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SUPRAMOLECULAR SYSTEMS INCORPORATING QUATERNARY AZAAROMATICS

Abstract: In the paper rotaxanes and catenanes incorporating quaternary azaaromatic moieties are presented, along with their synthetic procedures and properties.

Introduction

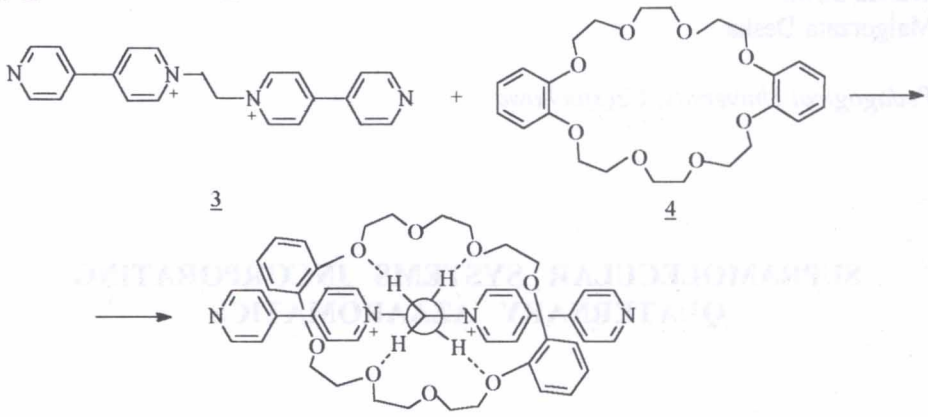
The area of supramolecular chemistry [1-5] is developing rapidly, systems containing rings threaded onto an acyclic fragment, i.e. rotaxanes [6] and compounds consisting of interlocked rings, i.e. catenanes [7] are of a special current interest. Synthetic approaches to these supramolecular assemblies involve their template-directed formation. Rotaxanes and catenanes are precursors to molecular machines, in which selected parts can be set in motion by a photochemical or electrochemical signal [8-10].

Quaternary azaaromatic salts are a topic of intense study due to their interesting properties [11-15]. These species are very often components of supramolecular systems, playing the role of a guest or of a host, i.e. they are incorporated into the thread [16], or they form the interlocked macrocycle [17-20].

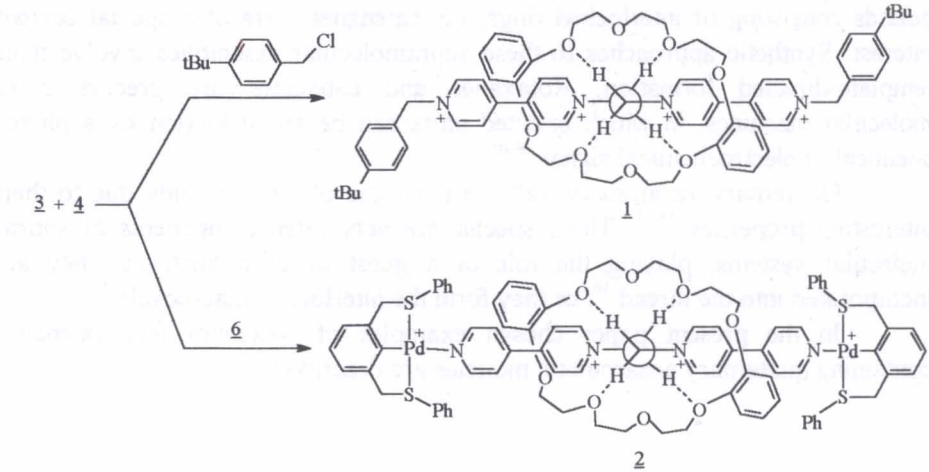
In the present paper chosen examples of rotaxanes and catenanes containing quaternary azaaromatic moieties are described.

