A Nomenclature and Structural Representation System for Ladder and Spiro Polymers

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A "ring-by-ring" nomenclature and structural representation system for ladder and spiro polymers is presented. This novel system differs markedly from the International Union of Pure and Applied Chemistry (IUPAC) and Chemical Abstracts Service (CAS) systems, which require ring fracture, naming of complete ring assemblies, and occasional use of nomenclature to determine final orientation of structural repeating units (SRUs). The advantages of the system presented are as follows: SRU identification and orientation are completely independent of nomenclature; no rings are fractured; and each individual ring is named separately (except in one rare and precisely defined situation) and thus names of complete ring assemblies are not required.

1. INTRODUCTION

SCION, a DuPont proprietary online database, contains a bibliographic file and a chemical structure file. The two files work in a manner that parallels the functions and interactions of File CA and File Registry published by the Chemical Abstracts Service (CAS) of the American Chemical Society (ACS). The chemical file of the SCION database, described in an earlier publication,[1] follows CAS structure conventions except in the polymer field, where appreciable differences exist. Among these major differences are conventions for ladder and spiro polymers, and these are described in this paper.

2. BACKGROUND

Registration of polymers is executed manually for DuPont by CAS keyboarding personnel. This paper is a description of nomenclature rules to accompany manual encoding of polymers, but the principles behind it might be used for an automated polymer registration system.

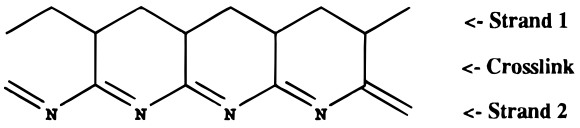
Ladder and spiro polymers present special nomenclature problems and database storage and retrieval challenges because of the absence of acyclic (open-chain) bonds in the backbone structure. Recommendations for their structural representation have been published by the International Union of Pure and Applied Chemistry (IUPAC),[2−4] and CAS representation of them is also documented.[5,6b,7] Both these basic representations frequently result in a constitutional repeating unit (CRU—IUPAC preferred name) or a structural repeating unit (SRU—CAS preferred name) that fractures at least one ring.

The alternative method described herein for the structural representation of ladder and spiro polymers does not fracture rings. Although never published previously, the method has been in use within the DuPont Company for over 25 years. The method enables indexers and searchers to identify the SRU of a ladder or spiro polymer unambiguously and (except in one rare and precisely defined situation) to derive for it a name based on the names of individual rings rather than on those of complex and possibly previously unknown fused-ring systems. At the same time, a topological record of the entire fused-ring structure is preserved and stored.

3. DEFINITION

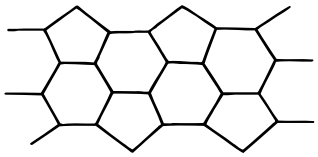
Ladder polymers are composed of two or more linear polymer backbones connected by cross-links repeated regularly along the multiple-strand backbone. All backbone atoms are thus in fused or spiro rings. Therefore this excludes ladder or so-called "stepladder" polymers in which most but not all of the backbone bonds are in rings. Examples 1−3 show some typical ladder and spiro polymers.

Example 1

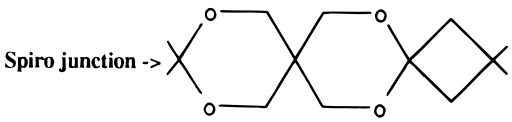


Note: for clarity, left- and right-limiting parentheses or brackets, and the customary sub-n to the right of the closing parenthesis or bracket, are omitted throughout this paper.

Example 2



Example 3



4. NOMENCLATURE

4.1. Identifying and Orienting the SRU. Examples are shown in section 4.3.

•*Rule 4.1.1*: Two or three sequences of the SRU are drawn.

† Retired.

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•*Rule 4.1.2*: Each SRU strand is identified. Two strands may not share atoms except in spiropolymers (see example 3 above).

•*Rule 4.1.3*: The SRU sequence is oriented according to the following rules in descending order of precedence.

•*Rule 4.1.3.1*: The minimum number of "points of connection" must be broken.

•*Rule 4.1.3.2*: The minimum number of bonds must be broken.

•*Rule 4.1.3.3*: The highest-priority atom is identified, according to the SCION database chemical file priority rules (see Appendix).

•*Rule 4.1.3.4*: The SRU is oriented so that the highest-priority atom (see Point 1) is in the top strand.

Point 1: See Rules 2, 3, and 4 in the Appendix.

•*Rule 4.1.3.5*: The individual ring (see Point 2) containing the highest-priority atom is oriented so that this highest-priority atom occurs as far to the LEFT in it as possible.

