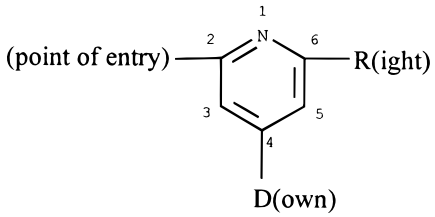
• *Rule 3.1.3:* By means of a suffix in the form of a parenthesized expression, indicate bonds that emanate from junction unit A. Indicate the direction of each bond that emanates from A, and, if necessary, preface it with an integer that indicates from which position or locant on the unit each bond emanates. The only choices are R (indicating "right") and D (indicating "down") because naming of the SRU began with the head atom in the upper, leftmost position.

Single-atom example (NITRILO):



Name: (←L)NITRILO(R;D)

Ring-system example (rings are numbered with the lowest-possible set of locants):



Name: (←L)2,6,4-PYRIDINETRIYL(6R;4D)

• *Rule 3.1.4:* Name the complete horizontal linear sequence BC that emanates from A. Name it in the direction of "radiating out from" A. Parenthesize compound sequences as necessary. Insert a hyphen between the junction unit suffix and the sequence BC.

Examples:

• (←L)NITRILO(R;D)-P-PHENYLENE

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(METHYLENE-P-PHENYLENEMETHYLENE)

Note on rule 3.1.4: Because A is a branch point, it is possible to alphabetize the names of the sequences BC and GD + EF that emanate from A, although further branching occurs at D. However, because further branching of the sequence GD occurs at point D, the name of the horizontal sequence BC may be displaced (for alphabetical reasons) to the remote end of the complete SRU name. Intellectually, it is easier to comprehend the name of the complete SRU when the name of the horizontal sequence BC follows

immediately after the branch point A, regardless of whether it alphabetizes before or after the rest of the SRU.

• *Rule 3.1.5:* Preface the name of the sequence BC named in rule 3.1.4 with the parenthesized symbol (R) to indicate that it emanated from the "right" position of the junction unit.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)

• *Rule 3.1.6:* Add the suffix (R→) to the linear sequence BC named in rule 3.1.4 to indicate that a bond emanates from the right of the sequence and becomes a crossing bond through the right-limiting bracket.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)

• *Rule 3.1.7:* Name the complete vertical linear sequence GD (if not already named per rule 3.1.1) that emanates downward from junction unit A. This includes the moiety that comprises the second junction unit D in the SRU. Name the sequence in the direction of "radiating out from" A. Parenthesize compound sequences as necessary. Preface the name of GD with a hyphen and add it to the name created per rules 3.1.1−3.1.6.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(P-PHENYLENEMETHYLIDYNE)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-1,3,5-BENZENE-TRIYL (see point 5)

Note on rule 3.1.7: See rule 3.1.1 for when the vertical linear sequence AGD is unitary.

Point 5: SCION uses CAS Eighth Collective nomenclature rules[6] (8CI) except for a few rare situations where 8CI fails to denote locants adequately, e.g., in *as*-phenenyl and *v*-phenenyl radicals. In these cases, points of entry into the ring cannot be described but have to be deduced from the cited locants of the groups beyond the phenenyl radical. Use of "benzenetriyl" here greatly clarifies the entry and exit locants, e.g., 1,2,4-; 2,1,4-; 4,1,2-, etc., because the first locant cited is always the ring entry point. Although this is probably unnecessary for *s*-phenenyl, for the sake of uniformity in nomenclature, SCION uses "benzenetriyl", vice "phenenyl" in all three cases.

• *Rule 3.1.8:* Preface the name of GD with the parenthesized symbol (D) to indicate that it emanated from the "down" position of A.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BEN-ZENETRIYL

• *Rule 3.1.9:* Add the suffix (L;R) to the GD name segment to indicate that bonds emanate left and right from D.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BENZENETRIYL(3L;5R)

Note on rule 3.1.9: In the case of the 1,3,5-benzenetriyl moiety, it is necessary to indicate ring locants as well as directions D or R. (3L;5R) is preferred to (5L;3R); this is explained below in the note on rule 3.1.10.

