Macromolecular Nomenclature Note No. 24

E. S. Wilks*
Nomenclature Committee
ACS Division of Polymer Chemistry, Inc.

Terminology and Nomenclature for Rotaxanes – A Progress Report

Although rotaxanes have been known for about 35 years, the development of a systematic nomenclature for them has been largely neglected. Rotaxanes were first proposed in 1961 [1], and shown to exist in 1967 [2-4]. Since then, many different types have appeared in the published literature.

Terminology

The term **rotaxane** is derived from the Latin words for a wheel and an axle [3, 4]. Generically speaking, a rotaxane is a chemical substance comprising one or more macrocyclic species threaded onto one or more "linear" species. "Linear" may be literally linear (I-shaped or bar-shaped), or it may be more complex, such as H-, X-, or Y-shaped.

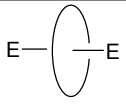
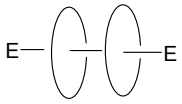
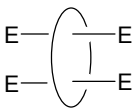
It is intellectually convenient to classify rotaxanes into two broad types: those which contain a macromolecular or polymeric component, and those which do not. Rotaxanes containing a macromolecular or polymeric component are generally called "**macromolecular rotaxanes**", "**polymeric rotaxanes**", or "**polyrotaxanes**". In contrast, rotaxanes containing no macromolecular or polymeric component are generally referred to simply as "rotaxanes". Since, hierarchically speaking, "rotaxanes" is a broad term to "macromolecular rotaxanes" or "polymeric rotaxanes", use of the word "rotaxanes" without further qualification is ambiguous, because, without further qualification, it is unclear whether the name refers to the whole family or only to "rotaxanes other than macromolecular or polymeric ones". Although the term "low-molar-mass rotaxanes" has been used previously [5], it is suggested that the term "**discrete rotaxanes**" should be adopted.

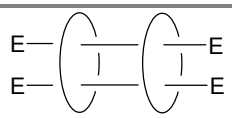
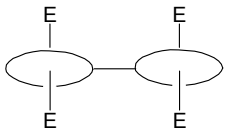
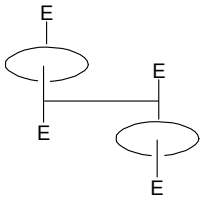
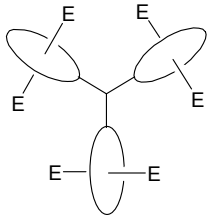
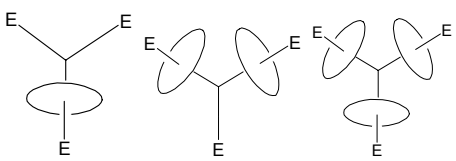
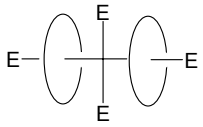
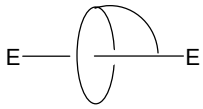
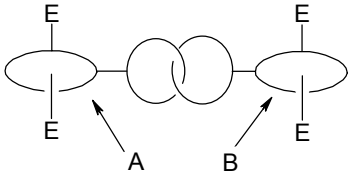
Rotaxanes differ from a closely related species, **pseudorotaxanes**, by the presence of bulky end-groups, frequently called **stoppers**, which prevent macrocyclic components from being threaded onto, or dethreading from, "linear" components. In contrast, pseudorotaxanes, which are often synthetic precursors to rotaxanes, have end-groups small enough to permit threading of "linear" components through macrocyclic components.

Examples of Types of Rotaxane Reported in the Literature

Tables 1 and 2 show examples of discrete and macromolecular rotaxanes, respectively, cited in the literature.