Rotaxanes

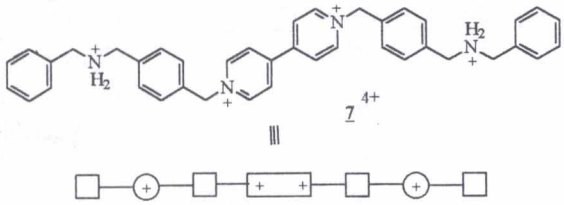
Rotaxanes in which the thread incorporates quaternary azaaromatics have been intensively studied [21,22], examples are rotaxanes 1 and 2. It was observed that the dication 3 threads through dibenzo-24-crown ether 4 to form [2]pseudorotaxane 5 .



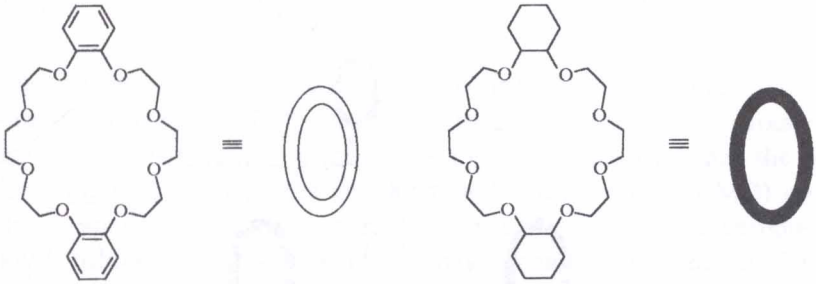
In order to obtain [2]rotaxanes 1 and 2 , stoppering by alkylation or coordination with a metal complex is necessary. In the following procedure the alkylation is performed with bulky t-butylbenzyl groups, and the coordination with $[Pd\{C_6H_3(PhSCH_2)_2\}(MeCN)]BF_4$ 6.



Acid - base controlled de/rethreading of pseudorotaxanes consisting of 7 $^{4+}$ as a thread and crown ethers 4 and 8 as macrocycles has been investigated[25].