• *Rule 3.1.10:* To the name generated by rules 3.1.1−3.1.9, add a hyphen and the parenthesized expression (L←); this indicates that the left position emanating from D becomes a crossing bond through the left-limiting bracket.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)-(L←)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BENZENETRIYL(3L;5R)-(3L←)

Notes on rule 3.1.10: (1) For moieties such as 1,3,5-benzenetriyl, where entry is by definition in the 1-position (because it is cited first), select the next lowest locant available and add it to the parenthesized expression; thus, (3L←), not (5L←). (2) For SRUs of the type illustrated by examples 3.1.1 and 3.1.2, in which the position emanating from D becomes a crossing bond through the left-limiting bracket, parenthesized expressions such as (L←) and (3L←) ***always precede*** further name segments added per rules 3.1.11−3.1.13.

• *Rule 3.1.11:* Name the complete horizontal sequence EF that emanates from the ***right*** position of D. Name EF in the direction of "radiating out from" D. Parenthesize compound sequences as necessary. Preface the EF name segment with a hyphen and add it to the rest of the name generated by rules 3.1.1−3.1.10.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)-(L←)-P-PHEN-YLENE

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BEN-ZENETRIYL(3L;5R)-(3L←)-(METHYLENE-P-PHEN-YLENEMETHYLENE)

• *Rule 3.1.12:* Preface the EF name segment with a parenthesized expression indicating that it emanated from the "right" position of D.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)-(L←)-(R)P-PHEN-YLENE

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BENZENETRIYL(3L;5R)-(3L←)-(5R)(METHYLENE-P-PHENYLENEMETHYLENE)

Note on rule 3.1.12: For METHYLIDYNE, (R) alone is sufficient. For junction units such as 1,3,5-benzenetriyl, it is necessary to add a locant to the parenthesized expression, e.g., (5R).

• *Rule 3.1.13:* Add the suffix (R→) to the name generated by rules 3.1.1−3.1.12 to indicate that a bond from the right of EF becomes a crossing bond that exits through the right-limiting bracket.

Examples:

• (←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)-(L←)-(R)P-PHEN-YLENE(R→)

• (←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-

BENZENETRIYL(3L;5R)-(3L←)-(5R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→)

• *Rule 3.1.14:* Preface the complete name generated per rules 3.1.1−3.1.13 with POLY-.

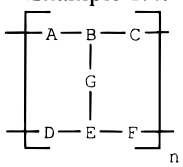
Examples:

• POLY-(←L)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEMETHYLIDYNE)(L;R)-(L←)-(R)P-PHENYLENE(R→) (see example 3.1.1 above for structure)

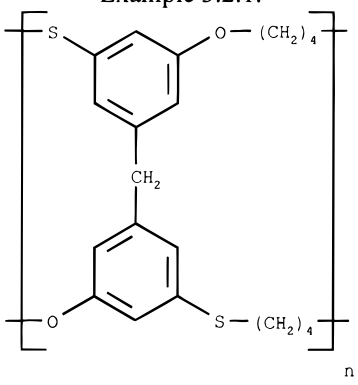
• POLY-(←L)2,6,4-PYRIDINETRIYL(6R;4D)-(R)-(METHYLENE-P-PHENYLENEMETHYLENE)(R→)-(D)1,3,5-BENZENETRIYL(3L;5R)-(3L←)-(5R)(METHYLENE-P-PHENYLENEMETHYLENE)(R→) (see example 3.1.2 above for structure)

3.2. Rules for the SRU of Example 1.4

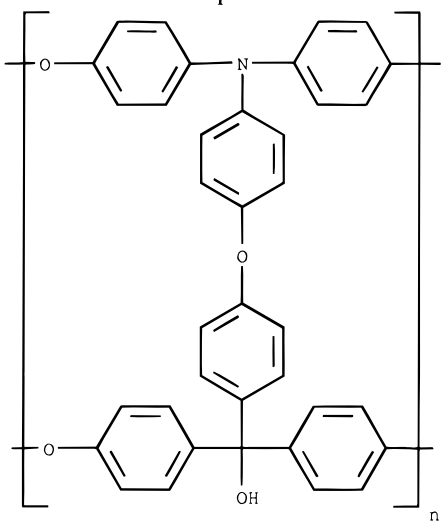
Example 1.4.



Example 3.2.1.



Example 3.2.2.