Table 1. Idealized Representations of Nine Generic Types of Discrete Rotaxanes

Type	Generic Structure[a]	Key Structural Features
D-1.1		[2]Rotaxane: a linear molecule, upon which is threaded a single macrocycle [6, 7].[b,c]
D-1.2		[3]Rotaxane: a linear molecule, upon which are threaded two identical or different macrocycles [6, 7].[d]
D-2.1		[3]Rotaxane: two identical or different linear molecules, upon which are threaded a macrocycle [6].[e]

D-2.2		[4]Rotaxane; two identical or different linear molecules, upon which are threaded two identical or different macrocycles [6, 8].
D-3		[2-2]Rotaxane;[f] two identical or different linear molecules, upon which are threaded two identical or different macrocycles, which are structurally linked [7, 9-11].
D-4		[2-2]Rotaxane;[f] two identical or different linear molecules, upon which are threaded two identical or different macrocycles; the linear molecules are structurally linked [7, 9, 10].
D-5		Tris[2]rotaxane: three identical or different ansate macrocycles are connected via their acyclic moieties to form a Y-shaped molecule; each macrocycle is threaded with a linear molecule; the linear molecules may be identical or different [7, 10].
D-6		[2], [3], and [4]rotaxanes: one, two, or three arms of a Y-shaped molecule are threaded with one, two, or three macrocycles, respectively [12-17].
D-7		[3]Rotaxane: two opposite arms of a four-armed, star-shaped molecule are each threaded with a macrocycle; the macrocycles may be identical or different [18].
D-8		[1]Rotaxane:* a linear molecule, upon which is threaded a macrocycle; the linear molecule and macrocycle are structurally linked [7, 11, 19]. *Also called a [2]rotaxane [9].
D-9		Catrotaxane:[g] a [2rot-2cat-2rot]axane; two interlocking rings are connected, via acyclic bridges, to two macrocycles, A and B, which may be identical or different; each macrocycle is threaded with a linear molecule; the linear molecules may be identical or different [7, 20].

[a]In these generic structures, E represents an end-group of any size. Nomenclature systems usually exclude any indication of end-groups as being specifically large (for rotaxanes) or small (for pseudorotaxanes).

[b]In [2]rotaxanes having both an asymmetrical linear component (e.g., one with two structurally different end-groups) and an asymmetrical macrocycle, two orientationally isomeric [2]rotaxanes are possible.

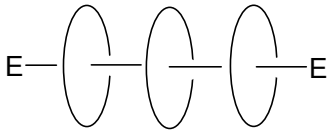
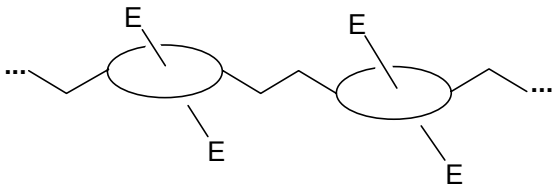
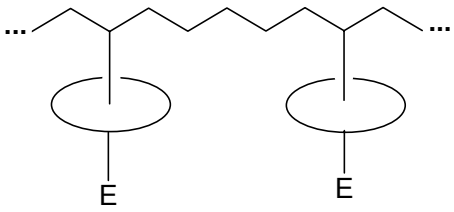
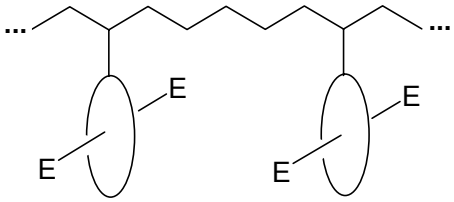
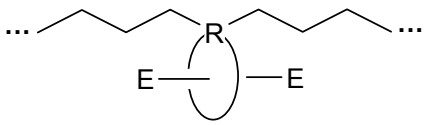
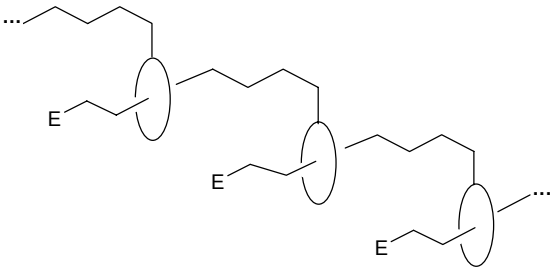
[c]A variation of the [2]rotaxane shown as Type 1 is a [2]rotaxane that functions as a linear molecular shuttle. A systematic nomenclature system for [2]rotaxane molecular shuttles needs to address this special feature.