Point 2: Even if the multiple-ring system has a name, it is critical to consider each individual ring, not the multiple-ring system. Thus benzene is an individual ring; naphthalene (drawn with the rings side-by-side) is a multiple-ring system.

•*Rule 4.1.3.6*: If Rule 4.1.3.5 leaves a choice, the ring containing the highest-priority atom is oriented so that the atom(s) of the top strand in that ring, if any, to the left of the highest-priority atom has higher priority than the atom-(s) to the right.

•*Rule 4.1.3.7*: If Rule 4.1.3.6 leaves a choice, e.g., if the highest-priority atom is part of a spiro junction (see example 3) or a cross-link, the SRU sequence is oriented so that top-strand neighbors to the RIGHT of the highest-priority atom have higher priority than those to the LEFT.

•*Rule 4.1.3.8*: If Rule 4.1.3.7 leaves a choice, the rule is reapplied to atoms of the closest bottom strand.

•*Rule 4.1.4*: Visualizing the SRU as a series of individual rings fused together, the ladder "SRU" (see Point 3) is identified by bracketing the oriented polymer chain in a left-to-right direction (from Rules 4.1.1 through 4.1.3) from the between-strands cross-link (or spiro junction) to the left of the highest-priority atom to the next occurrence of that cross-link. The ring containing the highest priority atom is thus the leftmost ring in the oriented SRU.

Point 3: Because the orientation process repeats one of the cross-links and shows it at both the left end and the right end, the ladder SRU is not an SRU in the same sense as a nonladder SRU.

4.2. Naming the SRU. Examples are shown in section 4.3.

This method of naming ladder and spiro SRUs was devised to circumvent the difficulties of the standard methods[2−5,6b] of naming large fused-ring systems.

In CAS and IUPAC rules[5,6b,9] for naming SRUs, nomenclature may be used to determine the final name of an SRU. In the SCION database chemical file, polymer nomenclature is never used in SRU identification and orientation. An SRU is named only after it has been completely identified and oriented. This rule is maintained even for ladder and spiro polymers.

•*Rule 4.2.1*: Each ***INDIVIDUAL*** ring in the oriented SRU is named from left to right except in the comparatively rare situation covered by Rule 4.2.1.1 below.

NOTE: Rule 4.2.1 is the key to the workability of the entire method, because (except for the situation covered by Rule 4.2.1.1 below) it circumvents the need to name complex, and possibly hitherto unknown, ring systems.

•*Rule 4.2.1.1*: If the breaking of an individual ring in the walk-through path along a side that it does not share with any other ring still leaves a ladder polymer (albeit different from the original one), then that ring is named as part of the **smallest and earliest** (see Point 4) possible fused-ring system rather than as an individual ring—see examples 16, 18, 19, and 26, and contrast these with example 17.

Point 4: **Smallest** means minimum number of rings, irrespective of individual ring sizes. **Earliest** means that the "breakable" ring is to be fused to the leftmost possible ring in the walk-through path.

•*Rule 4.2.2*: If a ring is substituted, the substituted ring name is written in running order (substituents followed by parent ring name); the resulting complex name is enclosed in parentheses or square brackets as required.

•*Rule 4.2.3*: Before each ring name, locants are written to show the positions of left fusion, i.e., attachments to the previous ring. The locant for the attachment at the top is written first. For the leftmost ring, of course, these are the positions of fusion to the rightmost ring of the preceding occurrence of the SRU. For a spiro junction both locants are the same. The set of locants is enclosed within parentheses to avoid confusion with numbers that may occur in the ring name itself.

•*Rule 4.2.4*: After each ring name, locants are written to show the positions of right fusion, i.e., fusions to the following ring. The locant for the fusion at the top is written first. For the rightmost ring these are, of course, the positions of fusion to the leftmost ring of the next occurrence of the SRU. For a spiro junction both locants are the same. As for Rule 4.2.3 above, the set of locants is enclosed within parentheses.

•*Rule 4.2.5*: If there is a choice of locants for equivalent positions in Rules 4.2.3 and 4.2.4, the lowest possible number is assigned that is consistent with whatever fixed numbering a ring itself may require, to the point of fusion at the top left. If this still leaves a choice for numbering the rest of the ring atoms, they are numbered counterclockwise so that the remaining left fusions receive the next lowest possible numbers.

•*Rule 4.2.6*: Assignments of locants for points of entry into a ring, points of exit from a ring, double bonds in a ring, and positions of hydrogenation are made according to the following rules in descending order of precedence.

•*Rule 4.2.6.1*: Lowest possible locants for points of entry into a ring are assigned.

•*Rule 4.2.6.2*: Lowest possible locants for points of exit from a ring are assigned.

•*Rule 4.2.6.3*: Lowest possible locants for double bonds in a ring are assigned.