• *Rule 3.2.1:* Name the horizontal moiety A, which may be the head atom, a ring containing the head atom, or a linear sequence of more than one diradical. If the vertical sequence BGE has a unitary name, it ***must*** be used. The junction unit B is excluded as part of A. Parenthesize compound sequences as necessary.

Examples:

• THIO (see example 3.2.1 above)

• (OXY-P-PHENYLENE) (see example 3.2.2 above)

• *Rule 3.2.2:* Preface the name generated by rule 3.2.1 with the parenthesized symbol (←L) to indicate that a crossing bond originates from the left-limiting bracket of the SRU and is connected to the left of the first moiety.

Examples:

• (←L)THIO

• (←L)(OXY-P-PHENYLENE)

• *Rule 3.2.3:* After the name of the SRU created per rules 3.2.1−3.2.2 add the name of the junction unit B.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL

• (←L)(OXY-P-PHENYLENE)NITRILO

• *Rule 3.2.4:* By means of a suffix in the form of a parenthesized expression, indicate bonds that emanate from junction unit B. Indicate the direction of each bond that emanates from B, and, if necessary, preface it with an integer that indicates from which position or locant on the unit each bond emanates. The only choices are R (indicating "right") and D (indicating "down") because naming of the SRU began with the head atom in the upper, leftmost position.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)

Notes on rule 3.2.4: (1) The designation (3R;5D) means that the bond emanating from the 3-position of the 1,3,5-benzenetriyl radical goes to the right, while the bond emanating from the 5-position goes vertically downward. In the complete SRU name, the horizontal moiety emanating from the 1,3,5-benzenetriyl radical is named before the vertical one; the 3-position is therefore linked to the R direction and cited before the 5-position, which is linked to the D direction. (2) As shown in the example under rule 3.1.3, the only choices for NITRILO are R (indicating "right") and D (indicating "down").

• *Rule 3.2.5:* Name the complete horizontal linear sequence C that emanates from junction unit B. Name it in the direction of "radiating out from" the junction unit. Parenthesize compound sequences as necessary. Insert a hyphen between the junction unit suffix and C.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(OXYTETRAMETHYLENE)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-P-PHENYLENE

Note on rule 3.2.5: Because B is a branch point, it is possible to alphabetize the names of the sequences C and GE + D + F that emanate from B, although further branching occurs at E. However, because further branching of the sequence GE occurs at point E, the name of the horizontal sequence C may be displaced (for alphabetical reasons) to the remote end of the complete SRU name. Intellectually, it is easier to comprehend the name of the complete SRU when the name of the horizontal sequence C follows immediately after the branch point B, regardless of whether it alphabetizes before or after the rest of the SRU.

• *Rule 3.2.6:* Preface the name of the sequence C named in rule 3.2.5 with a parenthesized expression that indicates that it emanated from the "right" position of the junction unit.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE

Note on rule 3.2.6: For NITRILO, (R) is sufficient; for 1,3,5-BENZENETRIYL(3R;5D), (3R) is necessary for the same reason that it was necessary to cite (3R), not (R), as a suffix after 1,3,5-BENZENETRIYL.

• *Rule 3.2.7:* Add the suffix (R→) to the linear sequence C named in rule 3.2.5 to indicate that a bond emanates from the right of the sequence and becomes a crossing bond through the right-limiting bracket.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)

• *Rule 3.2.8*: Name the complete vertical linear sequence GE that emanates downward from junction unit B (unless it has already been named per rule 3.2.1). This includes the moiety that comprises the second junction unit E in the SRU. Name the sequence GE in the direction of "radiating out from" B. Parenthesize compound sequences as necessary. Preface the name of GE with a hyphen and add the GE segment to the name created per rules 3.2.1−3.2.7.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(METHYLENE-1,3,5-BENZENETRIYL)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(P-PHENYLENEOXY-P-PHENYLENE-(HYDROXYMETHYLIDYNE)) (see point 6)

Note on rule 3.2.8: See rule 3.2.1 for when the vertical linear sequence BGE is unitary.

Point 6: The CASRS is currently unable to accept left and right square brackets "[" and "]" in names; therefore, multiple parentheses are used.