[d]In [3]rotaxanes having a symmetrical linear component and two identical, incongruently threaded, asymmetrical macrocycles, two orientationally isomeric [3]rotaxanes are possible. Two orientationally isomeric [3]rotaxanes are also possible when an asymmetrical linear component is threaded with two identical, incongruently threaded, asymmetrical macrocycles.

[e]Spontaneous self-assembly of a [4]pseudorotaxane and a [5]pseudorotaxane from large cyclic crown ethers and 4 or 5 equivalents, respectively, of dibenzylammonium hexafluorophosphate have been reported [6]. The corresponding rotaxanes have not been reported.

[f]The designation [2-2]rotaxane is derived according to the nomenclature system of Vögtle and co-workers [9].
[g]Catrotaxanes [9] were formerly called catrotanes [7, 21] or rotacatenanes [22]. The designation [2rot-2cat-2rot]axane is derived according to the nomenclature system of Vögtle and co-workers [9].

Table 2. Idealized Representations of Six Generic Types of Macromolecular Rotaxanes

Type	Generic Structure[a]	Key Structural Features
M-1		A linear macromolecule, upon which is threaded at least one macrocycle. A [4]rotaxane is shown [5, 23].
M-2		A linear macromolecule containing covalently bonded macrocycles, through each of which which is threaded at least one discrete linear molecule [5, 23].
M-3		A linear macromolecule containing linear side-groups or substituents; at least one macrocycle is threaded upon each side-group or substituent [5, 23].
M-4		A linear macromolecule containing side-groups or substituents, each of which contains a covalently bonded macrocycle; through each macrocycle is threaded at least one discrete linear molecule [5, 23].
M-5	 R = non-macrocyclic ring, e.g., benzene-1,2,4,5-tetrayl	A linear macromolecule containing macrocycles that are covalently attached to the linear backbone in cardo fashion, via either a single atom or a non-macrocyclic ring. Each macrocycle is threaded with a discrete linear molecule [5].
M-6		A linear macromolecule containing an attached covalently bonded macrocycle that is threaded with the linear moiety of another macromolecule having the same composition (homopolymer) or a different composition (copolymer) [23, 24].

[a]In these generic structures, E represents an end-group large enough to prevent dethreading.

Nomenclature

In 1971 Schill [25] introduced a nomenclature system for rotaxanes that comprised four parts:
(a) a prefix in the form of a bracketed integer indicating the total number of components in the rotaxane
(b) the name of the linear component, complete with end-groups

(c) the name of each macrocycle, regardless of whether it is chemically identical with, or different from, other macrocycles present
(d) the unitalicized suffix 'rotaxane'.

The generic format of Schill's systematic nomenclature was as follows:

[x]-[name of linear component]-[name of macrocycle$_1$]-[name of macrocycle$_2$]-rotaxane

wherein the integer *x* represents the total number of linear and macrocyclic components, and macrocycle$_1$, macrocycle$_2$, macrocycle$_3$, etc. represent structurally identical or different macrocyclic components.

Schill's nomenclature was thus designed for rotaxanes of Types D-1.1 or D-1.2 (Table 1), or Type M-1 (Table 2).

Schill's nomenclature principles have been used as the basis for macromolecular rotaxane nomenclature [26, 27]. Although Schill did not extend his nomenclature principles to macromolecular rotaxanes, they can be named by a logical extension of his nomenclature principles for discrete rotaxanes.

In 2000, the International Union of Pure and Applied Chemistry (IUPAC) initiated a project to develop systematic nomenclature for macromolecular rotaxanes [28]. A corresponding project was begun in 2001 for the development of systematic nomenclature for discrete rotaxanes [29]. Work is still in progress on both of these projects.

