

Nomenclature for Catenanes, Rotaxanes, Molecular Knots, and Assemblies Derived from These Structural Elements

O. Safarowsky, B. Windisch, A. Mohry, and F. Vögtle*

Bonn, Kekulé-Institut für Organische Chemie der Universität

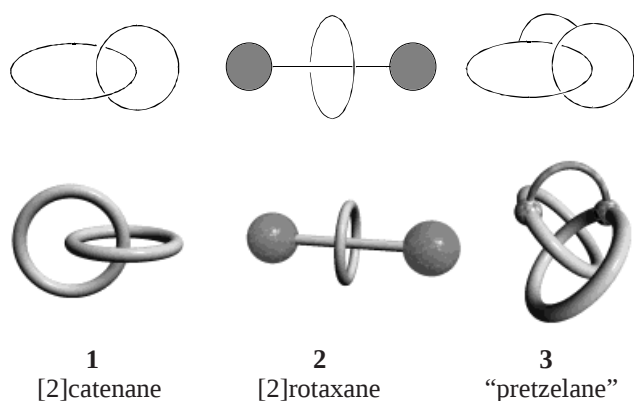
Received May 3rd, 2000

Keywords: Catenanes, Rotaxanes, Interlocked systems, Knots, Mechanical bonds

Abstract. We introduce a systematic nomenclature for mechanically linked molecules – such as catenanes, rotaxanes, and assemblies derived from these structural elements – which comes up to the increasing complexity of already synthesized interlocked molecules and the ones to be expected in future. Like in the naming of other substance classes (polycycles,

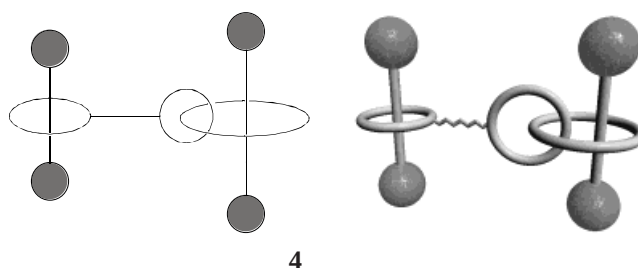
phanes, crown compounds, podands, dendrimers) we attach importance to the fact, that certain units in the name, *e.g.* expressions in brackets, quickly convey an idea of the molecular architecture. Furthermore, this modular nomenclature reveals as many analogies to the IUPAC nomenclature as possible.

The IUPAC notation system does not provide a nomenclature for interlocked, mechanically linked molecules beyond very simple catenanes and rotaxanes [1]. Whereas simple catenanes and rotaxanes like **1** and **2** can be named explicitly as [2]catenane and [2]rotaxane according to IUPAC, [1] one already brakes new ground with the naming of additionally bridged types of compounds – such as “pretzelanes” **3** [2] which are easily accessible nowadays.



Although it is likely to obtain concrete names of more complicated mechanically linked molecules, like for example “catrotaxane” **4**, basing on the IUPAC system by establishing additional rules and determinations of priorities, a problem occurs similar to that for phanes, crown ethers, podands, and dendrimers: The names become too abstract, long and difficult. Thus, they are not suggestive of the total structure or at least of a “cartoon” of the molecule only by flying over the name, and it takes more time to recognize the linking pattern or to draw a graph [2b]. Experience shows, however, that such nomenclatures are only adopted and frequent-

ly used by chemists, if they are constructed from easily comprehensible characteristic parts, basing on immediately convincing rules. Like in the former cases mentioned above a new nomenclature seems to be sensible, which contains – analogously to the bicyclo nomenclature of *von Baeyer* and to the crown compounds, cyclophanes [3], podands [4], and dendrimers [5] – a characteristic part of the name, for example in brackets, so that it indicates the “overall structure” and its most important features, such as *e.g.* the type, number, and sequence of the mechanical bonds particularly relevant in this case.



Hence, it is easy to understand that new mechanically linked molecular architectures have been given trivial names for years, as illustrated by the expressions “catenanes”, “rotaxanes”, “knotanes” [6], “pretzelanes” [7], “daisy rotaxanes” [8], “catrotanes” [9a], “rotacatenanes” [9b], “bonnanes” [10]. Without further rules and a hierarchy of rules it will be even more difficult to name more complicated catenanes and rotaxanes like **4**, built up from several rings and assemblies of covalently and mechanically linked units [11].

