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NOMENCLATURE FOR ROTAXANES AND PSEUDOROTAXANES

(IUPAC Recommendations 2008)

Developed by a Working Group consisting of
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Nomenclature for rotaxanes and pseudorotaxanes

(IUPAC Recommendations 2008)

Abstract: Expanded definitions of rotaxanes and pseudorotaxanes, their components, and other terms concerning rotaxanes are given. The uniform classification and nomenclature principles for naming different types of rotaxanes and pseudorotaxanes are described and illustrated with examples. Recommendations are provided for unambiguous description of rotaxane isomerism with special descriptors that include information about position of rotaxane components.

Keywords: IUPAC Chemical Nomenclature and Structure Representation Division; nomenclature; rotaxanes; pseudorotaxanes; molecular shuttles; terminology; threading component; threadable ring; rotaxane isomerism.

CONTENTS

INTRODUCTION

Rotaxanes were first represented pictorially in 1958 as in situ intermediates in the synthesis of [2]catenanes [1]. Rotaxanes were proposed as a new type of species (though not referred to as pseudorotaxanes or rotaxanes) in 1961 [2], and shown to exist in 1967 [3–5]. However, it was not until 1971 that Schill [6] introduced a nomenclature system for rotaxanes. In 2000, Vögtle and coworkers [7] proposed a generic nomenclature system in which Schill's description was extended to include information about

mechanical or covalent linkages within the components of the rotaxane to distinguish between intermolecular and intramolecular rotaxanes. Nevertheless, the proposed nomenclature cannot unambiguously describe the whole range of rotaxane structures reported in the literature. The current document specifies a systematic nomenclature for rotaxanes that includes the description of structure, composition, and isomerism of rotaxanes.

This document discusses only rotaxanes in which none of the components is macromolecular, but the naming principles specified in this document can also be used to name macromolecular rotaxanes. Specific recommendations for naming rotaxanes with at least one polymeric component will be published in a separate document.

Because the structures of rotaxanes are often large, in most cases throughout this document schematic presentations of rotaxanes and their components are used. Full chemical structures of rotaxanes and their systematic names are given in Section ROT-6 of this document.

The rotaxane literature has been extensively reviewed [8–19].

ROT-1. GLOSSARY

ROT-1.1 rotaxane (generic)

Molecular arrangement comprising at least one molecule with a linear section threaded through at least one macrocyclic part of another or the same molecule and having end-groups large enough to prevent dethreading.

An example of a rotaxane is given in Fig. 1.1.1.

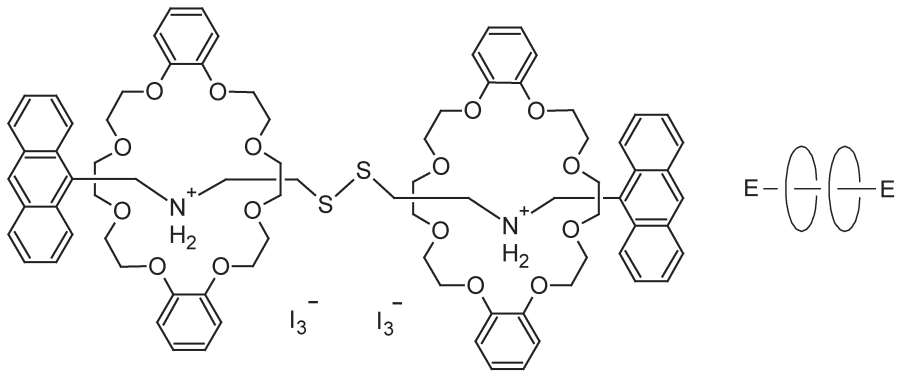


Fig. 1.1.1 Example of a [3]rotaxane and its schematic representation; E represents the end-groups of the threading molecule.

Note: The *IUPAC Compendium of Chemical Terminology* defines rotaxanes as molecules in which a ring encloses another rod-like molecule having end-groups too large to pass through the ring opening; the rod-like molecule is thus held in position without covalent bonding [20]. The definition given in this document is more general to accommodate the wide variety of reported rotaxane compounds.

ROT-1.2 macrocyclic component (macrocyclic molecule)

Molecule that has at least one ring large enough to be threaded onto a linear section of another molecule. Such large rings can be called threadable to distinguish them from other smaller cycles within a

complex macrocyclic component. A macrocyclic rotaxane component is sometimes called a "wheel". Examples of macrocyclic molecules are shown in Fig. 1.2.1.

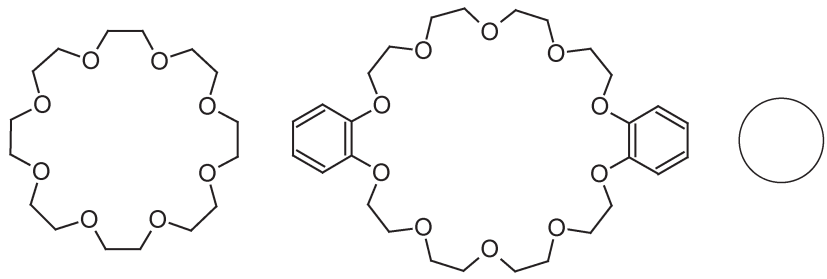


Fig. 1.2.1 Macrocyclic molecules and their schematic representation.

Note 1: In addition to simple macrocyclic components that include only one threadable ring, more complex macrocyclic components may contain several such rings connected with each other. Several generic types of such macrocyclic components are described in Sections ROT-3 and ROT-5, and specific examples are shown in Section ROT-6.

Note 2: The literature on rotaxanes frequently cites the word "macrocycle", which is, in rotaxane terminology, a contraction of (and an abbreviation for) macrocyclic molecule, rather than cyclic macromolecule. Cyclic macromolecules are virtually never used as cyclic components in rotaxane assemblies. Use of the word "macrocycle" in rotaxane terminology is incompatible with the IUPAC definition of a macrocycle, which is "a cyclic macromolecule or a macromolecular cyclic portion of a macromolecule" [21]. Figure 1.2.2 shows an example of a cyclic macromolecule.

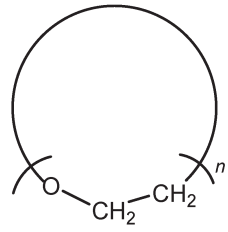


Fig. 1.2.2 An example of a cyclic macromolecule.

Therefore, because the term "macrocycle" is ambiguous, its use in the rotaxane literature is not recommended.

ROT-1.3 threading component (generic)

Molecule with at least one linear section onto which at least one macrocyclic molecule is threaded.

Note 1: The simplest threading component consists of one linear section and end-groups large enough to prevent dethreading of macrocyclic components; this is often called a "dumbbell" or sometimes an "axle".

Note 2: For rotaxanes, the word "linear" is to be interpreted broadly. The linear section of the threading component can be either an unbranched chain or include small cyclic fragments and substituents that do not prevent threading through a macrocyclic molecule.

More complex threading components may contain several linear sections separated by branch points or internal large groups, often called "stoppers", that prevent movement of macrocyclic components from one linear section to another. Threading components with several linear sections, such as "Y"-, "X"-, or "H"-shaped components that include three, four, or five linear sections, respectively, are discussed in Sections ROT-3 and ROT-5. Specific examples can be found in Section ROT-6.

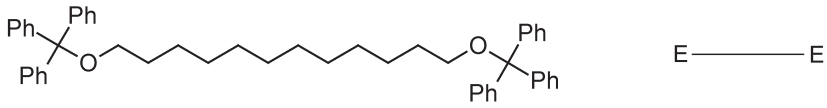


Fig. 1.3.1 An example of a threading component and its schematic representation.

ROT-1.4 pseudorotaxane (generic)

Rotaxane-like molecular assembly in which the threading component(s) has(have) ends small enough to permit threading or dethreading of the macrocyclic molecule(s).

The stability of pseudorotaxanes may arise not only from spatially hindered dethreading of their components, but also from interaction between threading and macrocyclic components, e.g., donor–acceptor or electrostatic.

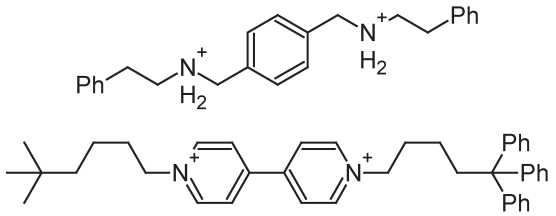


Fig. 1.4.1 Examples of threading components; the first has two small end-groups and the second has one small and one large end-group.

Note: Pseudorotaxanes in which only one end of a linear section is small enough to allow threading and dethreading of a macrocyclic component are sometimes called "semirotaxanes" or "half-capped pseudorotaxanes".

ROT-1.5 recognition site

Part of a threading component with which a macrocyclic component prefers to associate.

Note: Examples of recognition sites in threading components of rotaxane assemblies are ammonium and bipyridinediium units. For threading components possessing more than one recognition site, the sites may be either identical with, or different from, each other.

ROT-1.6 molecular shuttle

Rotaxane or pseudorotaxane assembly comprising a threading component upon which is threaded a macrocyclic component that can reside at a specific recognition site (see Section ROT-1.5) on the threading component.