As a broad principle, IUPAC proposes to name both discrete and macromolecular rotaxanes according to the generic format:

[p]-[x]-[name of "linear" component]-*rotaxa*-[name of macrocycle$_1$]-[name of macrocycle$_2$]-...

wherein the [x] represents the total number of linear and macrocyclic components, and macrocycle$_1$, macrocycle$_2$, macrocycle$_3$, etc. represent structurally identical or different macrocyclic components. [p] is an additional prefix that will probably be needed for complex rotaxanes, such as those that are H-, X-, or Y-shaped, and also for information about how asymmetric macrocycles, such as the cyclodextrins, are oriented, both with respect to each other and to the structural features of the "linear" component.

The name format will include:

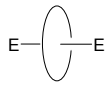
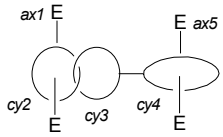
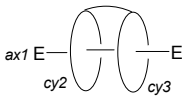
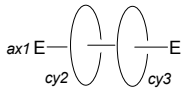
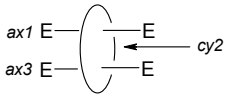
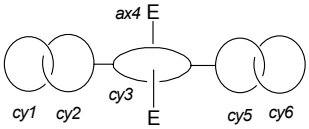
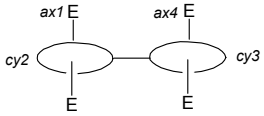
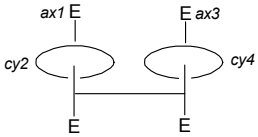
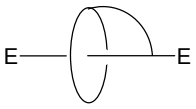
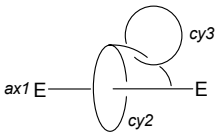
- A recommendation that name(s) of linear component(s) should precede name(s) of macrocyclic component(s). While there is no precedence for assigning seniority to linear components over macrocyclic components, adherence to this principle will follow Schill's original nomenclature principle, and will add consistency – wherever possible – to names generated for both discrete and macromolecular rotaxanes.

- Introduction of a new IUPAC connective, -*rotaxa*-, which is in keeping with use of other connectives in IUPAC nomenclature (30) and will serve to separate the names of the "linear" component(s) from the macrocyclic component(s).*

  *The only exception currently anticipated to use of -*rotaxa*- as a connective is rotaxanes of Type M-6 (see Table 2), which are formed from one component – a polymerizable monomer containing an attached macrocyclic moiety; for these, use of *rotaxa*- as a prefix will be recommended, since there is no logical place within a systematic name into which to insert -*rotaxa*- as a connective.

In May 2000, Vögtle and co-workers [9] proposed a generic nomenclature system in which Schill's prefix was extended to include information about mechanical (mec) or covalent (cov) linkages between the components of a rotaxane. Their nomenclature proposals are most easily understood by studying selected types, which are listed in Table 3 and reproduced with permission.

Table 3. Selected Examples of Rotaxanes and Catrotaxanes [9]

Type[a]	Generic Structure	Generic Nomenclature Style
1 (2)		[2]rotaxane
2 (4)		[3catrot$^{ax1\text{mec}cy2,\ cy2\text{mec}cy3}$-(*cy3*cov*cy4*)-2rot$^{cy4\text{mec}ax5}$]axane
3 (7)		[3]rotaxane, "bonnane" [3$^{ax1\text{mec}cy2,\ ax1\text{mec}cy3,\ cy2\text{cov}cy3}$]rotaxane
4 (8)		[3]rotaxane [3$^{ax1\text{mec}cy2,\ ax1\text{mec}cy3}$]rotaxane
5 (9)		[3]rotaxane [3$^{ax1\text{mec}cy2,\ cy2\text{mec}ax3}$]rotaxane
6 (10)		[2cat-2rot-2cat]enane [2cat$^{cy1\text{mec}cy2}$-(*cy2*cov*cy3*)-2rot$^{\text{cy3mecax4}}$-(*cy3*cov*cy5*)-2cat$^{cy5\text{mec}cy6}$]enane
7 (11)		[2-2]rotaxane [2$^{ax1\text{mec}cy2}$-(*cy2*cov*cy3*)-$^{cy3\text{mec}ax4}$]rotaxane
8 (13)		[2-2]rotaxane [2$^{ax1\text{mec}cy2}$-(*ax1*cov*ax3*)-2$^{ax3\text{mec}cy4}$]rotaxane
9 (14)		[2$^{1\text{cov}2}$]rotaxane
10 (15)		[3]rotaxane [3$^{ax1\text{mec}cy2,\ ax1\text{cov}cy2,\ (ax1\text{cov}cy2)\text{mec}cy3}$]rotaxane