• *Rule 3.2.9:* Preface the name of GE with a parenthesized expression to indicate that it emanated from the "down" position of B.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))

Note on rule 3.2.9: For NITRILO, (D) is sufficient; for 1,3,5-BENZENETRIYL(3R;5D), (5D) is necessary.

• *Rule 3.2.10:* Add to name segment GE a suffix in the form of a parenthesized expression to indicate that bonds emanate left and right from E.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)- (5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)

Note on rule 3.2.10: For (HYDROXYMETHYLIDYNE), (L;R) is sufficient; see note on rule 3.2.6 for why locants as well as directions are necessary for 1,3,5-BENZENETRIYL.

• *Rule 3.2.11:* Name the complete horizontal sequence D that emanates from the ***left*** position of E. Name D in the direction of "radiating out from" E. Parenthesize compound sequences as necessary. Preface the D name segment with a hyphen and add it to the rest of the name generated by rules 3.2.1−3.2.10.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-OXY

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(P-PHENYLENEOXY)

• *Rule 3.2.12:* Preface the segment D (added per rule 3.2.11) with a parenthesized expression indicating that it emanated from the ***left*** side of E.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)

Note on rule 3.2.12: For (HYDROXYMETHYLIDYNE), (L) is sufficient; see note on rule 3.2.6 for why locant as well as direction is necessary for 1,3,5-BENZENETRIYL.

• *Rule 3.2.13:* To the name generated per rules 3.2.1−3.2.12 add a parenthesized expression indicating that the ***left*** position emanating from D becomes a crossing bond through the ***left***-limiting bracket.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)- (5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)(L←)

• *Rule 3.2.14:* Name the complete horizontal sequence F that emanates from the ***right*** position of E. Name F in the direction of "radiating out from" E. Parenthesize compound sequences as necessary. Preface the F name segment with a hyphen and add it to the rest of the name generated by rules 3.1.1−3.1.13.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)-(THIOTETRAMETHYLENE)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)(L←)-P-PHENYLENE

• *Rule 3.2.15*: Preface name segment F (added per rule 3.2.14) with a parenthesized expression indicating that it emanated from the ***right*** side of E.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)-(5R)-(THIOTETRAMETHYLENE)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)(L←)-(R)P-PHENYLENE

Note on rule 3.2.15: for (HYDROXYMETHYLIDYNE), (R) is sufficient; see note on rule 3.2.6 for why locant as well as direction is necessary for 1,3,5-BENZENETRIYL.

• *Rule 3.2.16:* To the name generated per rules 3.2.1−3.2.15 add a parenthesized expression indicating that the ***right*** position emanating from F becomes a crossing bond through the ***right***-limiting bracket.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)- (5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)- (5R)-(THIOTETRAMETHYLENE)(R→)

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)(L←)-(R)P-PHENYLENE(R→)

• *Rule 3.2.17:* Examine the name segments D and F generated per rules 3.2.11−3.2.16; if the names of the segments emanating from the left and right sides of segment E are not alphabetized, rearrange them so that they are. If this rearrangement is necessary, it will also be necessary to reverse the letters within the parenthesized expression following the name of segment E.

Examples:

• (←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)- (5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)-(5R)-(THIOTETRAMETHYLENE)(R→)

In this case, the segments (3L)OXY(L←) and (5R)-(THIOTETRAMETHYLENE)(R→) are already alphabetized, and no corrections are needed.

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(L;R)-(L)(P-PHENYLENEOXY)(L←)-(R)P-PHENYLENE(R→)

In this case, (L)(P-PHENYLENEOXY)(L←) and (R)P-PHENYLENE(R→) are not alphabetized, and a correction ***is*** needed. The parenthesized expression (L;R) following ...METHYLIDYNE)) also needs correcting from (L;R) to (R;L) to agree with the order of the F and D segments. Thus, the name becomes the following:

• (←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(R;L)-(R)P-PHENYLENE(R→)-(L)(P-PHENYLENEOXY)(L←)

• *Rule 3.2.18:* Preface the complete name generated per rules 3.2.1−3.2.17 with POLY-.