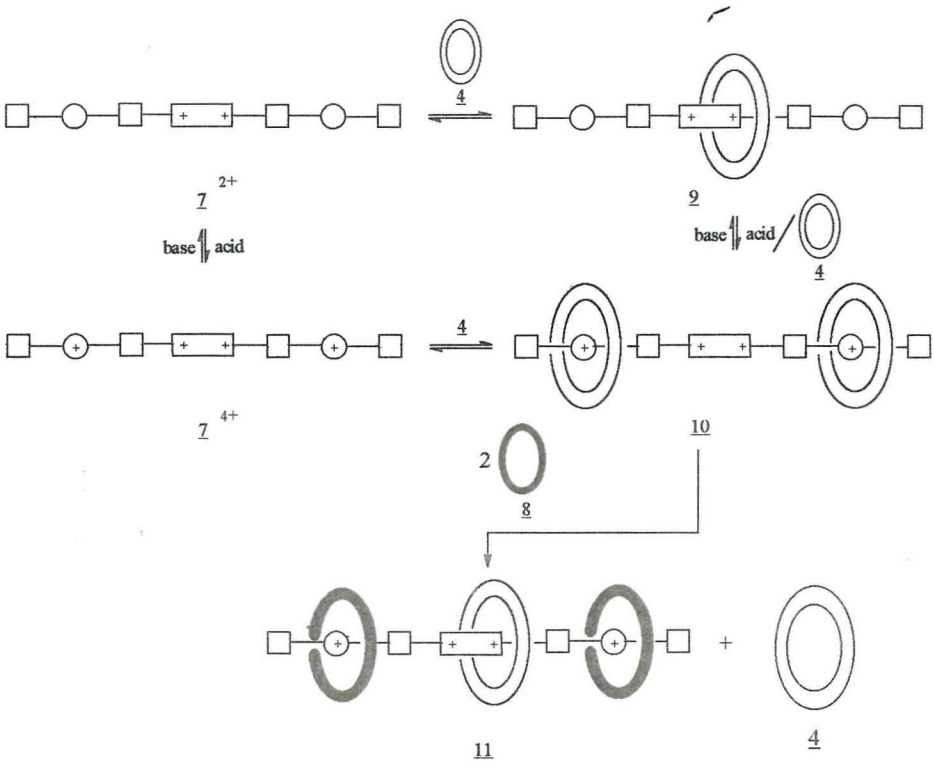


7 $^{4+}$



4 8

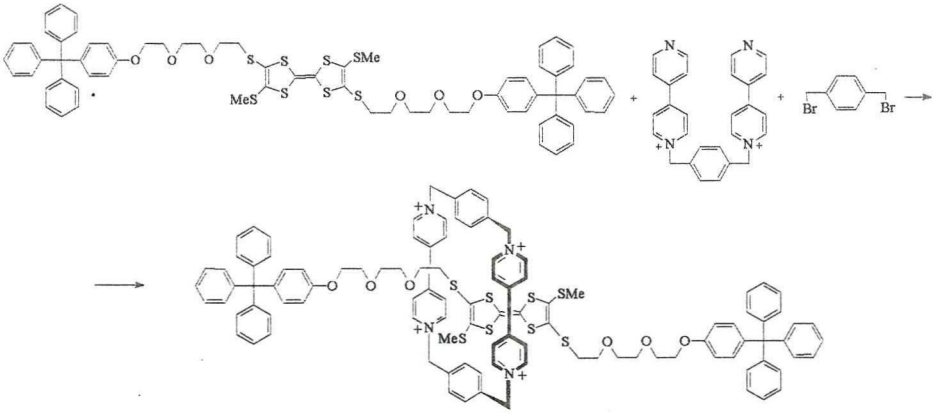
It was found that crown ethers self-assemble site-selectively with the 7 $^{4+}$. The conversion from one state to another is possible by means of external stimuli; the affinities of the bipyridinium unit can be suppressed by reduction, and those of NH_2^+ centers by deprotonation.



The reaction of 7 $^{2+}$ with 4 affords [2]pseudorotaxane 9, which by treatment with acid and the second molecule of 4 gives [3]pseudorotaxane 10. The conversion 9/ 10 is fully acid-base reversible.

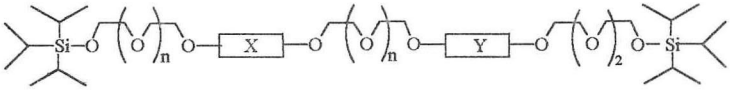
When 10 is treated with the surplus of 8, one molecule of 4 undergoes dethreading and [4]pseudorotaxane 11 is formed. The addition of acid to 7 $^{2+}$ results in its protonation affording 7 $^{4+}$ which reacts with 4 to give 10.

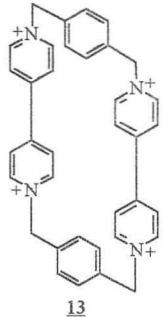
To rotaxanes in which the macrocycle has a character of quaternary azaaromatic belongs 12, obtained in a following procedure [26]:



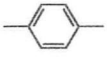
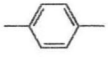
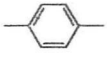
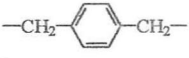
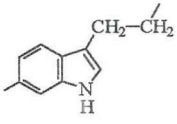
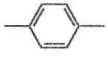
12

In rotaxanes the translational isomerism has been observed, i.e. the macrocycle can shuttle forth and back along the thread. For [2]rotaxanes consisting of cyclobis[paraquat]-*p*-phenylene 13 [27] as a macrocycle and the polyether chain 14a-c as a thread the computational study (MM and MD) on the translational isomerism has been made [27]. It was shown that the introduction of bulky substituents in the polyether chain enhances the energy barrier of shuttling.