Note: Depending on the specific structural features and conditions, such rotaxanes can exist either in a form in which macrocyclic components are associated with a specific fragment of threading component or in non-associated form where the macrocyclic component can move along a linear section. Figure 1.6.1 shows representations of typical molecular shuttles. E represents an end-group and "rs" represents a recognition site; the two recognition sites may be either identical or different.

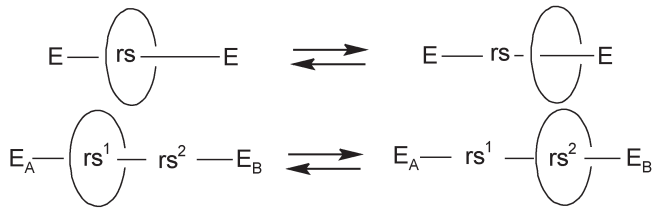


Fig. 1.6.1 Examples of [2]rotaxanes that function as molecular shuttles.

ROT-2. HISTORY OF THE NOMENCLATURE OF ROTAXANES

The first nomenclature system for rotaxanes was proposed by Schill in 1971 [6]. According to this system, the name of a rotaxane includes four parts:

a. a prefix in the form of a bracketed integer that indicates the total number of components in the rotaxane
b. the name of the threading component
c. the name of each macrocyclic molecule, regardless of whether it is chemically identical with, or different from, other macrocyclic molecules present
d. the unitalicized suffix "rotaxane"

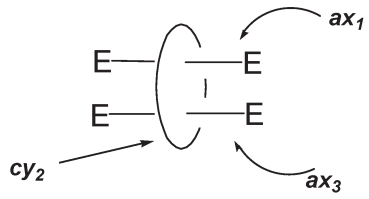
The following generic example summarizes Schill's nomenclature principle:

[*x*]-[name of threading component]-[name of macrocyclic molecule$_1$]-
[name of macrocyclic molecule$_2$]-[name of macrocyclic molecule$_3$]-...-rotaxane

Note: In the prefix [*x*], the integer *x* represents the total number of threading and macrocyclic components; macrocyclic molecule$_1$, macrocyclic molecule$_2$, macrocyclic molecule$_3$, etc. represent structurally identical or different macrocyclic molecules.

In 2000, Vögtle and coworkers [7] proposed a generic nomenclature system in which Schill's prefix was extended to include information about mechanical (mec) or covalent (cov) linkages within the components of the rotaxane to distinguish between intermolecular and intramolecular rotaxanes.

For example, for [3]rotaxanes of type 2.1 (see Table 3.1), Vögtle's system leads to the prefix [3^{ax1meccy2,cy2mecax3}].



ax_1, ax_3 = axles (components 1 and 3); cy_2 = macrocyclic molecule (component 2)

Fig. 2.1 A [3]rotaxane of type 2.1 (from Table 3.1).

For [1]rotaxanes of type 9 (see Table 3.1), Vögtle and coworkers proposed the generic nomenclature system [$2^{1cov2,1mec2}$]rotaxane, see Fig. 2.2.

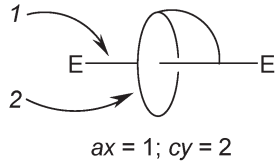


Fig. 2.2 A [1]rotaxane of type 9.

The nomenclature system described in this document is based on modifications of Schill's description of the rotaxane composition and Vögtle and coworkers' idea of a prefix that describes a specific arrangement of rotaxane components for each generic type of rotaxane.

ROT-3. TYPES OF ROTAXANES

Schematic representations of eleven generic types of rotaxanes described since the earliest-known pictorial representation of a pseudorotaxane [1] in 1958 are given in Table 3.1.

Table 3.1 Idealized representations of 11 generic types of rotaxanes.

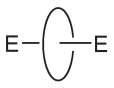
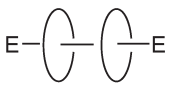
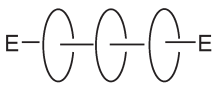
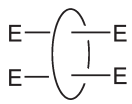
Type	Generic structure	Key structural features
1.1		[2]Rotaxane: a single linear molecule, upon which is threaded a single macrocyclic molecule.
1.2		[3]Rotaxane: a linear molecule, upon which are threaded two macrocyclic molecules.
1.3		[4]Rotaxane: a linear molecule, upon which are threaded three macrocyclic molecules.
2.1		[3]Rotaxane: two linear molecules, upon which is threaded a macrocyclic molecule.

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Table 3.1 (*Continued*).

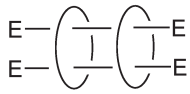
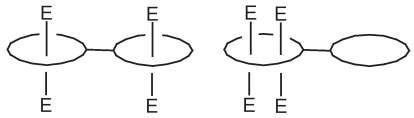
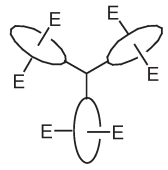
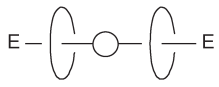
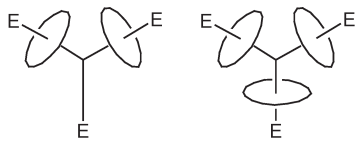
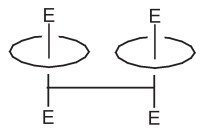
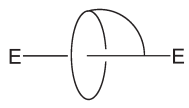
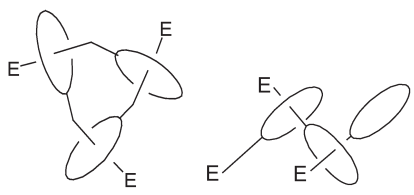
Type	Generic structure	Key structural features
2.2		[4]Rotaxane: two linear molecules, upon which are threaded two macrocyclic molecules.
3		Two covalently linked macrocyclic molecules that can be threaded by linear molecules. Two possible [3]rotaxanes are shown[a].
4		Three macrocyclic molecules are covalently linked to form a Y-shaped molecule; each macrocyclic fragment may be threaded with a linear molecule. A [4]rotaxane is shown.
5		Threading component with two linear sections separated by a group large enough to prevent cyclic components from moving between the two linear sections. A [3]rotaxane is shown.
6		Y-shaped molecule with three linear sections; macrocyclic molecules can be situated at any linear section. [3]- and [4]rotaxanes are shown.
7		X-shaped molecule with four linear sections; the macrocyclic molecules may be situated at any linear section. A [3]rotaxane is shown[a].
8		H-shaped threading component with five linear sections at which macrocyclic components may be situated. A [3]rotaxane is shown[b].
9		[1]Rotaxane: a linear part of a molecule threaded through a macrocyclic part of the same molecule.
10		Cyclic and acyclic "daisy chain" [3]rotaxanes: each molecule contains a linear section and a large cycle. The linear section of one molecule is threaded through the cyclic part of other molecule.

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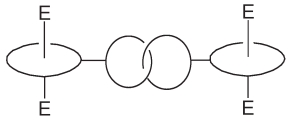
Table 3.1 (*Continued*).

Type	Generic structure	Key structural features
11		[4]Catenarotaxane or [4]rotacatenane: Two components each composed of two covalently linked large rings form a catenane; two large rings not involved in the catenane junction are threaded with a linear molecule to form a [3]rotaxane[c].

[a]In this table, and throughout the document, differences in length of representations of linear sections do not imply that they are structurally different.
[b]The designation [2-2]rotaxane may be used according to the nomenclature system of Vögtle et al. [7].
[c]Catenarotaxanes were formerly called "catrotanes" or "rotacatenanes" [7]. The designation [2rot-2cat-2rot]catenane was proposed according to the nomenclature system of Vögtle et al. [7].

Sections ROT-4 through ROT-6 present the IUPAC recommendations for systematic nomenclature of the 11 types of rotaxanes listed in Table 3.1. Section ROT-6 illustrates these principles for real examples of rotaxanes from the published literature.

ROT-4. GENERAL PRINCIPLES OF ROTAXANE NOMENCLATURE

Because each of the types listed in Table 3.1 is structurally different from the others, a single recommendation for naming rotaxanes cannot be given. On the other hand, names for all types of rotaxanes can be created according to the same basic principles with small variations for specific types of rotaxanes.

ROT-4.1 Names for rotaxanes and pseudorotaxanes

While rotaxane and pseudorotaxane are compound class terms, from the nomenclature point of view it is immaterial whether the ends of a threading component are large enough to prevent dethreading or not. Each systematic name defines a specific chemical structure that in the case of rotaxanes and pseudorotaxanes is an arrangement of the components in relation to each other. Information about the stability of a molecular arrangement is not normally included in a chemical name. Thus, rotaxanes and pseudorotaxanes may be named according to the same nomenclature principles.

ROT-4.2 Name styles

ROT-4.2.1 Use of systematic nomenclature

The name of a rotaxane should be constructed according to the IUPAC recommendations described in this document. The macrocyclic and threading components of rotaxanes should each be named according to IUPAC recommendations for the naming of organic or other corresponding classes of chemical structures [22,23].