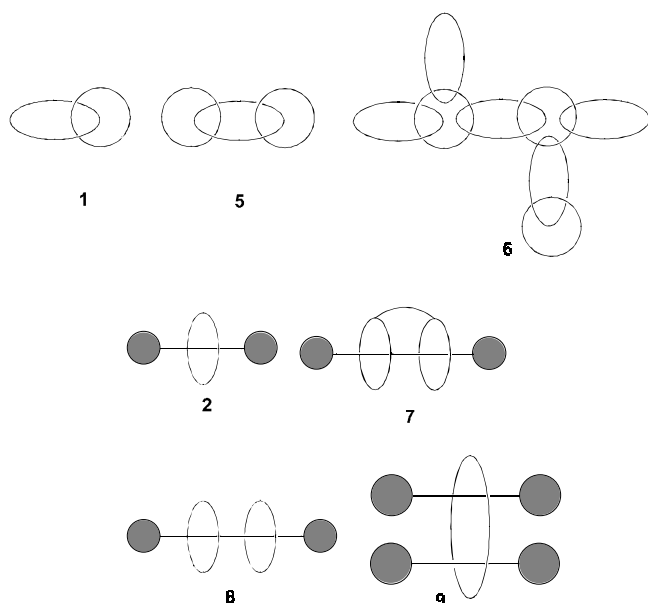
In the following the new nomenclature is explained with rules and formula examples. All examples mentioned in the text are also listed in table 1.

Rules and Examples

Rule 1: In an [n]catenane (and -rotaxane or -catrotaxane, respectively [12]) n describes the number of molecule parts (wheels, axles) participating in mechanical bonding.

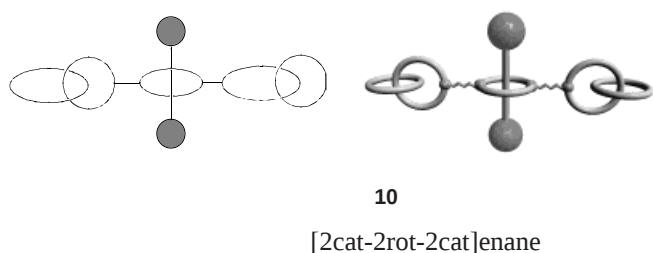
This rule is in accordance with the practice hitherto [1e].

The number of the molecule fragments which are not covalently, thus mechanically linked, are given in square brackets, e.g. **1** is named as a [2]catenane, **5** as a [3]catenane, and **6** as an [8]catenane, **2** as a [2]rotaxane, **7**, **8** and **9** as [3]rotaxanes.



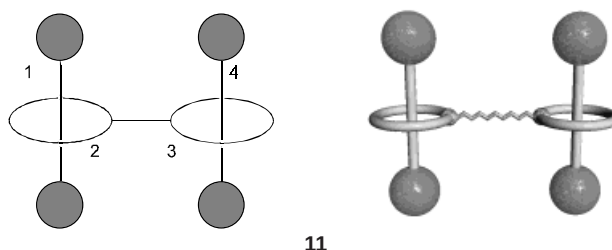
Hence, the names of more “simple” catenanes and rotaxanes which have been in use for many years – as for example **1** and **5** – maintain [1c,d, 2c].

Rule 2: The substances **4** and **10** containing both catenane and rotaxane elements are generally referred to as [n]catrotaxanes [9] (hitherto also named as catrotanes [9a] or rotacatenanes [9b]), **10** e.g. as a [2cat-2rot-2cat]enane. Each covalent bond is represented by a hyphen between the linked elements.