[a]Because this Macromolecular Nomenclature Note is limited to rotaxanes and catrotaxanes, the numbers in this Table do not correspond with the numbers in Table 1 of [9]; the parenthesized numbers are those in Table 1 of [9].

Conclusions

1. Schill's original nomenclature system is a good basis from which to develop a more comprehensive nomenclature system.

2. The nomenclature system proposed by Vögtle and co-workers [9] is a useful tool for generation of prefixes that are needed to cite the mechanical and covalent linkages between the components in complex rotaxanes and catrotaxanes, but – as the authors themselves imply – creation of a complete systematic nomenclature system for these substances will be a formidable task indeed.

References

1. Frisch, H. L.; Wasserman, E. "Chemical Topology". *J. Amer. Chem. Soc.* **83**, 3789-3795 (1961).
2. Harrison, I. T.; Harrison, S. "The Synthesis of a Stable Complex of a Macrocycle and a Threaded Chain". *J. Amer. Chem. Soc.* **89**, 5723-5724 (1967).
3. Schill, G.; Zöllenkopf, H. "Rotaxane"*. *Nachr. Chem. Tech.* **15**, 149 (1967). *Subject matter; the article is titleless.
4. Schill, G.; Zöllenkopf, H. "Rotaxan-Verbindingen, I". *Justus Liebigs Ann. Chem.* **721**, 53-74 (1969).
5. Gibson, H. W. "Rotaxanes" in *Large Ring Molecules* Semlyen, A. J., (Ed.), John Wiley and Sons, 1996, p.191.
6. Raymo, M.; Stoddart, J. F. "Organic Template-Directed Syntheses of Catenanes, Rotaxanes, and Knots" in *Molecular Catenanes, Rotaxanes and Knots* Sauvage, J.-P.; Dietrich-Buchecker, C., (Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany, 1999, 143-176.
7. Heim, C.; Udelhofen, D.; Vögtle, F. "Amide-Based Catenanes, Rotaxanes and Pretzelanes" in *Molecular Catenanes, Rotaxanes and Knots* Sauvage, J.-P.; Dietrich-Buchecker, C., (Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany, 1999, 177-222.
8. Glink, P. T.; Schiavo, C.; Stoddart, J. F.; Williams, D. J. "The Genesis of a New Range of Interlocked Molecules". *Chem. Comm.* 1483-1490 (1996).
9. Safarowsky, O.; Windisch, B.; Mohry, A.; Vögtle, F. "Nomenclature for Catenanes, Rotaxanes, Molecular Knots, and Assemblies Derived from These Structural Elements". *J. Prakt. Chem.* **342**, 437-444 (2000).
10. Dünnwald, T.; Jäger, R.; Vögtle, F. "Chemistry with Rotaxanes. II. Synthesis of Rotaxane Assemblies". *Chem. Eur. J.* **3**, 2043-2051 (1997).
11. Jäger, R.; Händel, M.; Harren, J.; Rissanen, K.; Vögtle, F. "Chemistry with Rotaxanes. Intra- and Intermolecularly Covalently Linked Rotaxanes". *Liebigs Ann.* 1201-1207 (1996).
12. Panova, I. G.; Topchieva, I. N. "Rotaxanes and Polyrotaxanes. Their Synthesis and the Supramolecular Devices Based on Them". *Russian Chem. Rev.* **70**, 23-44 (2001).
13. Philp, D.; Stoddart, J. F. "Self-Assembly in Natural and Unnatural Systems". *Angew. Chem. Int. Ed. Engl.* **35**, 1154-1196 (1996).
14. Amabilino, D. B.; Stoddart, J. F. "Interlocked and Intertwined Structures and Superstructures". *Chem. Rev.* **95**, 2725-2828 (1995).