ROT-4.2.2 Use of non-systematic name and acronyms

Systematic names for most macrocyclic and threading components of rotaxanes are usually long, complex, or both. The use of semi-systematic and trivial names, or acronyms, for components is therefore acceptable, provided that no ambiguity is thereby introduced.

Note that systematic names generated according to IUPAC nomenclature recommendations are preferred.

ROT-4.3 Name generation

ROT-4.3.1 Order of citation of component names in the complete name

It is recommended that in the complete name of the rotaxane the name(s) of the threading component(s) should precede the name(s) of the macrocyclic component(s). While there is no precedence for assigning seniority to threading components over macrocyclic components, adherence to this recommendation wherever possible will add consistency to names generated for rotaxanes.

Where several threading or macrocyclic components are to be listed, they are preferably cited in descending seniority of their compound classes as defined by IUPAC recommendations for the naming of organic compounds [22,23]. The order of citation does not depend on the number or position of a component in a rotaxane.

ROT-4.3.2 Generic names for rotaxanes of types 1–8

Systematic names for all rotaxane types listed in Table 3.1 are generated according to the same principles and include the names of rotaxane components and the number of each component in a rotaxane assembly. If different arrangements of rotaxane components are possible, the name also includes a prefix that describes the arrangement of the components and is specific for each type of rotaxane.

Systematic names for rotaxanes of types 1 to 8 are constructed according to the following generic format:

(*prefix*)-[*v*]{[*w*][name(s) for threading component(s)]-*rotaxa*-[*x*][name(s) for macrocyclic component(s)]}

wherein *prefix* indicates the position and orientation of rotaxane components with respect to each other if variants are possible and thus specifies the rotaxane isomer as described in Sections ROT-5 and ROT-6. If only the composition of a rotaxane is known or isomers are not possible the prefix part is omitted.

The main part of the name describes the structures of the rotaxane components and the rotaxane composition. This name part is generated in the same way for most types of rotaxanes:

- -*rotaxa*- is a connective that is used to join the names of the threading and macrocyclic components
- *v*, *w*, and *x* are positive integers that define the total number of rotaxane components, the number of threading components, and the number of macrocyclic components, respectively, as described in more detail below.

Note: The use of *pseudorotaxa* as a connective to distinguish between rotaxanes and pseudorotaxanes is illogical, because it would mean that a cyclic component is "pseudothreaded" by a linear component, which is clearly impossible.

If a rotaxane contains several different threading or macrocyclic components, each component is cited in the name only once and the number of each component is specified by the appropriate integer, which is enclosed in brackets before each component. If only one occurrence of a given kind of component is present in a rotaxane, citation of the integer [1] may be omitted.

For example, if a rotaxane contains one threading component and several macrocyclic components of different kinds, the generic name will be as follows:

[*v*]{[name of threading component]-*rotaxa*-[x_1][name of macrocyclic component$_1$]-[x_2][name of macrocyclic component$_2$]-…}

The total number of rotaxane components *v* in this example is: $v = 1 + x_1 + x_2 + \ldots$

For a rotaxane composed of several threading components and one macrocyclic component, the generic name will be:

[*v*]{[w_1][name of threading component$_1$]-[w_2][name of threading component$_2$]-…-*rotaxa*-[name of macrocyclic component]}

The total number of rotaxane components *v* in this example is: $v = w_1 + w_2 + \ldots + 1$.

Names for rotaxanes of types 1–8 are generated by following steps 1–10 in descending order:

1. Select the name for the threading component(s).
2. Enclose within square brackets the name generated in step 1.

   Note: IUPAC [22, R-0.1.5.1] recommends the nesting order of enclosing parentheses, square brackets, or braces in chemical names as follows: {[( )]}. However, because rotaxane names are often complex, a limited selection of enclosing marks for names of rotaxane components and for the entire rotaxane name is recommended here.

3. Enclose, within square brackets, a positive integer, *w*, that precedes the name generated in step 2 for the threading component(s); this indicates how many threading components there are in the rotaxane.
4. Add the italicized connective -*rotaxa*- after the name generated in step 3.
5. Add the name(s) for the macrocyclic component(s) after the italicized connective -*rotaxa*-.
6. Enclose within square brackets the name(s) generated in step 5.
7. Enclose, within square brackets, a positive integer, *x*, that precedes the name(s) generated in step 6 for the macrocyclic component(s); this indicates how many macrocyclic components there are in the rotaxane.
8. Enclose within braces the entire name generated in steps 1–7.
9. Enclose, within square brackets, a positive integer, *v*, that precedes the name generated in steps 1–8; this indicates the total number of components present in the rotaxane.
10. Add the italicized *prefix*, enclosed in parentheses, that describes the arrangement of rotaxane components and is generated as described in corresponding sections for each specific type of rotaxane.

Steps 1–10 given above are used to name rotaxanes of types 1–8. The generic name formats for rotaxanes of types 9–11 are described in Sections ROT-4.3.3 to ROT-4.3.5. The systematic names for specific examples are given in Section ROT-6.

ROT-4.3.3 Generic names for rotaxanes of type 9

Rotaxanes of type 9 are composed of a component that contains a macrocyclic part and a linear section connected to each other. The general name format specified in Section ROT-4.3.2 must be modified since there is no logical place within the complete name at which to insert -*rotaxa*- as a connector. Addition of *rotaxa*- as a prefix is therefore recommended.

Systematic names for rotaxanes of type 9 are written according to the generic format:

[1]{*rotaxa*-[name of the component]}

The integer [1] cannot be omitted for rotaxanes of type 9 because components that contain both a macrocyclic and a linear section can form other rotaxane arrangements, for example, type 10 rotaxanes (“daisy chains”).

ROT-4.3.4 Generic names for rotaxanes of type 10

The names for rotaxanes of type 10 are created in a similar way. Several identical components that consist of both a linear section and a threadable ring can form either acyclic or cyclic arrangements in which the linear section of one component is threaded through the macrocyclic part of another component to form so-called “daisy chains”.

Systematic names for rotaxanes of type 10 are written according to the following generic format:

[*n*]{*rotaxa*-[name of the component]}

for an acyclic arrangement; and

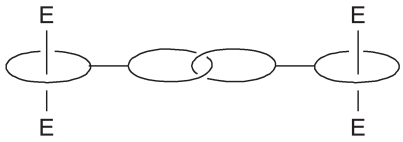
[*cyclo-n*]{*rotaxa*-[name of the component]}

for a cyclic arrangement. In both cases, *n* is the number of rotaxane components. Figure 4.3.4.1 shows examples of acyclic and cyclic [4]rotaxanes of type 10.

Fig. 4.3.4.1 Examples of acyclic and cyclic [4]rotaxanes of type 10.

ROT-4.3.5 Generic names for catenarotaxanes of type 11

Rotaxanes of type 11 shown below include a two-component catenane, each large ring of which has another large ring attached to it that can enclose a threading component or components. This type can be generically named as a [4]catenarotaxane or a [4]rotacatenane.



Note 1: The *IUPAC Compendium of Chemical Terminology* defines catenanes or catena-compounds as molecules having two or more rings connected in the manner of links of a chain, without a covalent bond [20].

The whole catenane component can be treated as a complex macrocyclic component. Thus, catenarotaxanes of type 11 that include two threading components and one macrocyclic catena component can be named according to the following generic format:

[3]{[2][name of threading component]-*rotaxa*-[name of the [2]catenane]}

Several nomenclature systems for catenanes have been proposed, but there is no universally recommended system. Use of -*catena*- as an italicized connective for the [2]catenane component of the generic name format is recommended in accord with use of -*rotaxa*- as a connective. The principles recommended in Section ROT-4.3.4 for "daisy-chain" rotaxanes can be followed to create names of catenanes composed of equal components. Thus, the [2]catenane composed of two equal components can be named according to the following generic format:

[2][*catena*-(name of the catena component)]

Analogously, the generic name for [3]rotaxanes of type 11 can be constructed according to the following format:

[3]{[2][name of threading component]-*rotaxa*-[2][*catena*-(name of the catena component)]}

This generic name unambiguously describes all components and the composition of catenarotaxanes of type 11. A specification of possible isomers of catenarotaxanes of type 11 with prefixes is described in Section ROT-5.4.

Note 2: Because a systematic nomenclature system for catenanes has not been developed yet, the name format proposed here for [2]catenanes and [3]rotaxanes of type 11 should be considered to be provisional.

ROT-5. SPECIFICATION OF ISOMERISM OF ROTAXANES

ROT-5.1 Types of isomerism in rotaxanes

Whereas the main part of the rotaxane name unambiguously describes the compositions of rotaxanes and isomerism of rotaxane components, the italicized prefix describes the isomerism specific to each rotaxane. Thus, the term "isomerism of rotaxanes" does not include isomerism of rotaxane components but describes different arrangements that can be formed by the same components.

The isomers of rotaxanes can differ in

a. positions of macrocyclic components at linear sections of complex threading components and/or positions of threading components at several macrocyclic parts of complex macrocyclic components;
b. the order in which several nonequivalent macrocyclic components are positioned at the same linear section of a threading component;
c. the position of a macrocyclic component at different recognition sites within the same linear section; and
d. the arrangement of unsymmetrical rotaxane components with respect to each other.