•*Rule 4.2.6.4*: Lowest possible locants for positions of hydrogenation are assigned.

•*Rule 4.2.7*: A hyphen is inserted between sets of locants occurring between ring names.

•*Rule 4.2.8*: When a multiple-ring system is broken into individual rings by Rule 4.2.1, the state of hydrogenation of the cross-link, i.e., the side(s) of fusion between them, is carried over into each individual ring. When an aromatic

ring is fused to a nonaromatic ring, the fusion side(s) of the nonaromatic ring is/are considered to have a double bond between the points of fusion.

•*Rule 4.2.9*: The final polymer name is formed by prefixing the class name POLY-, followed by the word LADDER-, to the SRU name.

If a copolymer contains more than one ladder or spiro SRU, the names of the individual SRUs are alphabetized on the word LADDER- and separated with slashes, and POLY- appears only once at the beginning of the final name. For copolymers that contain only ladder or spiro SRUs, the name format is

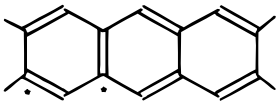
POLY-LADDER_A/LADDER_B/...

Nonladder and/or nonspiro SRUs, of course, may also be present in copolymers. In these cases, the name format is POLY-SRU_A/LADDER_B... (where the name for SRU_A alphabetically precedes the word LADDER) or POLY-LADDER_A/ SRU_B... (where the word LADDER alphabetically precedes the name for SRU_B)—see example 13 in section 4.3.

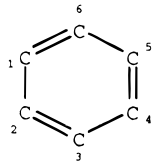
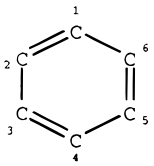
There is no separate category for spiro SRUs; both ladder and spiro SRU names begin LADDER-....

4.3. Examples. These examples show oriented ladder and spiro SRUs and the complete polymer names assigned to them. The beginning and end of each SRU are identified by asterisks. The examples given are theoretical and may or may not have been reduced to practice.

Example 4. POLY-LADDER-(1,2)BENZENE(5,4)



Each individual benzene ring in example 4 is depicted as shown below, and the atoms involved in the "fusion" take the lowest possible numbers.

Thus:  **not** 

Two key points of this nomenclature system need emphasizing:

•the method is easy to comprehend if the ladder is perceived as beginning "half-way" through the first vertical line of atoms (in this case, both atoms 1 and 2 are carbon atoms)

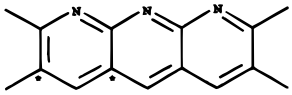
and proceeding to "half-way" through the second vertical line of atoms (again, in this example, both atoms are carbon atoms)

•atoms 5 and 4 of the first benzene ring moiety are cited again as atoms 1 and 2 of the second benzene ring moiety. Similarly, atoms 5 and 4 of the second benzene ring are cited again as atoms 1 and 2, respectively, of the third benzene ring and so on.

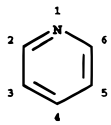
In strong contrast to IUPAC and CAS nomenclature,[2,5,6b] structures such as

are NOT used as ladder polymer representations in the SCION database chemical file, because they do not of themselves imply the essential conditions for a ladder polymer; that is, linear polymer backbones connected by crosslinks repeated regularly along a multiple-strand backbone.

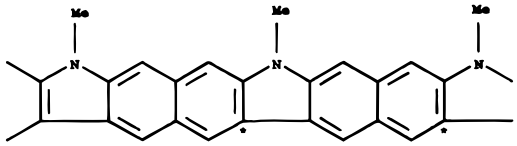
Example 5. POLY-LADDER-(2,3)PYRIDINE(6,5)



Each individual pyridine ring is depicted as shown below; the atoms involved in the "fusion" take the lowest possible numbers consistent with the normal numbering of the pyridine ring.

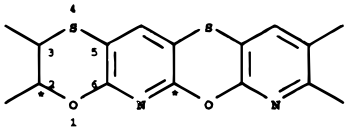


Example 6. POLY-LADDER-(2,3)(1-METHYLPYRROLE)(5,4)-(1,2)BENZENE(5,4)-(1,2)BENZENE(5,4)



Note: Individual rings are named rather than multiple-ring systems such as indole or naphthalene—see Rule 4.2.1.