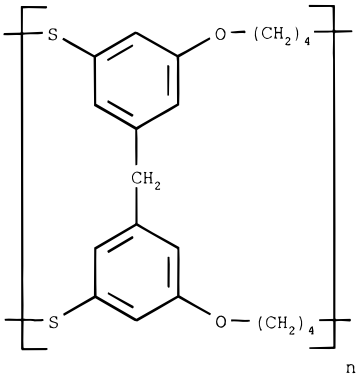
Examples:

• POLY-(←L)THIO-1,3,5-BENZENETRIYL(3R;5D)-(3R)-(OXYTETRAMETHYLENE)(R→)-(5D)(METHYLENE-1,3,5-BENZENETRIYL)(3L;5R)-(3L)OXY(L←)-(5R)-(THIOTETRAMETHYLENE)(R→) (See example 3.2.1 above for structure) (see point 7)

• POLY-(←L)(OXY-P-PHENYLENE)NITRILO(R;D)-(R)P-PHENYLENE(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENE(HYDROXYMETHYLIDYNE))(R;L)-(R)P-PHENYLENE(R→)-(L)(P-PHENYLENEOXY)(L←) (See example 3.2.2 above for structure) (see point 8)

Point 7: At first glance, the structure of example 3.2.1 appears to be a misrepresentation of the symmetrical structure of example 3.2.3:

Example 3.2.3.



However, it must be remembered that (1) the acyclic moieties represented are −S−$(CH_2)_4$−S− and −O−$(CH_2)_4$−O−, ***not*** −O−$(CH_2)_4$−S− and −S−$(CH_2)_4$−O− and (2) example 3.2.1 is a representation of a hyperbranched polymer, ***not*** a ladder polymer.

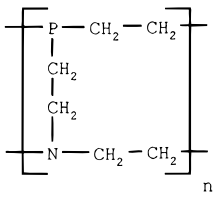
Point 8: Notice in the polymer name that the parenthesized expression following the HYDROXYMETHYLIDYNE moiety is (R;L), not (L;R); this is because the moieties that follow are alphabetized. Thus, P-PHENYLENE, which is placed to the ***right*** of the METHYLIDYNE moiety, is cited before (P-PHENYLENEOXY).

3.3. Rules for the SRUs of Examples 1.5 and 1.6. The rules for the SRUs of examples 1.5 and 1.6 are similar in format to those described above for examples 1.3 and 1.4; their detailed presentation is considered unnecessary here.

4. FURTHER EXAMPLES OF ASYMMETRICAL "I"-SHAPED SRUS

Four structures have already been used as examples in section 3 above; this section gives four more.

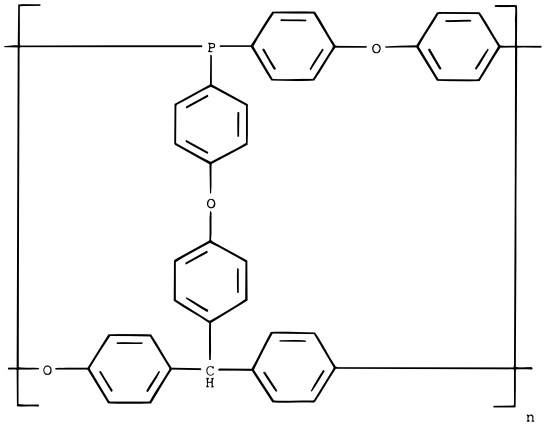
Example 4.1. POLY-(←L)PHOSPHINIDYNE(R;D)-(R)-ETHYLENE(R→)-(D)(ETHYLENENITRILO(L;R)-(L←)-(R)ETHYLENE(R→)



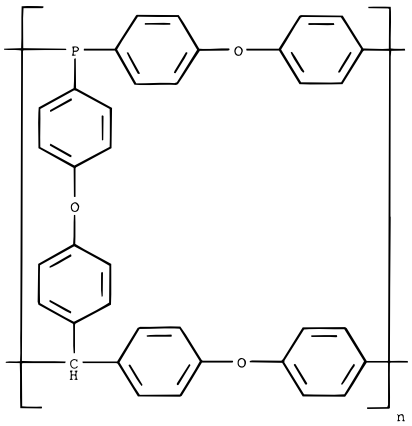
Note on example 4.1: In SCION, phosphorus is senior to nitrogen; it is therefore chosen as head atom and placed as close as possible to the top, left-hand corner of the SRU.