Figure 5.1.1 shows examples of isomerism in rotaxanes.

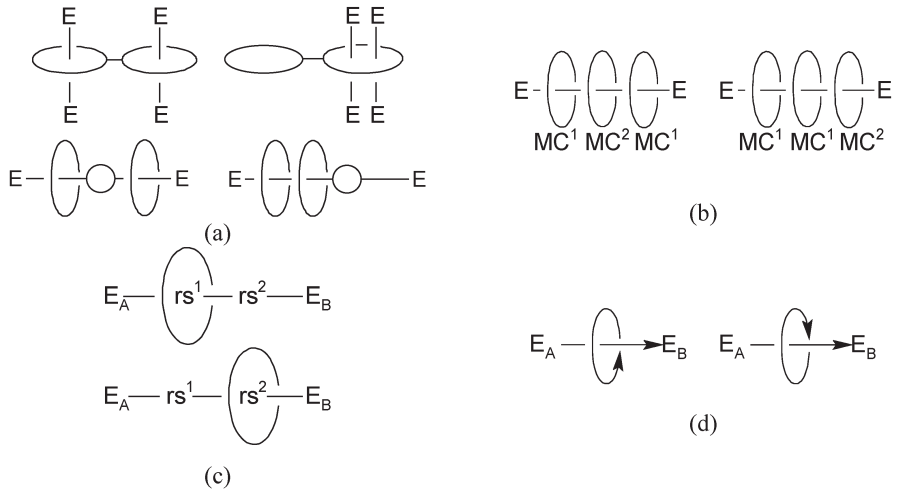


Fig. 5.1.1 Types of rotaxane isomerism (E_A and E_B designate nonequivalent ends and arrows define specific symmetry properties of a component, MC designates macrocyclic component).

Isomers of types a, b, and c can exist for rotaxanes irrespective of symmetry properties of rotaxane components. The naming conventions for these types of isomers are described in the section below for the corresponding classes of rotaxanes. Being relatively rare, the rotaxane isomers of type d are only

possible for the rotaxane components with certain specific symmetry properties. This and other types of stereoisomeric rotaxanes will be treated in the separate recommendations that are currently under preparation [24].

ROT-5.2 Position of threading components in several threadable rings (types 3 and 4)

For rotaxanes of type 3, isomers that differ in the position of the threading components in different threadable rings are possible. The position of the threadable components, which can be unambiguously specified by the italicized prefix part of the name, is designated by two numbers cited in decreasing order that indicate the number of threading components in each ring of the macrocyclic component. Examples of rotaxanes of type 3 and their corresponding prefixes are shown in Fig. 5.2.1.

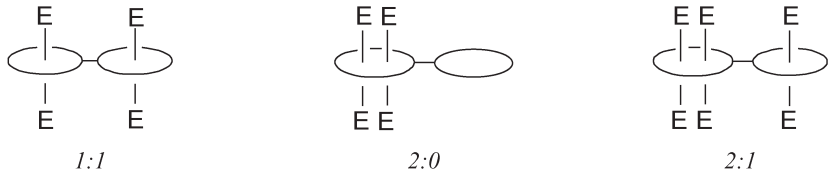


Fig. 5.2.1 Examples of isomeric rotaxanes of type 3 and their corresponding prefixes.

The isomers of rotaxanes of type 4 that differ in positions of the threading components in three rings are defined in the same way; a minor difference is that the prefix in this case is composed of three numbers that indicate the number of threading components in each threadable ring. Figure 5.2.2 shows examples of [4]rotaxanes of type 4 and their corresponding prefixes.

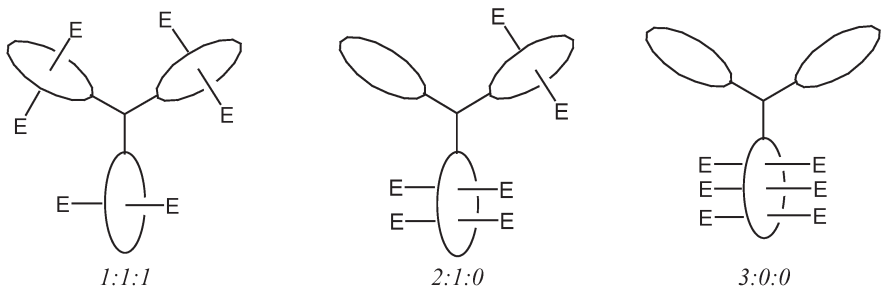


Fig. 5.2.2 Examples of isomeric [4]rotaxanes of type 4 and their corresponding prefixes.

The prefixes for more complex macrocyclic components can be created according to the principles specified above and in Section ROT-5.3.2 for rotaxanes with complex threading components.

Note 1: The numbers of threading components are cited in decreasing order if the threadable rings are structurally identical. If the threadable rings are not identical the numbers of components are cited in decreasing order of seniority of threadable rings. Thus, for [3]rotaxanes of type 3 with identical symmetrical threading components three isomers with prefixes *2:0*, *0:2*, and *1:1* are possible. The procedure to establish the seniority of threadable rings will be defined in a separate publication on stereoisomerism of rotaxanes [24].

Note 2: For citation of nonequivalent threading components see Section ROT-5.5.2.

ROT-5.3 Position of macrocyclic components on several linear sections (types 5–8)

The positions of simple macrocyclic components on threading components with several linear sections are specified in a manner similar to that given in Section ROT-5.2. The prefix in this case indicates the number of components threaded on each linear section.

ROT-5.3.1 Specification of the position of macrocyclic components for rotaxanes of type 5

Type 5 rotaxanes have an unbranched threading component with two or more linear sections separated from each other by large groups that prevent movement of a macrocyclic component from one section to another. In rotaxanes of type 5, the numbers of components threaded onto sections are cited successively starting from one terminal linear section and proceeding through all internal sections, finally to the other terminal section. Sections containing the greatest number of components should be cited as early as possible. Examples of [3]rotaxanes of type 5 are shown in Fig. 5.3.1.1.

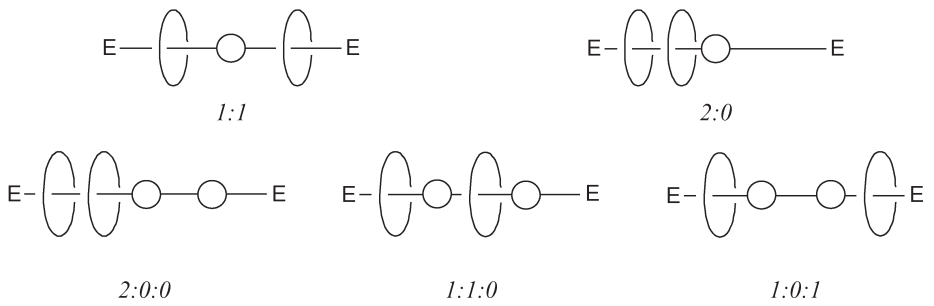


Fig. 5.3.1.1 Examples of [3]rotaxanes of type 5 and their corresponding prefixes.

For citation of nonequivalent macrocyclic components, see Section ROT-5.5.1.

ROT-5.3.2 Specification of the position of macrocyclic components for rotaxanes with branched threading components (types 6–8)

The isomers for rotaxanes of type 6 with a Y-shaped threading component are specified in a manner similar to that described above for type 5. Providing that the linear sections are equivalent, the prefix consists of three numbers that are cited in descending order. Examples of isomeric [4]rotaxanes of type 6 and their corresponding prefixes are shown in Fig. 5.3.2.1.

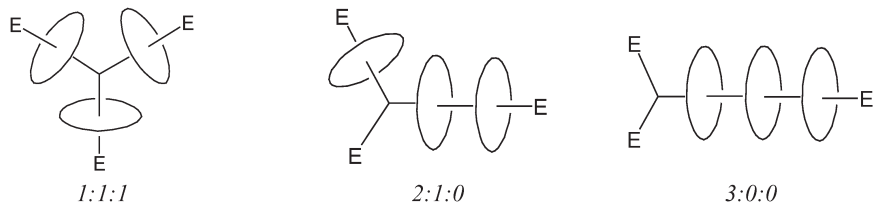


Fig. 5.3.2.1 Examples of isomeric [4]rotaxanes of type 6 and their corresponding prefixes.

In rotaxanes of type 7 with X-shaped threading components containing four topologically equivalent linear sections, the prefix consists of four numbers that indicate the number of macrocyclic components in each section. The order of citation of numbers for X-shaped threading components depends on the spatial structure of the X-shaped component. For tetrahedral X-shaped components, the numbers are cited simply in decreasing order, but for X-shaped components with square-planar configuration, the sections are listed sequentially clockwise or counterclockwise. Sections with the greatest number of components should be cited as early as possible. Figure 5.3.2.2 shows examples of [3]rotaxanes of type 7 and their corresponding prefixes.