Example 7. POLY-LADDER-(3,2)1,4-OXATHIIN(5,6)-(3,2)PYRIDINE(5,6)



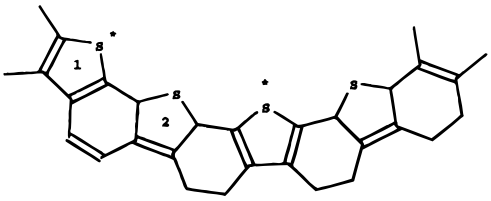
Note 1: By SCION database chemical file priority rules (see Appendix), the 1,4-oxathiin ring is senior to the pyridine

ring because the highest-priority atom is sulfur. In contrast, the pyridine ring is the senior ring by CAS and IUPAC rules.[6a,8]

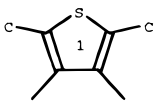
Note 2: Per Rule 4.2.1, individual rings are named rather than multiple-ring systems; thus, consideration of the complete 1,4-oxathiino(2,3-*b*)pyridine fused-ring system is not required. (See note 2 under example 14 for why (2,3-*b*), vice [2,3-*b*], is used.)

Note 3: Per Rule 4.1.3.4, the sulfur (highest-priority atom) is placed in the top strand.

Example 8. POLY-LADDER-(2,3)THIOPHENE (5,4)-(1,2)CYCLOHEXENE(6,5)-(2,3)(2,5-DIHYDROTHIOPHENE)(5,4)-(3,4)CYCLOHEXENE(2,1)

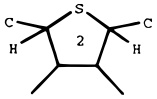


Note: By SCION database chemical file priority rules (see Appendix), a heterocyclic ring is senior to a cyclohexene ring. Therefore, the SRU begins with either ring 1 or ring 2. In ring 1, examination of either carbon atom adjacent to the S atom shows that both are connected to "three" other carbon atoms:



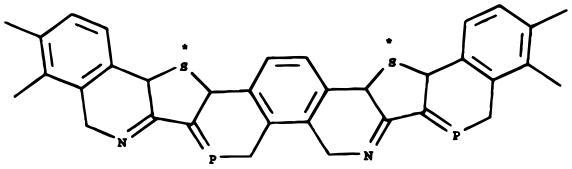
(Appendix Rule 5a: Q=X is treated as Q-X)

In contrast, in ring 2, examination of either carbon atom adjacent to the S atom shows that each is connected to two other carbon atoms and a hydrogen atom:



Therefore, by Appendix Rule 5a, ring 1 is senior to ring 2.

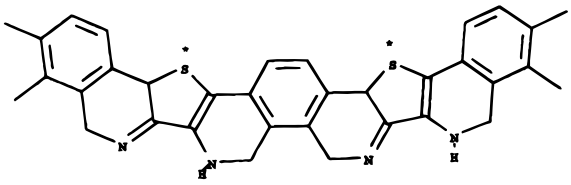
Example 9. POLY-LADDER(2,3)(TETRA-HYDROTHIOPHENE)(5,4)-(3,2)(3,6-DIHYDRO-PHOSPHORIN)(4,5)-(1,2)BENZENE(4,3)-(4,3)(2,5-DIHYDROPYRIDINE)(5,6)



Note 1: By SCION database chemical file priority rules (see Appendix Rule 1), S has higher priority than both N and P; therefore the sulfur-containing ring is the senior ring.

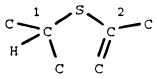
Note 2: The possible paths from the head sulfur atom are of equal seniority until either a P atom (in one path) or an N atom (in the other path) is reached; therefore, the choice of whether to proceed from the sulfur-containing ring to the phosphorus-containing ring or to the nitrogen-containing ring is determined by Appendix Rule 1 (P is senior to N).

Example 10. POLY-LADDER-(2,3)(2,3-DIHYDROTHIOPHENE)(5,4)-(3,2)(1,6-DIHYDROPYRIDINE)(4,5)-(1,2)BENZENE(4,3)-(4,3)(2,5-DIHYDROPYRIDINE)(5,6)



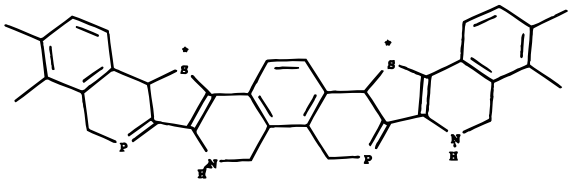
Note 1: By SCION database chemical file priority rules (see Appendix Rule 1), S has higher priority than N; therefore the sulfur-containing ring is the senior ring.

Note 2: The orientation of the SRU is determined by Appendix Rule 5a. In the sulfur-containing ring, consideration of the two carbon atoms adjacent to the S atom leads to the conclusion that atom C2, which is connected to "three" other carbon atoms (see diagram below), is senior to atom C1, which is connected to two other carbon atoms and a hydrogen atom. Thus, in this example, the nitrogen atoms play no part in the determination of the SRU identification and orientation.