Example 4.2. POLY-(←L)PHOSPHINIDYNE(R;D)-(R)-(P-PHENYLENEOXY-P-PHENYLENE)(R→)-(D)(P-PHENYLENEOXY-P-PHENYLENEMETHYLIDYNE)(R;L)-(R)P-PHENYLENE(R→)-(L)(P-PHENYLENEOXY)(L←)

Example 4.2.

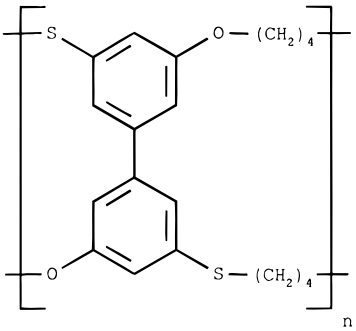


Example 4.2a.



Notes on example 4.2: (1) This example is of the type shown above as example 1.5, and it illustrates application of rule 2.6. Rules 2.1−2.5 result in the structure of example 4.2a, which must be changed to the structure of example 4.2 so that the oxygen atom, the senior atom in the lower horizontal sequence, is the ***leftmost*** atom in that sequence. (2) Because of an SRU structural situation similar to that of example 3.2.2 above, the parenthesized expression following the METHYLIDYNE moiety is (R;L), not (L;R); as in example 3.2.2, (R)P-PHENYLENE(R→) is cited before (L)-(P-PHENYLENEOXY)(L←) because it alphabetizes first. This illustrates application of rule 3.2.17.

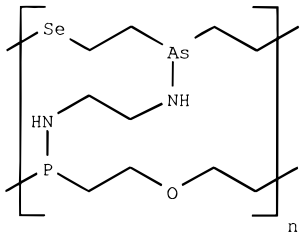
Example 4.3. POLY-(←L)THIO-3,5,3′,5′-BIPHENYLTETRAYL(5R;3′L;5′R)-(3R)(OXYTETRAMETHYLENE)-(R→)-(3′L)OXY(L←)-(5′R)(THIOTETRAMETHYLENE)-(R→)



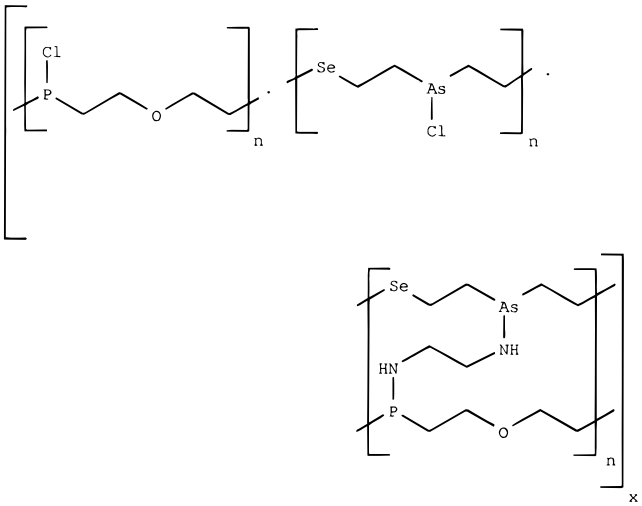
Note on example 4.3: this example is unusual in that the vertical bridge is a bond, and the entire vertical sequence BGE (see example 1.4 above, the model for this example) is unitary and must be named as such. The locants preceding the BIPHENYLTETRAYL name segment indicate precisely the point of entry into the ring system (3), and the points of exit from it (5,3′,5′), in the exact order in which they are cited again later in the name of the complete polymer.

Example 4.4. POLY-(CHLOROPHOSPHINIDENE)-ETHYLENEOXYETHYLENE, AFTERTREATED WITH POLY-SELENOETHYLENE(CHLOROARSYLENE)-ETHYLENE TO (←L)SELENOETHYLENEARSYLIDYNE-(R;D)-(R)ETHYLENE(R→)- (D)(IMINOETHYLENEIMINOPHOSPHINIDYNE(L;R)-(L←)-(R)ETHYLENEOXYETHYLENE(R→) (point 9)

The structure of the hyperbranched SRU is

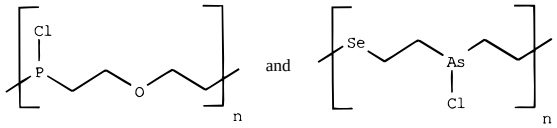


The structure of the entire polymer is



Point 9: Nomenclature for situations where one polymer aftertreats another has been described elsewhere.[1]