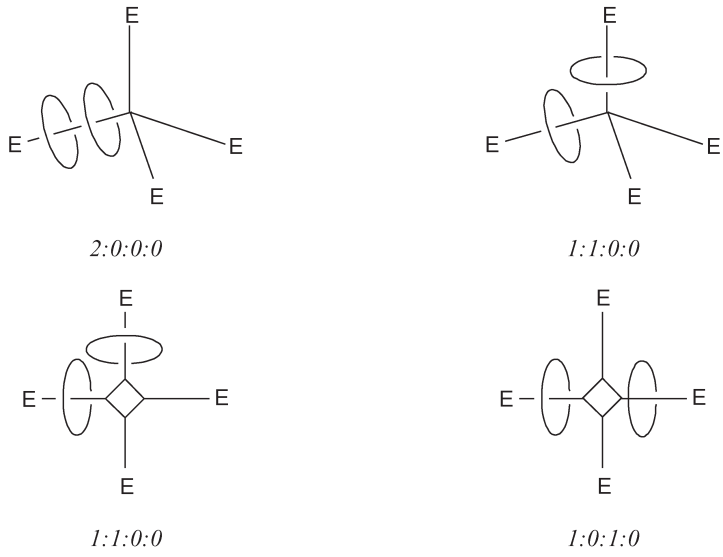


Fig. 5.3.2.2 Examples of [3]rotaxanes of type 7 and their corresponding prefixes (the square in the center of the X-shaped component is added to indicate the square-planar configuration).

If rotaxanes of types 5–7 with equivalent threading sections contain a single macrocyclic component, the prefixes *1:0, 1:0:0*, and *1:0:0:0*, respectively, are not cited, unless isomers are possible.

The prefix for rotaxanes of type 8 that include an H-shaped threading component with five topologically nonequivalent linear sections is composed of five numbers. For unambiguous specification of isomers, the numbers of macrocyclic components are cited in a fixed order: (1) the two adjacent terminal sections; (2) the internal section; (3) the remaining two adjacent terminal sections. Among several possible prefixes, the one that specifies the most populated terminal section earliest is chosen. Figure 5.3.2.3 shows the order of sections with numbers placed near the corresponding section and examples of isomeric [3]rotaxanes of type 8 with their prefixes.

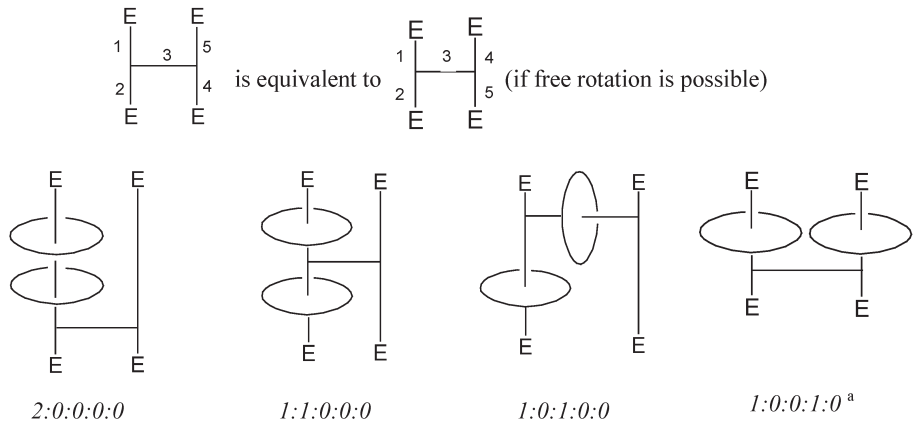


Fig. 5.3.2.3 Order of citation of linear sections in an H-shaped threading component and type 8 isomeric [3]rotaxanes with corresponding prefixes.
[a]The prefix *1:0:0:1:0* given for the last structure implies free rotation along the internal linear section. If such rotation is not possible the prefix will be *1:0:0:0:1* in accordance with the order of citation of the linear section.

Note 1: The principles specified in this section imply that topologically equivalent sections are also structurally equivalent. For rotaxanes of Types 5–8 with structurally nonequivalent linear sections the numbers of components are cited first with respect to the topological order stated here, and then in decreasing order of seniority of linear sections. The principles for establishing the seniority of structurally nonequivalent sections will be defined in a separate publication on stereoisomerism of rotaxanes [24].

Note 2: For citation of nonequivalent macrocyclic components, see section ROT-5.5.1.

ROT-5.4 Position of threading components for catenarotaxanes of type 11

Catenarotaxanes of type 11 contain a catena macrocyclic component that includes four large rings that can be potentially threaded with linear components. To specify the structure, the prefix for rotaxanes of type 11 consists of four numbers that indicate how many threading components are positioned in each threadable ring. Figure 5.4.1 shows two examples of isomeric [3]rotaxanes of type 11 and their corresponding prefixes.

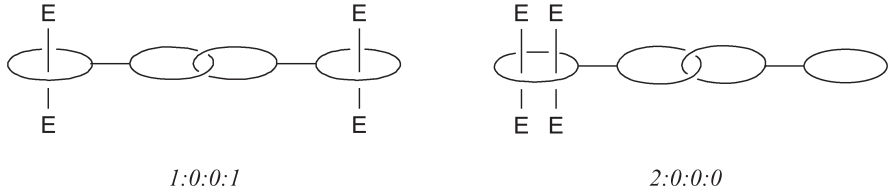


Fig. 5.4.1 Examples of [3]rotaxanes of type 11 and their corresponding prefixes.

Each catena component of a rotaxane of type 11 contains two large rings; thus, two different isomeric catenanes are possible. To indicate that only one large ring of each component forms a catena junction, the prefix *(1-1)* can be added in front of the catenane name. This prefix indicates that the first

ring of one component forms a catena junction with the first ring of another component. Thus, the whole name of a [2]catenane will be:

(*1-1*)-[2][*catena*-(name of the catena component with two large rings)]

Thus, the generic name for the first isomer of [3]rotaxanes of type 11 shown in Fig. 5.4.1 will be:

1:0:0:1-[3]{[2][name of threading component]-*rotaxa*-[(*1-1*)-[2][*catena*-(name of the catena component with two large rings)]]}

Note 1: For catena components with two equivalent rings this generic name unambiguously indicates the structure of a catenane. The principles pertinent to isomers of nonequivalent components will be established in a separate publication [24].

Note 2: Because a systematic nomenclature for catenanes has not yet been developed, the name format proposed here for [2]catenane and thus for [3]rotaxanes of type 11 should be considered to be provisional.

ROT-5.5 Positions and order of nonequivalent components of the same type

For rotaxanes with different components of the same type, isomers that differ in position or order of components are possible. For an unambiguous description of positions of rotaxane components, the prefix part of the rotaxane name includes designations of specific rotaxane components in accordance with the order in which they are cited in the name as described below.

ROT-5.5.1 Specification of arrangement of nonequivalent macrocyclic components

For rotaxanes of type 1 with more than one type of macrocyclic component, isomers differing in the order of macrocyclic components are possible. To define an arrangement of macrocyclic components, they are indicated by MC^n designations that define different macrocyclic components. *MC* is an abbreviation for "macrocyclic component" and *n* is the position of this component name in the whole name of the rotaxane. Thus, the macrocyclic component cited first in the name is designated in the prefix part by MC^1, the second by MC^2, and so on.

For the [4]rotaxane of type 1.3 composed of two equal macrocyclic components cited earlier in the name, and a third, different macrocyclic component, and having the generic name

[4][(name of threading component)-*rotaxa*-[2](name of macrocyclic component$_1$)-[1](name of macrocyclic component$_2$)],

two isomers are possible. Figure 5.5.1.1 shows two possible isomers and their corresponding prefixes for this type of rotaxane.

MC^1, MC^1, MC^2 (*not* MC^2, MC^1, MC^1) MC^1, MC^2, MC^1

Fig. 5.5.1.1 Examples of isomeric [4]rotaxanes of type 1 and the corresponding prefixes.

The prefix part of the rotaxane name cites the designations of components in the order in which they are positioned on the threading component. If there is a choice, the prefix that cites the components with lower indexes earlier is chosen, as shown for the first structure in Fig. 5.5.1.1.

For rotaxanes of types 5–8, composed of threading components with several linear sections and different macrocyclic components, each possible isomer is specified by the prefix that cites the specific macrocyclic component designations MC^n instead of numbers for each linear section. The linear sections for specific rotaxane types are listed in the order defined in Section ROT-5.3. If there is a choice, the most populated sections are cited first, then earlier cited macrocyclic components. For rotaxanes of type 5, the macrocyclic components are cited sequentially, beginning with the outermost one. For rotaxanes of types 6–8, the components are cited from the outermost one for each linear section. Examples of rotaxanes of types 5 and 6 and their corresponding prefixes are shown in Fig. 5.5.1.2.