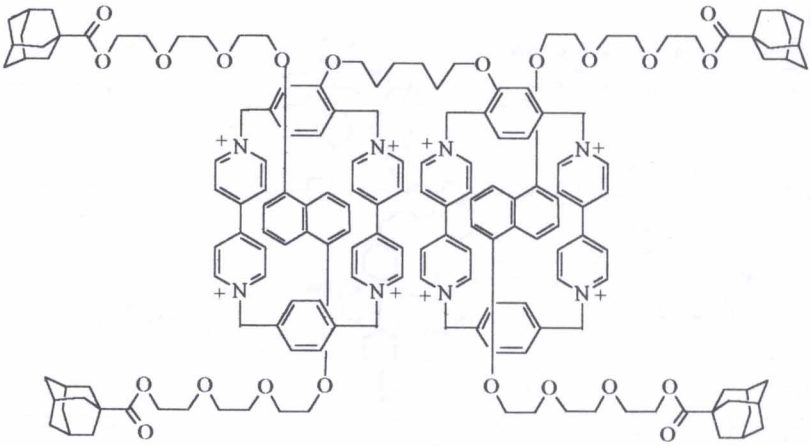




13

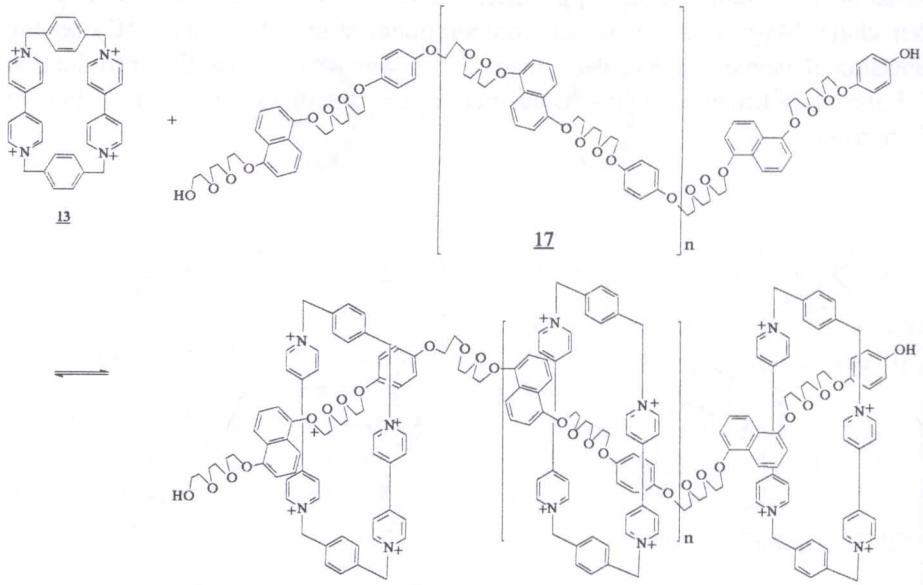
	n	X	Y
a	3		
14 b	5		
c	2		

An example of a bis[2]rotaxane is 15 [28].



15

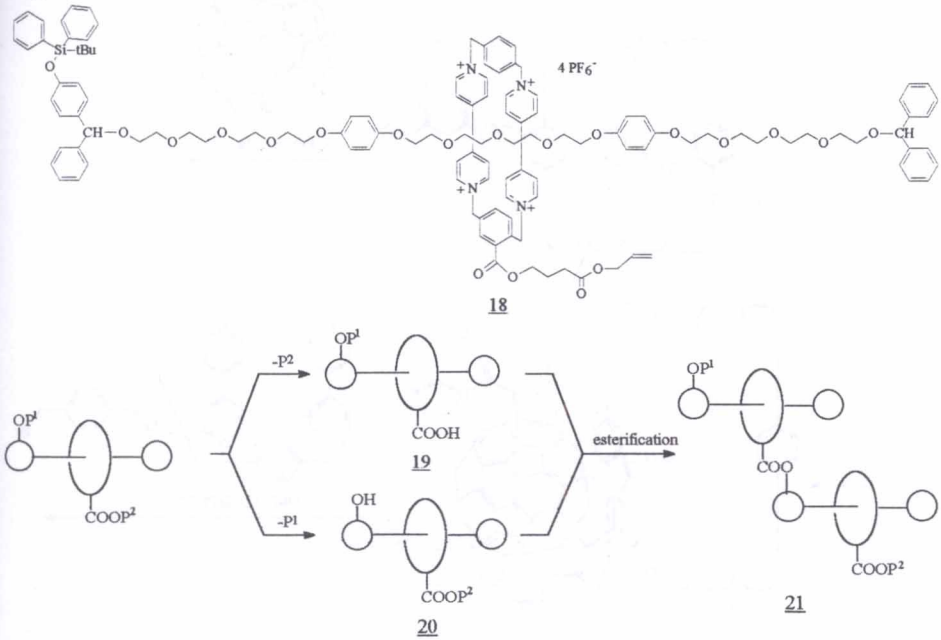
The formation of the pseudo[n]polyrotaxane 16 from cyclophane 13 and the polymer 17 is shown below [29].