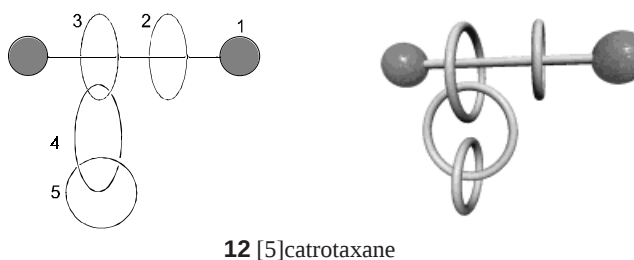
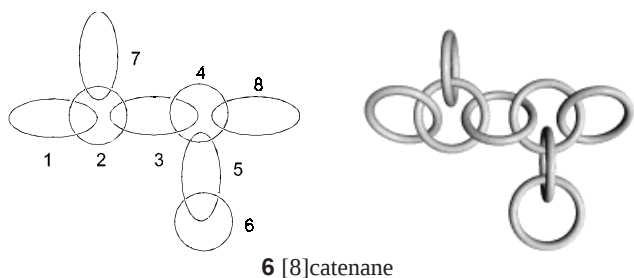
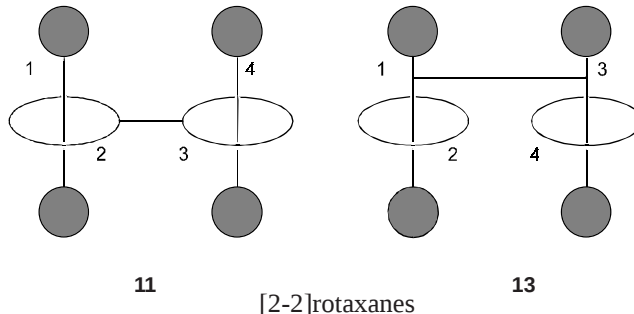


In this way shorter family names will result, which are useful to combine compounds with similar structural elements.

Rule 3: For a standardized naming of complex molecules it appears sensible to proceed analogously to the IUPAC nomenclature of alkanes and include mechanical bonds of highest priority into a main chain:



Rule 4: If one or more structural elements connected by a covalent bond like in rotaxanes **7** (table 1) and **11**, then it must be stated, which molecular elements are linked by covalent bonding and in which way. For this, the numbering of the building blocks (wheel, axle) is required.



Thus, the building units of the main chain are not written as indices, but as normal numbers. The covalent bond is indicated symbolically as a hyphen between the numbers (as already mentioned in rule 2).

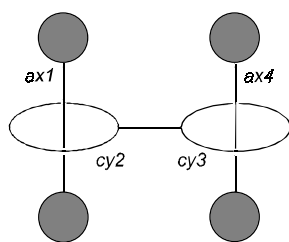
Rule 5: a) The longest chain has the chain including the maximum number of mechanical and covalent bonds (in this order).

b) The axle is prior to the cycle (wheel) in the case that both is equally possible.

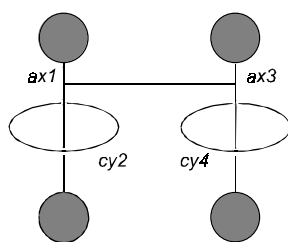
c) After that mechanically or covalently linked side chains are numbered.

d) Groups covalently bonded to the main chain (including bridges and (host) cycles) count as substituents.

Rule 6: In front of the cycle name a *cy* (for cycle) is written in *italics*, in front of the axle name an *italic ax* (for axle). This is only necessary for rotaxanes and catrotaxanes.



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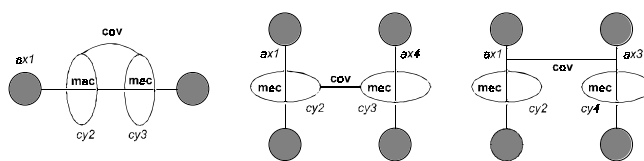
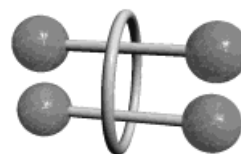
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Molecular fragments are numbered similar to the alkanes without taking into account the bridging of the units. One starts at the fragment at the beginning of a chain-like molecule, regardless of whether it is covalently or mechanically linked. Only the priority of the beginning and of the end is important like for alkanes.

Rule 7: a) Beyond the priorities explained above (only valid for the starting point of the molecule) the following priorities are established: axle units before macrocycles; otherwise the order once determined is valid.

b) The linked fragments are listed in numeral pairs which are separated by “mec” for mechanical bonds in catenanes and rotaxanes and by “cov” for covalent bonds. c) In the preceding square brackets roughly describing the molecular structure, the connectivity within the supramolecular subunit is given in superscripts, the description of the structural elements connected (*ax* or *cy*) and their numbers in superscript *italics*. The connectivity between two subunits is written in normal size and put in round brackets.