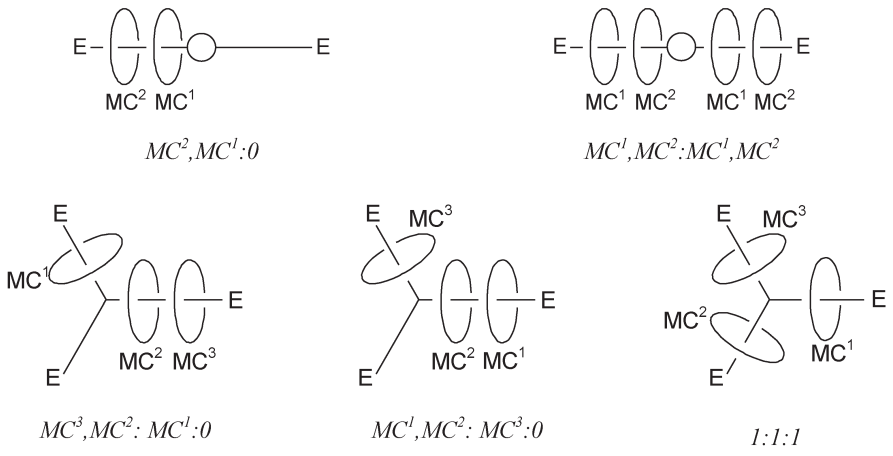


Fig. 5.5.1.2 Examples of rotaxanes of types 5 and 6 with different macrocyclic components and their corresponding prefixes.

Note that for the last example of [4]rotaxanes of type 6 no isomers are possible when one macrocyclic component is threaded onto each threading section and components are symmetrical. Thus, the simplified prefix described in section ROT-5.3 unambiguously describes the structure of the rotaxane. If no isomers are possible, or if the exact position of each component is unknown, simplified prefixes can be used for other types of rotaxanes with nonequivalent components.

ROT-5.5.2 Specification of positions of nonequivalent threading components

The positions of different threading components for isomeric rotaxanes with macrocyclic components with several threadable rings are specified by modification of the prefixes described in Section ROT-5.2. Instead of numbers that define the number of threading components in each threadable ring, the italicized designations TC^n are used, where *TC* is an abbreviation for "threading component" and *n* is the position of the threading component name within the complete name of a rotaxane.

Figure 5.5.2.1 shows two isomeric [4]rotaxanes of type 3 and their corresponding prefixes. The designations TC^1 and TC^2 indicate different threading components. TC^1 designates a component cited earlier in the complete name.

Fig. 5.5.2.1 Examples of isomeric [4]rotaxanes of type 3 and their corresponding prefixes.

If the threadable rings in a complex macrocyclic component are equivalent, the designations of threading components are cited starting from the more populated threadable ring, which results in citation of lower-numbered threading components as early as possible.

ROT-5.5.3 Specification of rotaxanes that function as molecular shuttles

The recommended method for indicating the association of a macrocyclic component with a specific recognition site is to add a prefix comprising italicized indications rs^n-*MC*, where *rs* is an abbreviation for "recognition site", *n* is a number assigned to the recognition site by consecutive numbering from one end of the threading component, and *MC* is an abbreviation for "macrocyclic component". The procedures pertinent to nonequivalent recognition sites will be established in a separate publication [24]. Figure 5.5.3.1 shows several examples of molecular shuttles and their corresponding prefixes.

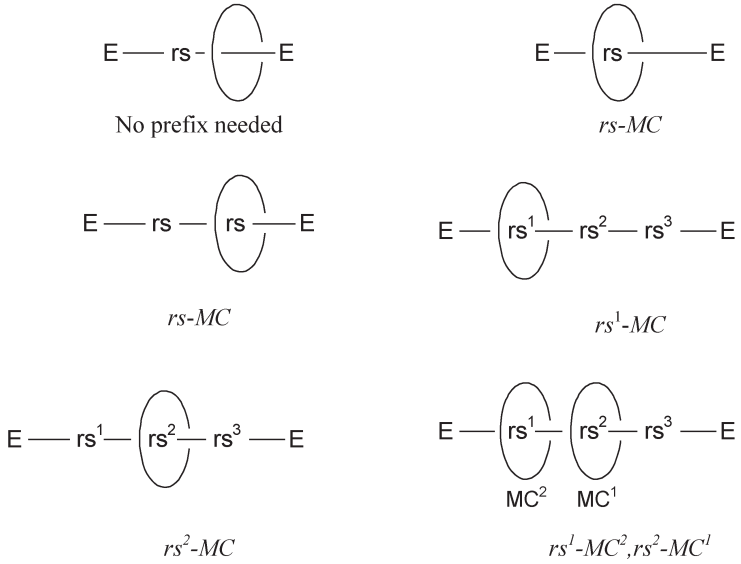


Fig. 5.5.3.1 Examples of [2]rotaxanes that function as molecular shuttles and their corresponding prefixes.

For rotaxanes with a single recognition site or two identical recognition sites, the designation is unnecessary. However, if it is important to distinguish between associated and non-associated forms of a rotaxane, the prefix *rs-MC* is added to indicate that a macrocyclic component resides at a recognition site (see Section ROT-1.6).

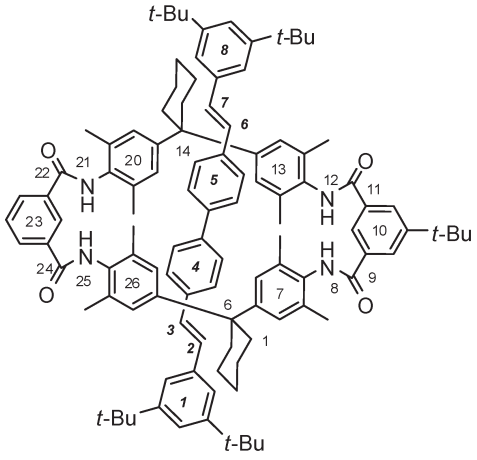
Different macrocyclic components are indicated by the addition of MC^n designations that are assigned as described in Section ROT-5.5.1 (see the last structure in Fig. 5.5.3.1).

ROT-6. EXAMPLES OF ROTAXANES AND THEIR SYSTEMATIC NAMES

This section illustrates the above-stated principles of rotaxane nomenclature for several examples of rotaxanes reported in the literature. Names are created according to the IUPAC recommendations for the nomenclature of organic compounds [22,23]. Because the rotaxane components very often contain several cyclic fragments, many compounds are named using phane nomenclature principles [25,26]. In all cases where new nomenclature principles lead to different systematic names the new organic nomenclature rules are followed [23].

Alternate, less formal names for complete rotaxanes are acceptable for general use when one or more components have semi-systematic names, trivial names, or acronyms, provided that the semi-systematic or trivial names are in common usage in the scientific literature and the acronyms are defined.

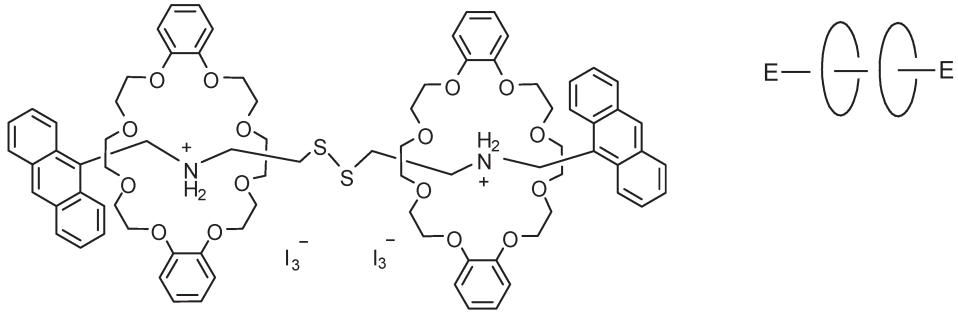
Example 1



A type 1.1 [2]rotaxane composed of symmetrical components. Isomers are not possible.

[2]{[(2*E*,6*E*)-1^3,1^5,8^3,8^5-tetra-*tert*-butyl-1,8(1),4,5(1,4)-tetrabenzenaoctaphane-2,6-diene]-*rotaxa*-[10^5-*tert*-butyl-7^3,7^5,13^2,13^6,20^3,20^5,26^3,26^5-octamethyl-8,12,21,25-tetraaza-7,13,20,26(1,4),10,23(1,3)-hexabenzenadispiro[5.7.5.7]hexacosaphane-9,11,22,24-tetrone]}

Example 2



A type 1.2 [3]rotaxane with symmetrical components. Isomers are not possible.