15. Amabilino, D. B.; Ashton, P. R.; B□lohradsky, M.; Raymo, F. M.; Stoddart, J. F. "The Self-Assembly of Branched [n]Rotaxanes – the First Step Towards Dendritic Rotaxanes". *J. Chem. Soc. Chem. Commun.* 751-754 (1995).
16. Ashton, P. R.; B□lohradsky, M.; Philp, D.; Spencer, N.; Stoddart, J. F. "The Self Assembly of [2]- and [3]-Rotaxanes by Slippage". *J. Chem. Soc. Chem. Commun.* 1274-1277 (1993).
17. Asakawa, M.; Ashton, P. R.; Iqbal, S.; Stoddart, J. F.; Tinker, N. D.; White, A. J. P.; Williams, D. J. "The Self-Assembly of Some Novel [2]Rotaxanes and their Alkali Metal Cation Complexation". *J. Chem. Soc. Chem. Commun.* 483-486 (1996).
18. Manka, J. S.; Lawrence, D. S. "Template-Driven Self-Assembly of a Porphyrin-Containing Supramolecular Complex". *J. Am. Chem. Soc.* 2440-2442 (1990).
19. Reuter, C.; Mohry, A.; Sobanski, A.; Vögtle, F. "[1]Rotaxanes and Pretzelanes: Synthesis, Chirality, and Absolute Configuration". *Chem. Eur. J.* **6**, 1674-1682 (2000).
20. Jäger, R. Ph.D. Thesis, Universität Bonn, 1997.
21. Jäger, R.; Vögtle, F. "A New Synthetic Strategy towards Molecules with Mechanical Bonds: Nonionic Template Synthesis of Amide-Linked Catenanes and Rotaxanes". *Angew. Chem.* **109**, 965-980 (1997); *Angew. Chem. Int. Ed. Engl.* 36, 930-944 (1997).
22. Amabilino, D. B.; Ashton, P. R.; Bravo, J. A.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. "Molecular Meccano, 52. Template-Directed Synthesis of a Rotacatenane". *Eur. J. Org. Chem.* 1295-1302 (1999).
23. Gong, C.; Gibson, H. W. "Polyrotaxanes – Syntheses and Properties" in *Molecular Catenanes, Rotaxanes and Knots* Sauvage, J.-P.; Dietrich-Buchecker, C., (Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany, 1999, 277-321.
24. Werts, M. P. L. "Mechanically Linked Oligorotaxanes". Ph.D. Thesis, University of Groningen, Netherlands, 2001. ISBN 90-367-1425-7.
25. Schill, G. "Nomenclature of Catenanes and Rotaxanes" in *Catenanes, Rotaxanes, and Knots*, Academic Press, New York (1971).
26. Lipatov, Yu. S.; Lipatova, T. E.; Kosyanchuk, L. F. "Synthesis and Structure of Macromolecular Topological Compounds". *Adv. Polym. Sci.* **88**, 49-76 (1989).
27. Sun, X.; Amabilino, D. B.; Ashton, P. R.; Parson, I. W.; Stoddart, J. F.; Tolley, M. S. "Towards the Self-Assembly of Polyrotaxanes". *Macromol. Symp.* **77**, 191-207 (1994).
28. IUPAC Project No. 2002-037-1-800 (formerly Project No. 35/2000). Task leader, E. S. Wilks.
29. IUPAC Project No. 2002-007-1-800. Task leader, E. S. Wilks.
30. IUPAC. "Source-Based Nomenclature for Copolymers (Recommendations 1985)". *Pure Appl. Chem.* **57**, 1427-1440 (1985); reprinted as Chapter 7 in *Compendium of Macromolecular Nomenclature* (The Purple Book), W. V. Metanomski, (Ed.), Blackwell Scientific Publications, Oxford, 1991.

*Mailing address: 113 Meriden Drive, Canterbury Hills, Hockessin, DE 19707. E-mail address: tedwilks@juno.com