Rule 8: In the case of several mechanically linked building blocks (wheel, axle) in succession, the first and the last mechanical element are connected by *n* cat (rule

7 [3^{ax1meccy2,ax1meccy3,cy2covcy3}]rotaxane11 [2^{ax1meccy2-(cy2covcy3)-2cy3mecax4}]rotaxane13 [2^{ax1meccy2-(ax1covax3)-2ax3meccy4}]rotaxane

9

[3^{ax1meccy2,cy2mecax3}]rotaxane

5

[3^{n1mec3}]catenane

8

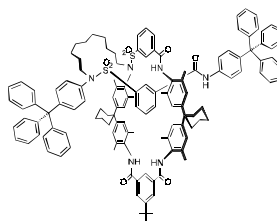
[3^{n1mec3}]rotaxane

4.1) and *n* rot (rule 4.2), respectively, where *n* is derived from the IUPAC *neo*. (Please note that *n* has a slightly different meaning for catenanes and rotaxanes).

This is only valid for linear assemblies (see 5 and 8) and macrocyclic polycatenanes [13].

Employing the rules 1–9 the formula names and family names can be derived for all molecular structures mentioned above (see table 1).

Rule 9: Covalent linkings – like in the bridged rotaxane 14 below – are positioned at the beginning of the name joint by the binding sites. The exact position of a covalent bridge follows from the notation of the whole name.



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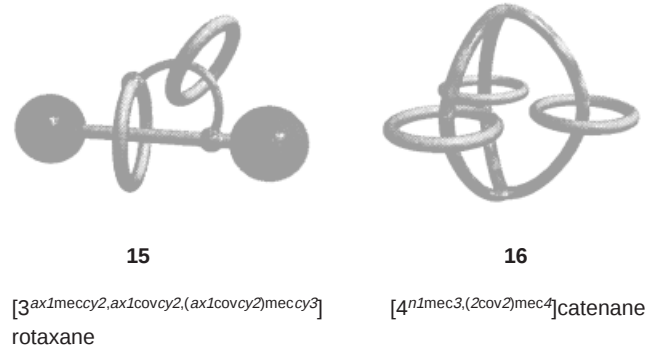
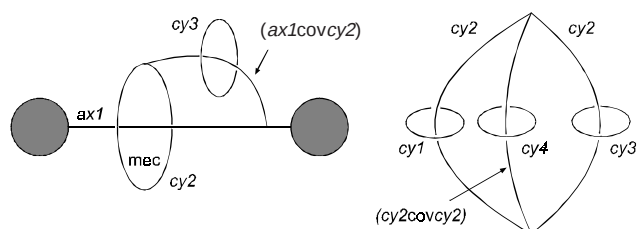
[2^{1cov2,1mec2}][N',7'-[1,10-decamethylene]][N-[4-(triphenylmethyl)phenyl]-3-{[4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide]-[29'-*tert*-butyl-5',17',23',35',38',40',43',45'-octamethyl-8',8',14',26',32'-pentaoxo-

Table 1 Names of molecules 1–16

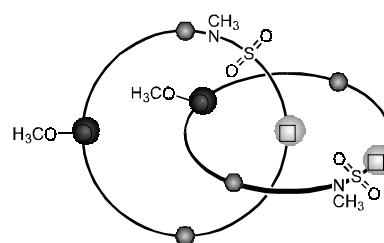
No.	Names for all formulae according to the rules proposed above	short characterization of principle connections (family name)
1	[2]catenane	
2	[2]rotaxane	
3	[2 ^{1cov2}]catenane	[2]catenane, “pretzelane” [2c]
4	[3catrot ^{ax1mecy2, cy2mecy3} -(cy3covcy4)-2cot ^{cy4mecax5}]axane	[3catrot-2rot]axane
5	[3 ^{n1mec3}]catenane	[3]catenane
6	[8 ^{n1mec6,2mec7,4mec8}]catenane	[8]catenane
7	[3 ^{1cov2}]rotaxane	[3]rotaxane, “bonnane”
8	[3 ^{ax1mecy2, ax1mecy3}]rotaxane	[3]rotaxane
9	[3 ^{ax1mecy2, cy2mecax3}]rotaxane	[3]Rotaxane
10	[2cat ^{cy1mecy2} -(cy2covcy3)-2rot ^{cy3mecax4} -(cy3covcy5)-2cat ^{cy5mecy6}]enane	[2cat-2rot-2cat]enane
11	[2 ^{ax1mecy2} -(cy2covcy3)-2 ^{cy3mecax4}]rotaxane	[2-2]rotaxane
12	[5 ^{ax1mecy2, ax1mecy3, cy3mecy4, cy4mecy5}]catrotaxane	[5]catrotaxane
13	[2 ^{ax1mecy2} -(ax1covax4)-2 ^{cy3mecax4}]rotaxane	[2-2]rotaxane
14	[2 ^{1cov2}]rotaxane	[2]rotaxane (formerly [1]rotaxane [2c])
15	[3rot ^{ax1mecy2, ax1covcy2, (ax1covcy2)mecy3}]axane	[3]rotaxane
16	[4 ^{n1mec3, (2cov2)mec4}]catenane	[4]catenane