[3]{[2,2'-disulfanediylbis{*N*-[(anthracen-9-yl)methyl]ethan-1-aminium}]-*rotaxa*-[2][6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine]} bis(triiodide)

Alternatively, the following less formal names may be used:

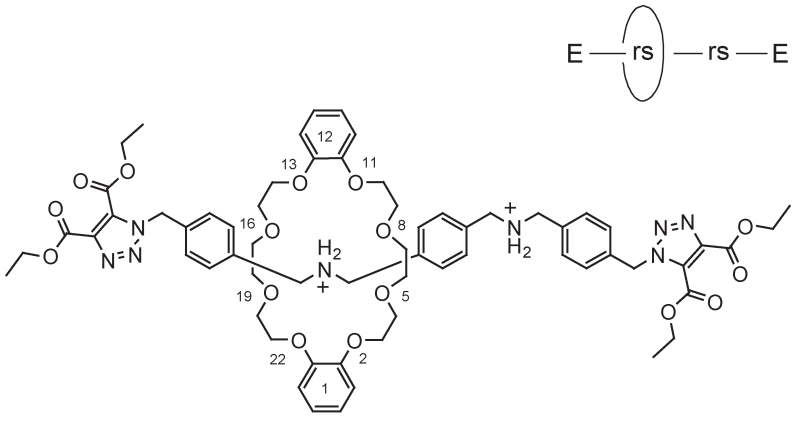
[3]{[2,2'-disulfanediylbis{*N*-[(anthracen-9-yl)methyl]ethan-1-aminium}]-*rotaxa*-[2][dibenzo-24-crown-8]} bis(triiodide)

or

[3]{[2,2'-disulfanediylbis{*N*-[(anthracen-9-yl)methyl]ethan-1-aminium}]-*rotaxa*-[2][DB24C8]} bis(triiodide)

wherein DB24C8 is an acronym for dibenzo-24-crown-8

Example 3

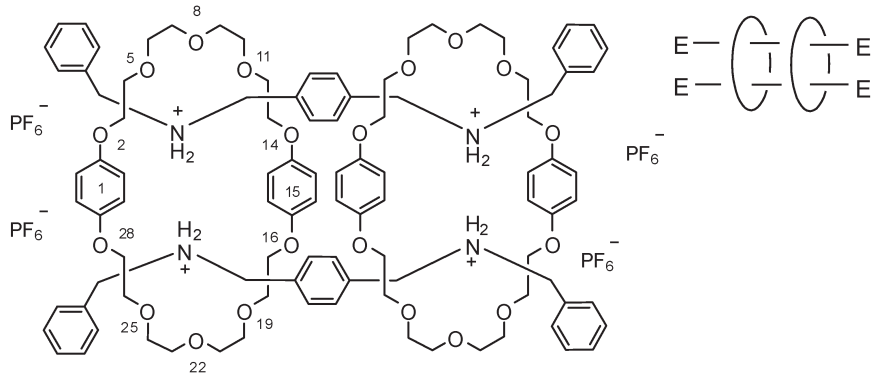


A type 1.1 [2]rotaxane composed of symmetrical components that can function as a molecular shuttle. Recognition sites are equivalent. Isomers are not possible.

[2]{[1,1'-(1,4-phenylene)bis[*N*-(4-{[4,5-bis(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]methyl}benzyl)methanaminium]]-*rotaxa*-[6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine]]

Note: To highlight that the macrocyclic component is associated with one of two equivalent recognition sites the prefix (*rs-MC*) may be added.

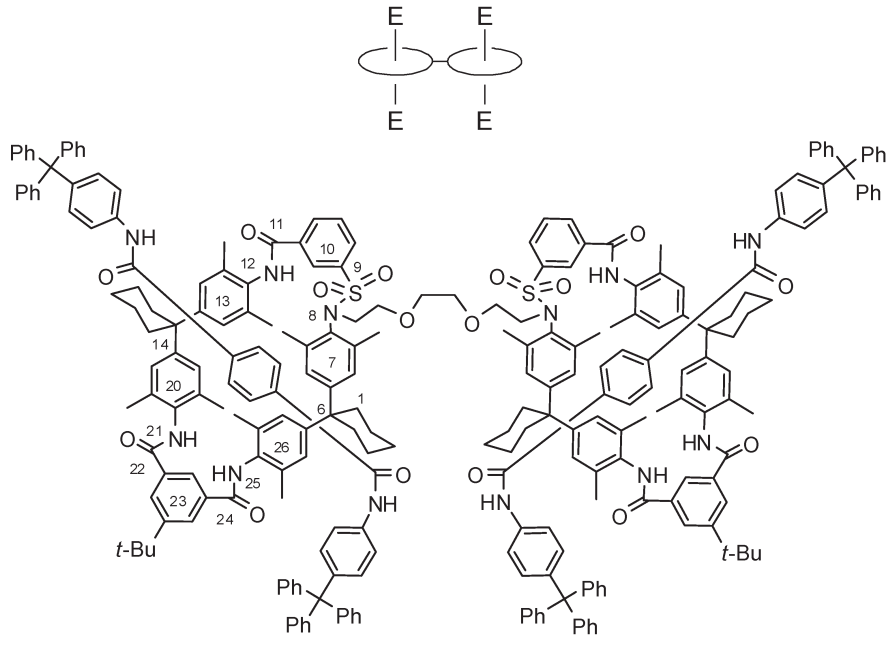
Example 4



A type 2.2 [4]pseudorotaxane with symmetrical components. Isomers are not possible.

[4]{[2][1,1'-(1,4-phenylene)bis(*N*-benzylmethanaminium)]-*rotaxa*-[2][2,5,8,11,14,16,19,22,25,28-decaoxa-1,15(1,4)dibenzenacyclooctacosaphane]} tetrakis(hexafluoridophosphate)

Example 5

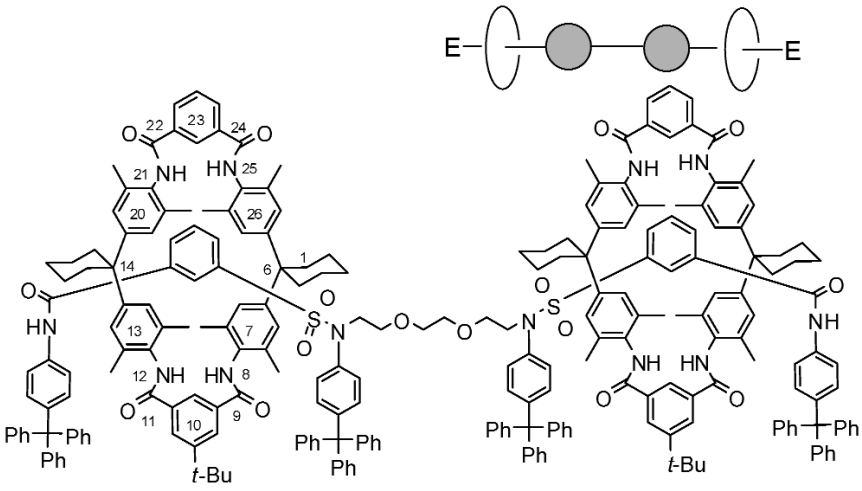


A type 3 [3]rotaxane composed of macrocyclic component with two threadable rings and two threading components. Isomers with different positions of threading components are possible. The prefix (*1:1*) is needed to specify the isomer.

(*1:1*)-[3]{[2][*N*,*N*'-bis(4-tritylphenyl)benzene-1,4-dicarboxamide]-*rotaxa*-[8,8'-[ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis[23^5-*tert*-butyl-7^3,7^5,13^2,13^6,20^3,20^5,26^3,26^5-octamethyl-9λ^6-thia-8,12,21,25-tetraaza-7,13,20,26(1,4),10,23(1,3)-hexabenzenadispiro[5.7.5.7]hexacosaphane-9,9,11,22,24-pentone]]}

Note: Here and in other examples the name "ethane-2,1-diyl" for the multiplicative substituent group –CH_2–CH_2– is used [23] instead of the traditional, currently recommended name "ethylene" [22]. The citation of oxo groups at sulfur atoms as suffixes follows new organic nomenclature rules [23].

Example 6

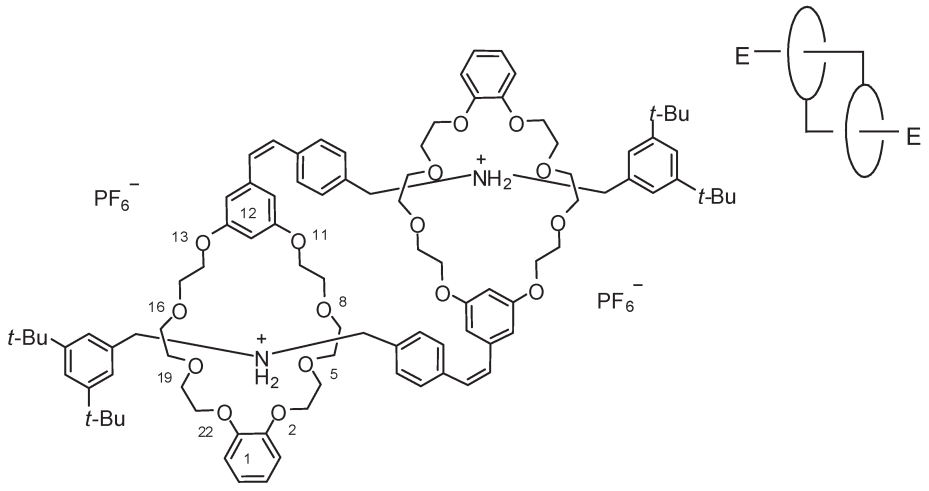


A type 5 [3]rotaxane composed of two symmetric macrocyclic components and threading component with three linear sections. Isomers are possible. The number of macrocyclic components at each linear section must be specified.