13 17 16

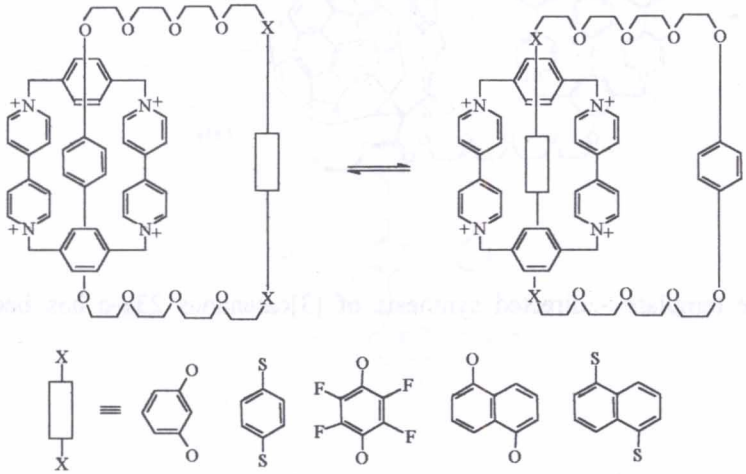
Mechanically linked polypseudorotaxanes [30-34] have been studied. In order to obtain mechanically linked polyrotaxanes, the bisprotected rotaxane 18 has been synthesized as a monomer used for the formation of a dimer by deprotection - coupling sequence [35].

The deprotection of the ester group in 18 leads to 19 bearing a free carboxyl, and the deprotection of the silyloxyphenyl affords 20 containing free phenol unit. The subsequent esterification of 19 with 20 yields the bisprotected dimer 21, which by the same deprotection - coupling procedure can give higher oligomers.