dispiro[cyclohexane-1,2'-[7,15,25,33]tetraaza-[8]-thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}] hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane]]rotaxane [15]

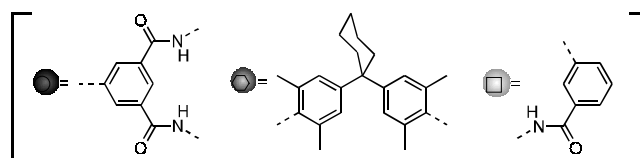
Rule 10: A covalent bridge can be indicated as a molecule part by (x1 cov x2), without including it in the numbering. Mechanical bonds can be determined by giving the position, similar as for covalent bonds. The covalent bridge can be additionally connected to other parts of the molecule by “mec” or “cov” like in 4.



Rule 11: Analogous to the IUPAC (and phane) nomenclature, the explicit numbering of axles and macrocycles follows.



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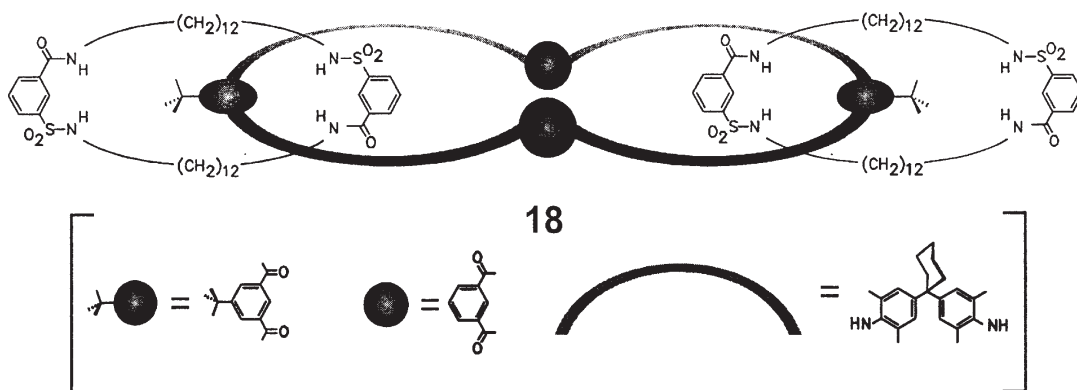


Rule 12: For symmetric catenanes with wheels of the same kind, *in*-orientated cycles have priority over *out*-orientated ones [16].

[2](*S*)-*in*-[29'-methoxy-5',7',17',23',35',38',40',43',45'-nonamethyl-8',8',14',26',32'pentaaxodispiro[cyclohexane-1,2'[7',15',25',33']tetraaza-[8]-thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3',5',9',11',13'(39),16',18',21',23',27',29',31'(44'),34',36',37',40',42',45']octadecaene-20',1''-cyclohexane]]-*out*-[29'-methoxy-5',7',17',23',35',38',40',43',45'-nonamethyl-8',8',14',26',32'-pentaaxodispiro[cyclohexane-1,2'-[7,15,25,33]tetraaza-[8]-thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(39),16,18,21,23,27,29,31(44),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane]]catenane

Rule 13: The ending of the name is based upon the cat] or rot] listed last before the square bracket ends and is called -enane and -axane, respectively (see table 1).

Rule 14: In the explicit molecule name the number of each cycle and each axle, respectively, is given in curved brackets and proceeds the name of the corresponding cycle and axle. (For reasons of clarity the corresponding numbers are given in bold in the example below.)