(*1:0:1*)-[3]{[3,3'-(ethane-1,2-diylbis{oxyethane-2,1-diyl[(4-tritylphenyl)azanediyl]sulfonyl})bis[*N*-(4-tritylphenyl)benzamide]]-*rotaxa*-[2][10^5-*tert*-butyl-7^3,7^5,13^2,13^6,20^3,20^5,26^3,26^5-octamethyl-8,12,21,25-tetraaza-7,13,20,26(1,4),10,23(1,3)-hexabenzenadispiro[5.7.5.7]hexacosaphane-9,11,22,24-tetrone]}

Note: If the threading component in this case is treated as having only two linear sections where macrocyclic component can reside, the prefix will be (*1:1*).

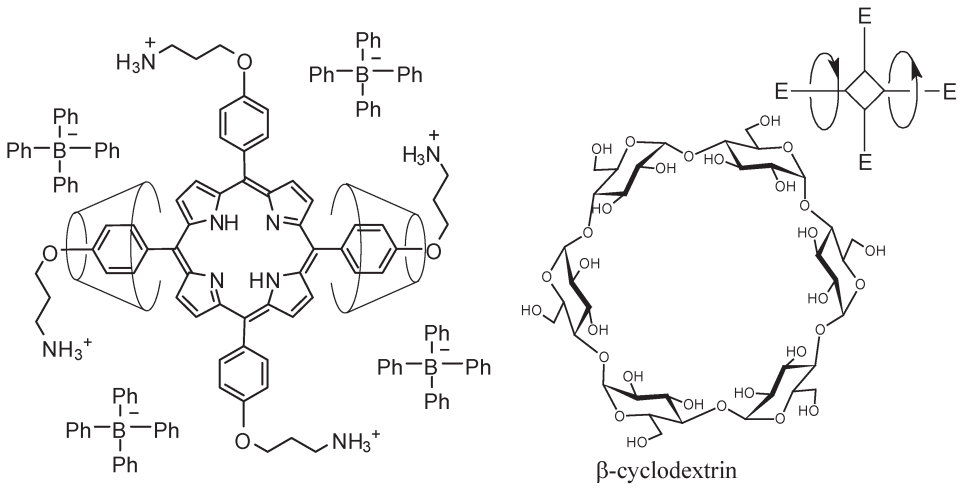
Example 7



A type 10 cyclic daisy-chain [2]rotaxane composed of two symmetrical components. Isomers are not possible.

[*cyclo*-2]{*rotaxa*-[*N*-(3,5-di-*tert*-butylbenzyl)-1-(4-{(*Z*)-2-[2,5,8,11,13,16,19,22-octaoxa-1(1,2),12(1,3)-dibenzenacyclodocosaphan-12^5-yl]ethenyl}phenyl)methanaminium]}
bis(hexafluoridophosphate)

Example 8



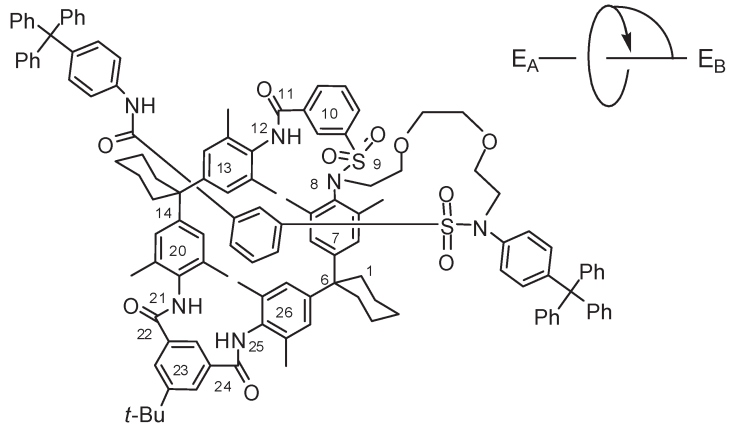
A type 7 [3]pseudorotaxane composed of two macrocyclic components and an X-shaped threading component with four linear sections and square-planar topology. Isomers with different position of macrocyclic components are possible. The number and position of the macrocyclic components must be specified. Cones at the diagram designate β-cyclodextrin molecules with wider rim with two hydroxyl groups (2,3-rim) directed to the porphyrin fragment.

(*1:0:1:0*)-[3]{[3,3',3'',3'''-[(porphyrin-5,10,15,20-tetrayl)tetrakis(4,1-phenyleneoxy)]tetra(propan-1-aminium)]-*rotaxa*-[2][β-cyclodextrin]} tetrakis(tetraphenylboranuide)

Note 1: Note that isomers with different orientation of cyclodextrin components are possible. The specification of such isomers and more detailed discussion of the structure of cyclodextrin components will be given in a separate publication [24].

Note 2: The more commonly used additive name "tetraphenylborate" may be used as an alternative name for the anion.

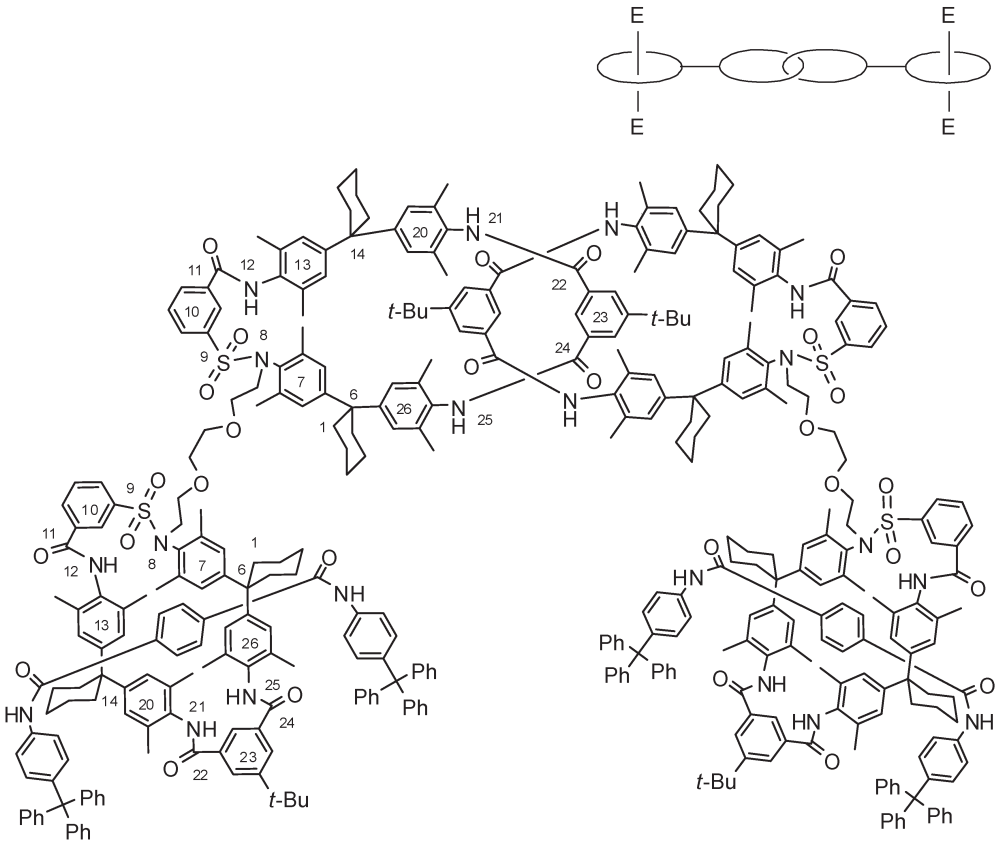
Example 9



A type 9 [1]rotaxane. Stereoisomers are possible; the specification of these isomers will be described in a separate publication [24].

rotaxa-[1][3-{[2-(2-{2-[23^5-*tert*-butyl-7^3,7^5,13^2,13^6,20^3,20^5,26^3,26^5-octamethyl-9,9,11,22,24-pentaoxo-9λ^6-thia-8,12,21,25-tetraaza-7,13,20,26(1,4),10,23(1,3)-hexabenzenadispiro[5.7.5.7]hexacosaphan-8-yl]ethoxy}ethoxy)ethyl][(4-tritylphenyl)amino]sulfonyl}-*N*-(4-tritylphenyl)benzamide]

Example 10



A type 11 [3]rotaxane ([4]catenarotaxane) composed of two symmetrical threading components and a two-component catenane macrocyclic component. The catenane component has four macrocyclic sections. Isomers are possible. An indication of the number of threading components in each macrocyclic section is needed.

(*1:0:0:1*)-[3]{[2][*N*,*N*'-bis(4-tritylphenyl)benzene-1,4-dicarboxamide]-*rotaxa*-[(*1-1*)-[2](*catena*-{8,8'-[ethane-1,2-diylbis(oxyethane-2,1-diyl)]bis[23^5-*tert*-butyl-7^3,7^5,13^2,13^6,20^3,20^5,26^3,26^5-octamethyl-9λ^6-thia-8,12,21,25-tetraaza-7,13,20,26(1,4),10,23(1,3)-hexabenzenadispiro[5.7.5.7]hexacosaphane-9,9,11,22,24-pentone]})]}

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