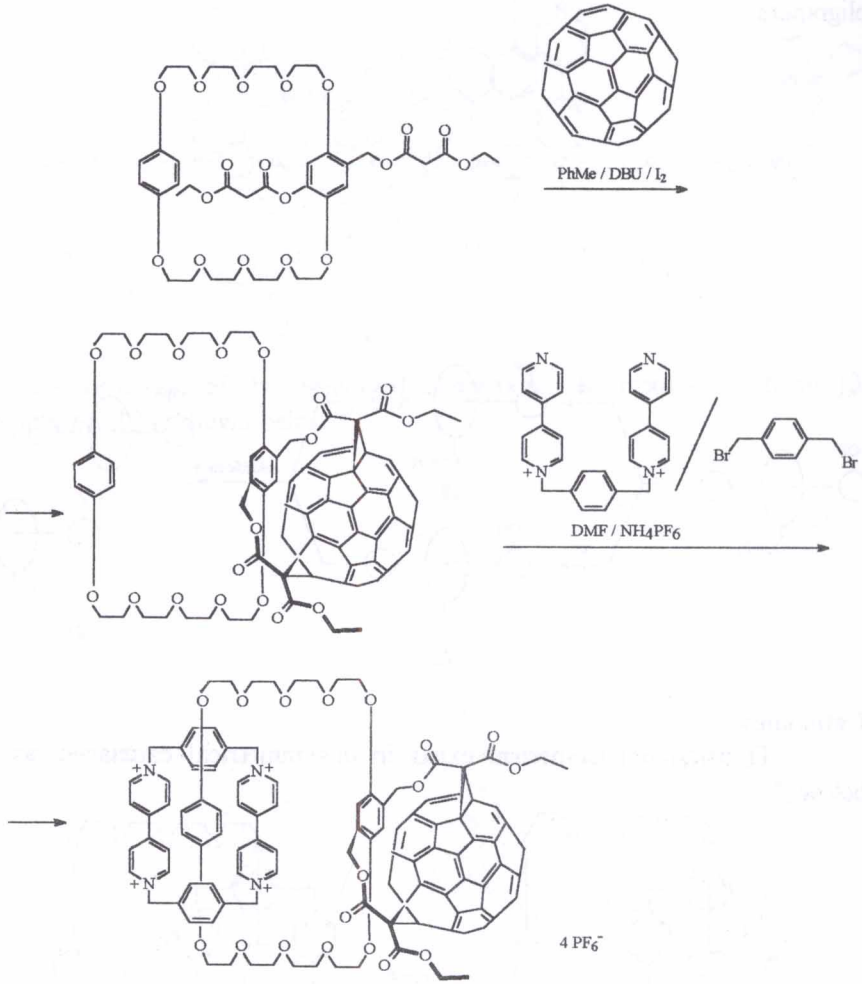


Catenanes

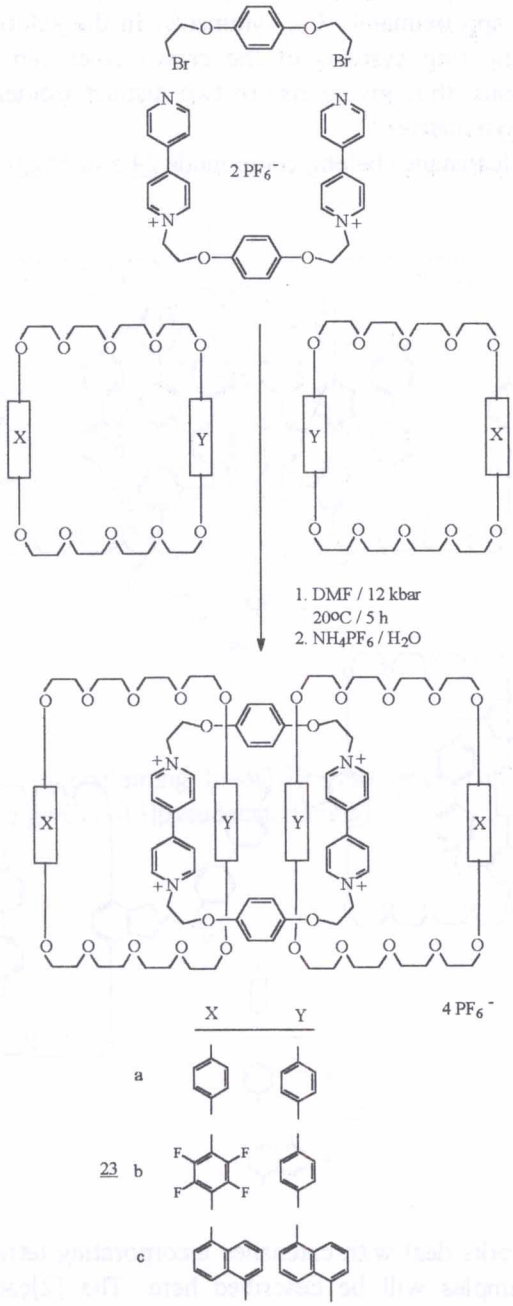
Translational isomerism exists in unsymmetrical catenanes, as shown below [36].



The fullerene - containing [2]catenane 22 has been synthesized by the following procedure [37].

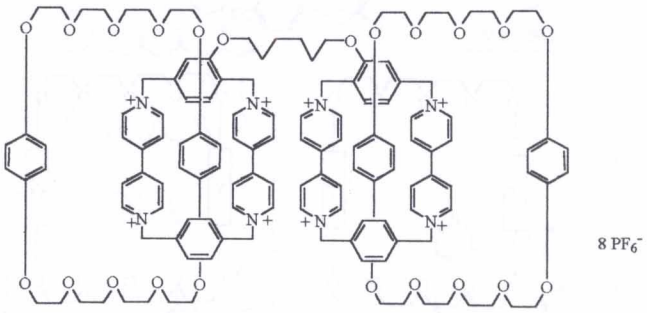


The template - directed synthesis of [3]catenanes 23a-c has been reported [38].