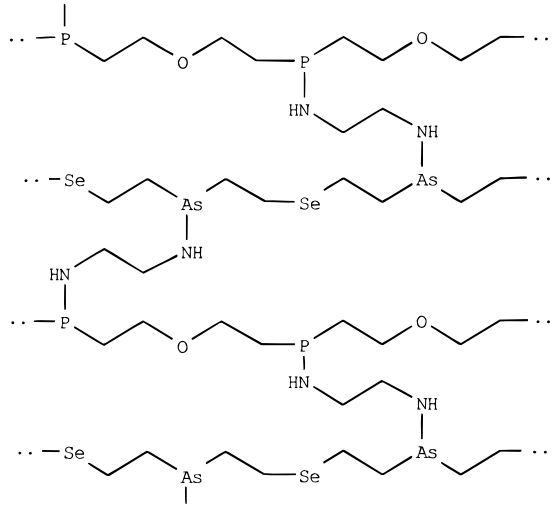
Notes on example 4.4: (1) This example is of the type shown above as example 1.6, and it illustrates application of rule 2.6. Selenium is the atom of highest atomic number in the SRU and is therefore the head atom; the upper horizontal sequence must therefore be as shown. In the lower horizontal sequence, phosphorus is senior to oxygen and must therefore be as far to the left as possible. (2) This hyperbranched polymer is different from the others in this paper in that it was formed by cross-linking two linear, single-strand polymers



and this is reflected in the name, which indicates that an aftertreatment (post-treatment) took place. Nevertheless, the hyperbranched SRU shown as example 4.4 exists within the polymer. There is a fundamental difference between this example and the others in this paper, which is revealed by drawing several sequences of the hyperbranched SRU.

- In this example, the upper horizontal sequence never contains any of the lower horizontal sequence and vice versa.

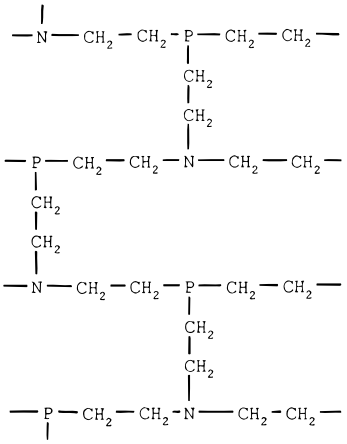
Thus, when several sequences of example 4.4 are joined, the result is as shown below, and the horizontal linear, single-strand sequence -P-C-C-O-C-C-Se-C-C-As-C-C- does not exist.



There is also the possibility of macrocycles forming during the cross-linking, whereas in the other types of hyperbranched polymer discussed in this paper, macrocycles cannot form.

- In the other examples, both horizontal, single-strands of the hyperbranched SRU contain both the upper and lower atom sequences.

Thus, when several sequences of example 4.1 are joined, the result is as shown below; the horizontal sequence is always either -P-C-C-N-C-C- or -N-C-C-P-C-C-, and the sequences -P-C-C-P-C-C- and -N-C-C-N-C-C- do not exist.



5. SUMMARY

A structural repeating unit (SRU) orientation and nomenclature system has been described for registration of asymmetrical, "I"-shaped hyperbranched polymers in SCION, a DuPont proprietary database that operates by use of the Chemical Abstracts Service Registration System for registration and Messenger software for searching. Detailed rules for the orientation and nomenclature of these novel polymers are included, and applications of the rules are illustrated by examples.

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GLOSSARY: Terms used in the nomenclature system for asymmetrical, hyperbranched, "I"-shaped SRUs.

Symbol	Meaning
(←L)	a bond begins as a crossing bond through the left-limiting bracket and connects with the left side of the first moiety to be cited in the SRU name
(L←)	a bond emanates from the left side of the junction unit and terminates as a crossing bond through the left-limiting bracket
(L→)	a bond emanates from the left side of the junction unit and terminates as a crossing bond through the right-limiting bracket
(R→)	a bond emanates from the right side of the junction unit and terminates as a crossing bond through the right-limiting bracket

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