(Appendix Rule 5a: Q=X is treated as Q-X)

Example 11. POLY-LADDER-(2,3)(2,3-DIHYDROTHIOPHENE)(5,4)-(3,2)(1,6-DIHYDROPYRIDINE)(4,5)-(1,2)BENZENE(4,3)-(4,3)(2,5-DIHYDRO-PHOSPHORIN)(5,6)

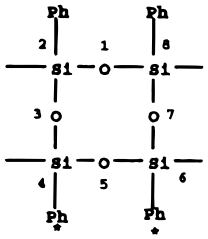


Note 1: By SCION database chemical file priority rules (see Appendix Rule 1), S has higher priority than both N and P; therefore the sulfur-containing ring is the senior ring.

Note 2: A cursory look at this structure might lead to the conclusion that, because P is senior to N, the SRU should be oriented with the phosphorin ring immediately to the right of the sulfur-containing ring. However, in this polymer neither the nitrogen atom nor the phosphorus atom play any

part in determinating the SRU identification and orientation. As in example 10, orientation of the SRU is determined by Appendix Rule 5a (see note 2 under example 10).

Example 12. POLY-LADDER-(2,4)(2,4,6,8-TETRAPHENYLCYCLOTETRASILOXANE)(8,6)

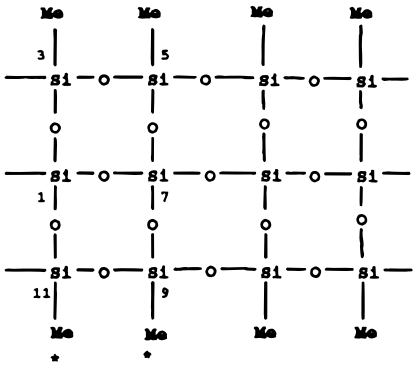


Example 13. Because "(dimethylsilylene)..." alphabetically precedes "ladder-" (see second paragraph after Rule 4.2.9), the name of the copolymer of example 12 with (Si(Me)$_2$-O-)*n*, POLY-(DIMETHYLSILYLENE)OXY (see Point 5), is

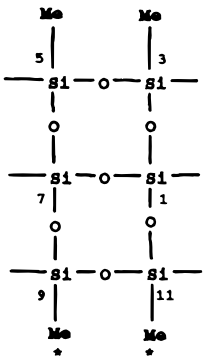
POLY-(DIMETHYLSILYLENE)OXY/LADDER-(2,4)(2,4,6,8-TETRAPHENYLCYCLO-TETRASILOXANE)(8,6)

Point 5: SCION database chemical file priority rules (see Appendix) result in the name given for this polymer. Compare the CAS 8CI nomenclature name POLY[OXY-(DIMETHYLSILYLENE)].

Example 14. POLY-LADDER-(3,1,11)(3,5,9,11-TETRAMETHYLBICYCLO(5.5.1)HEXASILOXANE)(5,7,9)



(a)



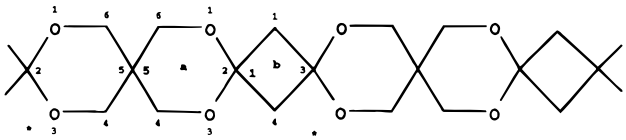
(b)

Note 1: The multiple points of fusion here are of special interest in this "double-ladder" polymer.

Note 2: Because of STN MESSENGER software limitations for SCION, square brackets in polymer names are replaced with parentheses; thus, the traditional BICYCLO-[5.5.1]... is replaced by BICYCLO(5.5.1)....

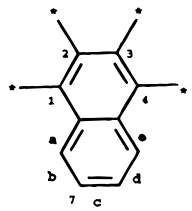
Note 3: Since numbering of the bicyclo(5.5.1)hexasiloxane ring system starts with a bridgehead silicon atom, structure 14(a) results in the name given above, whereas structure 14-(b) results in the name (5,7,9)(3,5,9,11)TETRAMETHYL-BICYCLO(5.5.1)HEXASILOXANE)(3,1,11). Because (3,1,11)... begins with the lower locant 3, versus 5 in (5,7,9)..., the numbering is as shown above in structure 14-(a); the numbering in structure 14(b) is incorrect.

Example 15. POLY-LADDER-(2,2)M-DIOXANE(5,5)-(5,5)M-DIOXANE(2,2)-(1,1)CYCLOBUTANE(3,3)



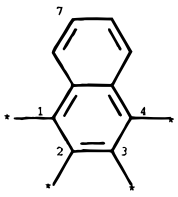
Note: Spiro carbon atom 2 in ring a is cited again as carbon atom 1 in ring b.