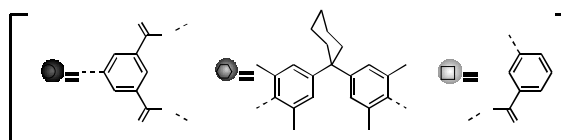
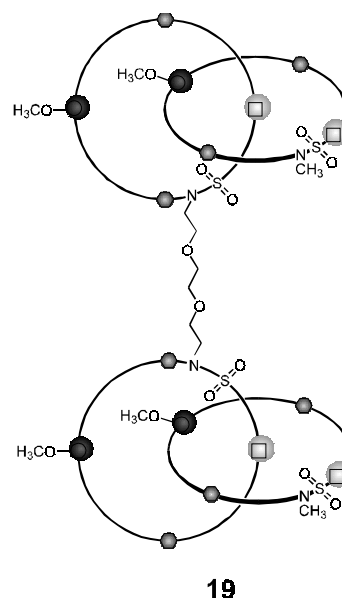


n-[3]{2}[11",47"-di-*tert*-butyl-5",17",23",35",41",53",59",71",74",76",79",81",84",86",89",91"-hexadecamethyl-8",14",26",32",44",50",62",68"-octaoxotetraspiro[dicyclohexane-1,2"-1',20"-[7,15,25,33,43,51,61,69]octaazatridecacyclo[68.2.2.2^{3,6}.2^{16,19}.2^{21,24}.2^{34,37}.2^{39,42}.2^{52,55}.2^{57,60}.1^{9,13}.1^{27,31}.1^{45,49}.1^{63,67}]dononaconta[3,5,9,11,13(90),16,18,21,23,27,29,31(85),34,36,39,41,45,47,49(80),52,54,57,59,63,65,67(75),70,72,73,76,81,83,86,88,91]hexatriacontaene-1"',38"-1''',56"-dicyclohexane]{1,3}bis[2,17,17,23,38,38-hexaoxo-17,38-dithia-3,16,24,37-tetraazatricyclo[37.3.1.1^{18,22}]tetratetraconta-1(43),18,20,22(44),39,41-hexaene]catenane.

Rule 15: The specification of the supramolecular stereochemistry (topological chirality, cycloenantio-merism) proceeds the whole name [17]. The one of the euclidian chirality is added to the name of the corresponding molecule part.

[2^{1mec2}-(2cov3)-2^{3mec4}][<{cy2,7'}-1, ω -1,2-bis(ethoxy)ethane-{cy3,7'}>(R)-{1}-in-[29'-methoxy-5',7',17',23',35',38',40',43',45'-nonamethyl-8',8',14',26',32'-pentaaxodispiro[cyclohexane-1,2'-[7,15,25,33]tetraaza-[8]-thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(39),16,18,21,23,27,29,31(44),34,36,37,40,42,45]octadecaene-20',1"-cyclohexane]]-{2}-out-[29'-methoxy-5',17',23',35',38',40',43',45'-octamethyl-8',8',14',26',32'-pentaaxodispiro[cyclohexane-1,2'-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(39),16,18,21,23,27,29,31(44),34,36,37,40,42,45]octadecaene-20',1"-cyclohexane]]-(S)-{3}-out-[29'-methoxy-5',17',23',35',38',40',43',45'-octamethyl-8',8',14',26',32'-pentaaxodispiro[cyclohexane-1,2'-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(39),16,18,21,23,27,29,31(44),34,36,

37,40,42,45]octadecaene-20',1"-cyclohexane]]-{4}-in-[29'-methoxy-5',7',17',23',35',38',40',43',45'-nonamethyl-8',8',14',26',32'-pentaaxodispiro[cyclohexane-1,2'-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(39),16,18,



21,23,27,29,31(44),34,36,37,40,42,45]octadecaene-20',1"-cyclohexane]]catenane.

Rule 16: As in the IUPAC-nomenclature, indices, connectivity, etc. can be omitted for reasons of simplification, if this does not restrict the naming or the understanding of the formula.

Knotanes: Molecular Knot Compounds

Knot compounds, which have already been mathemati-

cally systematized [18], are dealt with in the following, although they are experimentally less known than catenanes and rotaxanes [1e, 6]. The application of rules from the set of rules above on molecular knot structures ("knotanes" [6]) is explained below.

The naming of knot-like molecular topologies requires a description corresponding to the knot table [18]. The knot graphs defined in this table present all possible monocyclic knots, which are conceivable. To achieve a chemically sensible nomenclature based on this graph, the following steps are necessary:

Rule 17: According to Tait's method the areas arising from overlaps are labeled [18]. The peripheral areas are hatched in such a manner that two hatched areas only meet at crossings, but do not possess any joint edge.