Example 16. POLY-LADDER-(2,1)NAPHTHALENE(3,4)



Note 1: This example, together with examples 18 and 19, illustrate application of Rule 4.2.1.1. In this example, the breaking of an individual ring in the walk-through path along a side that it does not share with any other ring—i.e., any one of sides a, b, c, d, or e—still leaves a ladder polymer. Therefore, ring y is named as part of (in this case) the only possible fused-ring system, i.e., naphthalene, rather than as an individual ring.

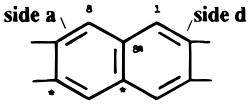
Note 2: the orientation of the naphthalene ring system is as shown above, and not



Were this correct, it would be named POLY-LADDER-(1,2)-NAPHTHALENE(4,3), which would have, as its initial pair of locants, lower numbers than POLY-LADDER-(2,1).... However, SRU orientation—which precedes naming and here follows Rule 4.1.3.4—determines that the head atom in the most crowded environment is placed in the topmost and

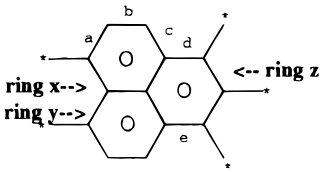
leftmost position possible. Carbon C2, which is connected to "four" other carbon atoms (the fourth one being in the adjacent SRU), outranks carbon C7, which is connected to "three" other carbon atoms (see Appendix).

Example 17. POLY-LADDER-(1,2)BENZENE(5,4)
[not POLY-(2,3)NAPHTHALENE(7,6)]



Note: in this example, the breaking of an individual ring in the walk-through path along a side that it does not share with any other ring means that only a side such as a, b, c, or d may be broken. Sides a and d are indicated by letters a and d in the diagram; side b lies between atoms 8 and 8a; side c lies between atoms 8a and 1. The breaking of any one of these four sides destroys the ladder and creates an acyclic (open-chain) bond in the polymer. Therefore a fused-ring name is not used.

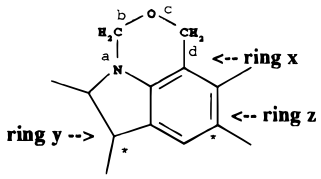
Example 18. POLY-LADDER-(1,8A,8)NAPHTHALENE-(4,4A,5)-(1,2,3)BENZENE(6,5,4)



Note 1: Using conventional single/double bonds, the aromaticity of the three rings in example 18 does not work out exactly; therefore, an O in the rings indicates aromaticity.

Note 2: Breaking any one of the sides a, b, or c still leaves a ladder polymer; therefore, by Rule 4.2.1.1, ring x is named as part of the smallest (which means "rings x + y" or "rings x + z") and earliest (which eliminates the "rings x + z" combination) ring system. The "rings x + y" combination is named naphthalene. In contrast, breaking side d (in ring z) destroys the ladder and changes side e into an acyclic bond; therefore, ring z must be named as an individual ring, not as part of the fused ring system comprising "rings x + y + z".

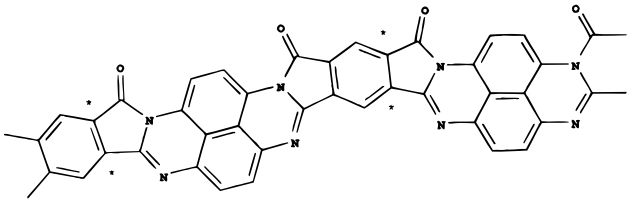
Example 19. POLY-LADDER-(7,6)(3,4-DIHYDRO-1H-PYRROLO(1,2-C)(1,3)OXAZINE(4,4A,5)-(1,2,3)BENZENE(6,5)



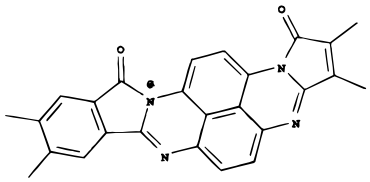
Note 1: The SRU is oriented so that (a) the minimum number of "points of connection" and bonds are broken (Rules 4.1.3.1 and 4.1.3.2); (b) the highest-priority atom, oxygen, is in the top strand (Rule 4.1.3.4); (c) the individual ring containing the highest-priority atom is oriented so that this highest-priority atom occurs as far to the left in it as possible (Rule 4.1.3.5); and (d) with the pyrrole ring (y) to the LEFT of the benzene ring (z) (Rule 4.1.3.7).

Note 2: breaking ring x along a side that it does not share with the other two rings, i.e., breaking side a, b, c, or d, still leaves a ladder polymer; therefore, ring x is named as part of the smallest and earliest possible fused-ring system rather than as an individual ring (Rule 4.2.1.1). Thus, rings x and y are named as the 1*H*-pyrrolo(1,2-*c*)(1,3)oxazine ring system. The benzene ring z is named separately.

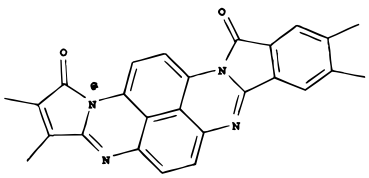
Example 20. POLY-LADDER-(3,4)(2-OXO-3-PYRROLINE)(1,5)-(1,2)(1,4-DIHYDRO-PYRIMIDINE)(6,5,4)-(1,8A,8)NAPHTHALENE(4,4A,5)-(4,5,6)(3,6-DIHYDROPYRIMIDINE)(3,2)-(1,5)(5-OXO-3-PYRROLINE)(4,3)-(1,2)BENZENE(5,4)



Note 1: Per Rules 4.1.3.1 and 4.1.3.2, the only places that the SRU for this ladder polymer can begin are either side of the benzene ring. The SRU must therefore begin either with the benzene ring, which gives the structure of example **20a**, or the pyrroline ring, which gives the structure of example **20b**:



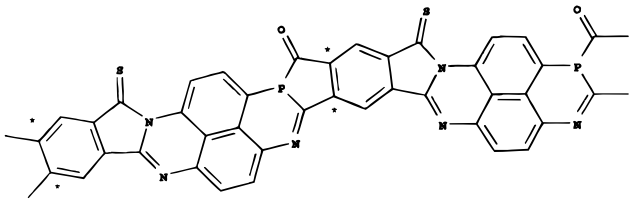
(20a)



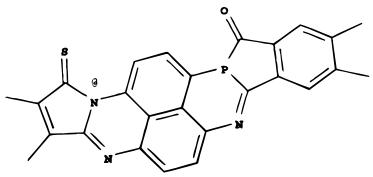
(20b)

The nitrogen atom marked with an @ symbol in examples **20a** and **20b** is the head atom because it is closer to the carbonyl oxygen than the other nitrogen atom. The SRU is oriented so that the @-symbol nitrogen is in the top strand and as far to the left as possible. The SRU shown as example **20b** is therefore the correct structure. In example **20**, therefore, the SRU starts at the first pair of asterisks (on the left) and terminates at the second pair (on the right).

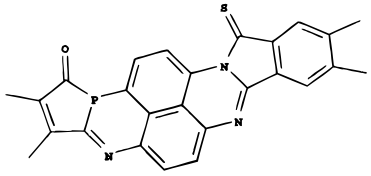
Example 21. POLY-LADDER-(3,4)(2-OXO-3-PHOSPHOLENE)(1,5)-(3,2)(3,6-DIHYDRO-1,3-AZAPHOSPHORINE)(4,5,6)-(1,8A,8)NAPHTHALENE(4,4A,5)-(4,5,6)(3,6-DIHYDROPYRIMIDINE)(3,2)-(1,5)(5-THIO-3-PYRROLINE)(4,3)-(1,2)BENZENE(5,4)



Note 1: It follows from example **20**, in which it was explained that the SRU in example **20b** is correct (i.e., the pyrroline ring is the leftmost ring), that the leftmost ring of the SRU in this example must be either the pyrroline ring or the phospholine ring. Therefore, the only possibilities are the SRUs shown as examples **21a** and **21b**:



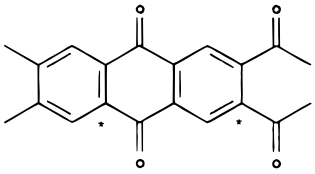
(**21a**)



(**21b**)

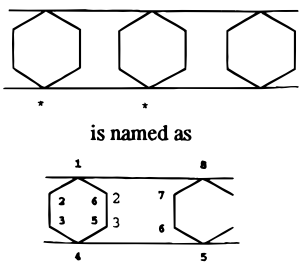
Per SCION priority rule 1 (see Appendix), the structure shown as example **21b** is correct, because P has higher atomic number than the N marked with the @ symbol.

Example 22. POLY-LADDER-(1,2)(3,6-DIOXO-1,4-CYCLOHEXADIENE)(5,4)-(1,2)BENZENE(5,4)

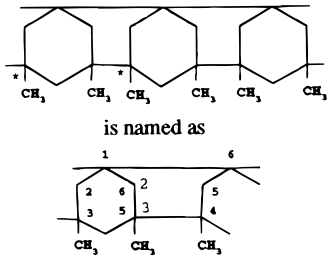


Note: The aromatic bonds of fused benzenes count as double bonds in deriving the name of 1,4-cyclohexadiene—see Rule 4.2.8.