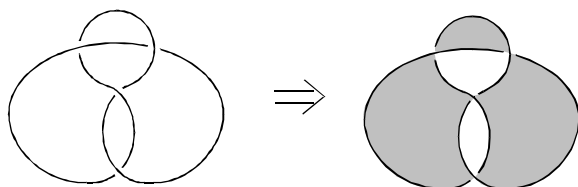
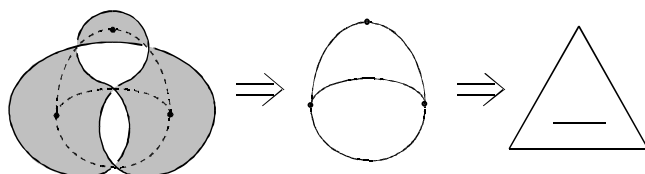


Fig. 1 Division of the nodal area

Rule 18: The centers of two hatched areas which have a joint crossing are connected by a line which goes through the crossing site between these two areas. By looking at these new connecting lines and slightly distorting them a description results which is analogous to a standard molecular drawing. If two centers are connected by two different lines, i.e. if they have two joint crossings, this is equivalent to a double bond. The molecular sketch is named according to IUPAC rules. The total number of bonds proceeds the name, as it does for catenanes and rotaxanes:



[4]cyclopropane knotane

Fig. 2 Transfer of the knot depiction into a 'molecular graph' [19]

Rule 19: The resulting molecular graph is turned in such a way that the 'bond' of highest order points to the top. In case that there are more than one 'bond' of the same higher order, the graph is turned in such a way that the higher order bonds follow each other as close as possible in a clockwise manner. If there is no 'bond' of highest order, a corner of the polygon is chosen to point to the top (they are all equal). The knot description is turned

correspondingly. Then the crossings are numbered starting at the top. If there is no top, it starts at the top left position. First, all the crossings on the 'knot periphery' are numbered clockwise followed by the ones in the inside of the knot which are also numbered clockwise. These numbers are assigned to the crossings in the knot depiction and written to the bond centers in the molecular graph.

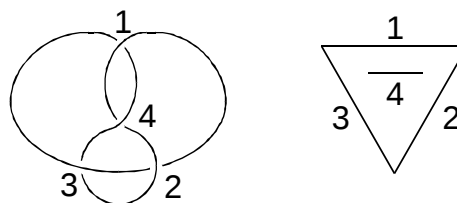


Fig. 3 Numbering of the sites of crossing in the nodal graph

Rule 20: The sense of crossing is labeled by 'p' or 'm' according to definition. Then starting from number 1 one follows the knot graph in the direction in which smaller numbers appear first. The sequence of the crossings and their sense is determined. Crossing met a second time are only characterized by their number. The sequence is denoted in superscripts and added to the total number of bonds in the name of the molecule.

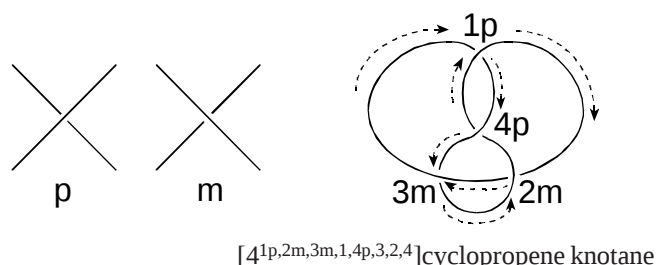
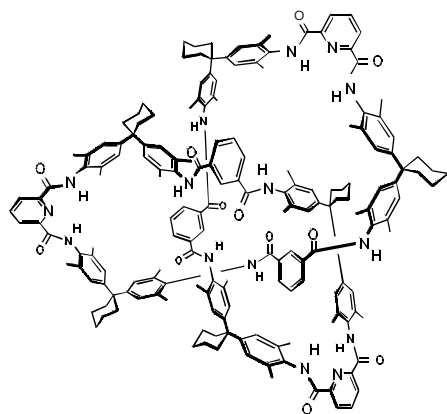


Fig. 4 Numbering of the crossing sites

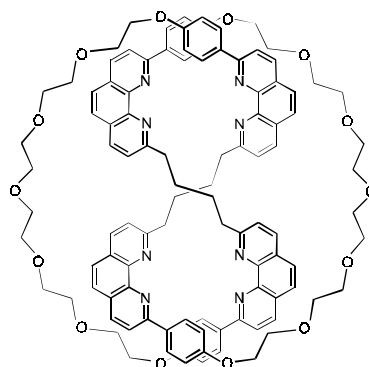
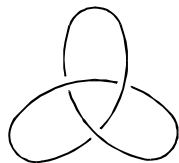
Rule 22: The IUPAC name of the corresponding non-interlocked macrocycle is determined and the total name finished with '-knotane'.