Example 23. POLY-LADDER-(1,1,4,4)CYCLOHEXANE(1,1,4,4)-(1,1,4,4)CYCLOOCTANE(8,8,5,5)

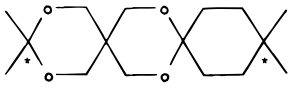


Example 24. POLY-LADDER-(1,1,3)(3,5-DIMETHYLCYCLOHEXANE)(1,1,5)-(1,1,3)(3,4-DIMETHYLCYCLOHEXANE)(6,6,4)

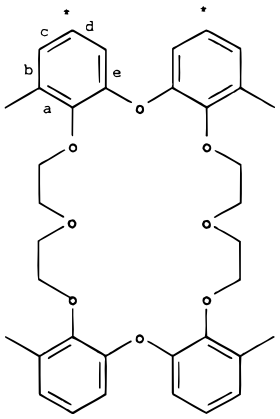


Note: A substituent on a fusion point is named twice (once for each of the fused rings).

Example 25. POLY-LADDER-(2,2)M-DIOXANE(5,5)-(5,5)M-DIOXANE(2,2)-(1,1)CYCLOHEXANE(4,4)



Example 26. POLY-LADDER-(1,25)(11,12,14,15,27,28,30,31-OCTAHYDRO-TETRABENZ(B,E,N,Q)(1,4,7,10,13,16,19,22)-OCTAOXACYCLOTETRACOSIN)(9,17)



Note: Breaking any of the sides of the four phenyl rings that are not shared with the "crown ether" ring (e.g., a, b, c, d, or e in the diagram) still leaves a ladder polymer; therefore, by Rule 4.2.1.1, the SRU is named as a fused-ring system.

5. SUMMARY

A nomenclature and structural representation system for ladder and spiro polymers has been presented. The system is used in the proprietary DuPont SCION database chemical file. Key points of the system are as follows:

•The structural representation system presented retains the integrity of all rings.

•Except in one rare and precisely defined situation, each ring is named separately, which circumvents the need to name complex and possibly previously unknown fused-ring systems.

•SRU identification and orientation are completely independent of nomenclature rules.

APPENDIX. SCION DATABASE CHEMICAL FILE: ATOM PRIORITY RULES

These rules are used to determine priority among two or more sites that are more or less chemically equivalent or to determine which site is most highly substituted.

Priority is used for such purposes as the following:

•orienting a polymer SRU

•localizing a charge or connection that is really delocalized or whose actual location is unknown. Such localization is necessary when topological coding requires a fixed connection even though the result may not describe chemical "reality".

Priority is determined by the following rules in descending order of preference.

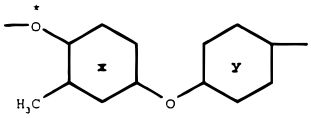
•*Rule 1*: HIGHEST atomic number. Thus, in the SCION database chemical file the order is Pb, Hg, Te, Sb, Sn, Se, As, Ge, S, P, Si, O, N, and B.

Note: This contrasts sharply with CAS and IUPAC rules that rank atoms in the following order: O, S, Se, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, and Hg.[3,6b]

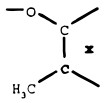
•*Rule 2*: If Rule 1 leaves a choice, priority is assigned to the atom with "directly attached" atoms of highest atomic number. In polymer SRUs, "directly attached" atoms include both lateral attachments and adjacent backbone atoms. Thus, OCl precedes OF; PCl_2 precedes PF_4; and PF_4 precedes PH_4.

•Rule 3: If Rule 2 leaves a choice, priority is assigned to the atom with the greatest number of directly attached atoms of high atomic number. Thus, PI_4 precedes PI_2 and PI_2 precedes PF_4.

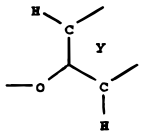
•*Rule 4*: If Rule 3 leaves a choice, Rules 2 and 3 are applied at successively further levels out from the atom in question. Thus, in the structure



the oxygen atom marked with an asterisk takes priority over the other oxygen atom because



in the left hand structure **x** takes priority over



in the right-hand ring structure **y**.

•*Rule 5*: In reapplying Rules 2, 3, and 4, multiple-bonded atoms are treated as follows (Q is the atom in question; = denotes a double bond; # denotes a triple bond):

- Rule 5a: **Q=X** is treated as **Q-X**
  ****
  X
- Rule 5b: **Q#X** is treated as **Q-X**
  **/ **
  X X
- Rule 5c: **Q-phenyl** is treated as

```
          CH
          /
Q-C-CH
     \
     C-CH
     |
     CH   (and so on)
```

- Rule 5d: True **Q-X** precedes the artificial **Q-X** derived from **Q=X**

```
|        |
X        X
```

- Rule 5e:

```
// <-true double bond          / <-aromatic (alternating) bond
Q-C                  precedes Q-C
\ <-true single bond           \ <-aromatic (alternating) bond
```

6. REFERENCES

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