These rules are illustrated by the following examples.

20: [3^{1m,2p,3m,1,2,3}]cyclopropane[5^{'''},17^{'''},23^{'''},35^{'''},41^{'''},53^{'''},59^{'''},71^{'''},77^{'''},89^{'''},95^{'''},107^{'''},110^{'''},112^{'''},115^{'''},117^{'''},120^{'''},122^{'''},125^{'''},127^{'''},130^{'''},132^{'''},135^{'''},137^{'''}-tetracosamethyl-8^{'''},14^{'''},26^{'''},32^{'''},44^{'''},50^{'''},62^{'''},68^{'''},80^{'''},86^{'''},98^{'''},104^{'''}-dodecaoxohexaspiro[tricyclohexane-1,2^{'''}-1',20^{'''}-1',38^{'''}]-[7,15,25,33,43,51,61,69,79,87,97,105,116,126,136]pentadecaazanonadecacyclo[104.2.2.2^{3,6,2}16,19.2^{21,24,2}34,37.2^{39,42,2}52,55.2^{57,60,2}70,73.



20



21

$2^{75,78}.2^{88,91}.2^{93,96}.1^{9,13}.1^{27,31}.1^{45,49}.1^{63,67}.1^{81,85}.1^{99,103}$]octatriacontahectane[3,5,9,11,13(136),16,18,21,23,27(131),28,30,34,36,39,41,45,47,49(126),52,54,57,59,63,65,67(121),70,72,75,77,81,83,85(116),88,90,93,95,99,101,103(111),106,108,109,112,114,117,119,122,124,127,129,132,134,137]tetrapentacontane-1''',56'''-1''',74'''-1''',92'''-tricyclohexane]knotane.

21: [$3^{1m,2p,3m,1,2,3}$]cyclopropane[30,33,36,39,42,45,48,81,84,87,90,93,96,101-tetradeca-105,108,109,112,117,120,121,124-octaazaheptadecacyclo[98.2.2.42.11.416.25.453.62.46 7,76.226.29.277.80.05,106.08,107.019,110.022,111.056,118.059,119.070,122.073,123]hectahexacos[2(105),3,5(106),6,8(107),9,11(108),16(109),17,19(110),20,22(111),23,25(112),26(113),27,29(114),49(115),50,52(116),53(117),54,56(118),57,59(119),60,62(120),67(121),68,70(122),71,73(123),74,76(124),77(125),78,80(126)]tetracontane]knotane [1d,e].

This nomenclature proposal for knots can be combined with the rules for catenanes and rotaxanes described above, in order to name, for example, covalently bridged molecular knots.

Final Remarks

Novel architectures have always required new rules and proposals; one of the oldest examples is the 'bicyclo nomenclature' by von Baeyer.

The rules describe a special nomenclature for catenanes and rotaxanes. This seems to be justified nowadays thinking of the manifold possibilities of mechanical and covalent linkings and bridgings. Also in other fields more specialized molecule-specific nomenclatures have proven to be useful and have been successful, as the phane and the dendrimer nomenclature.

General proposals for a nomenclature, such as the nodal nomenclature [19], could – in principle – be applied to catenanes, rotaxanes, and knots as well (collapsing of each mechanical bonding unit into a point

and their subsequent breakdown). They usually have, however, the disadvantage of requiring many rules and complex explanations to be broadly applicable, and this makes them difficult to remember. Nomenclatures like the one introduced here, which might be less general, often benefit from the fact that the barrier of their application is lower, since architecture and name are analyzed less formalistically and the structure principle can be recognized more rapidly from characteristic parts of the name.

We thank Dr. Ch. Seel and Dr. C. Schalley for any advice and critical comments.

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Address for correspondence:
Prof. Dr. F. Vögtle
Kekulé-Institut für Organische Chemie und Biochemie
Universität Bonn
Gerhard-Domagk-Str. 1
D-53121 Bonn
Fax: Internat. code (0)228-735662
e-Mail: voegt@uni-bonn.de