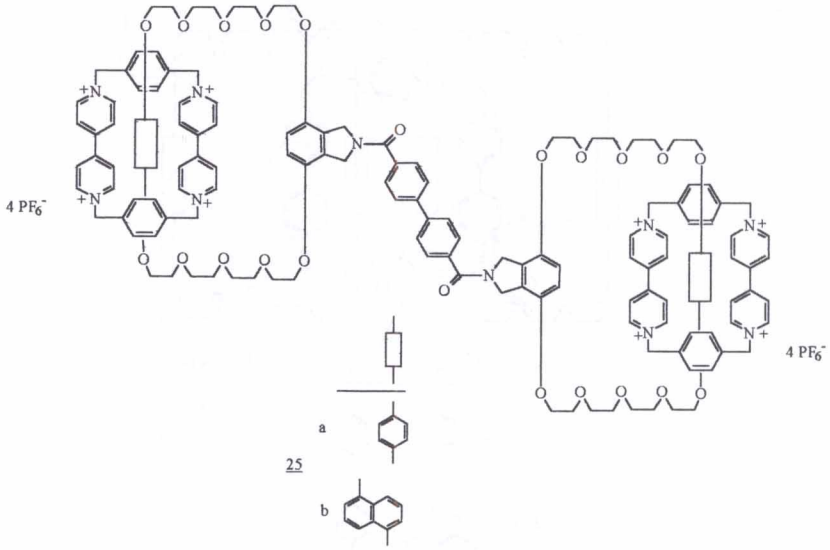

Br
Br
2 PF6⁻
X
Y
Y
X
1. DMF / 12 kbar
20°C / 5 h
2. NH4PF6 / H2O
X
Y
Y
X
4 PF6⁻
X
Y
a
23 b
c

The X-ray crystallography study of the solid - state structures of 23a-c has shown their approximately C_{2h} symmetry. In the solution state, the π-electron rich aromatic ring systems of the crown ether can adopt two different relative orientations, thus giving rise to two distinct isomeric forms possessing either C_{2h} or D_2 symmetries [38].

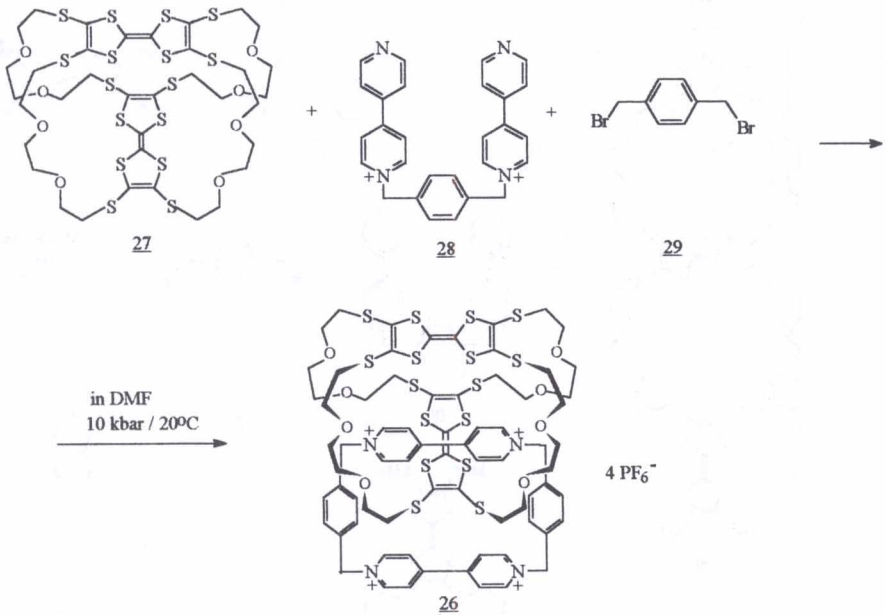
To bis[2]catenanes belong compounds 24 and 25a,b [28].



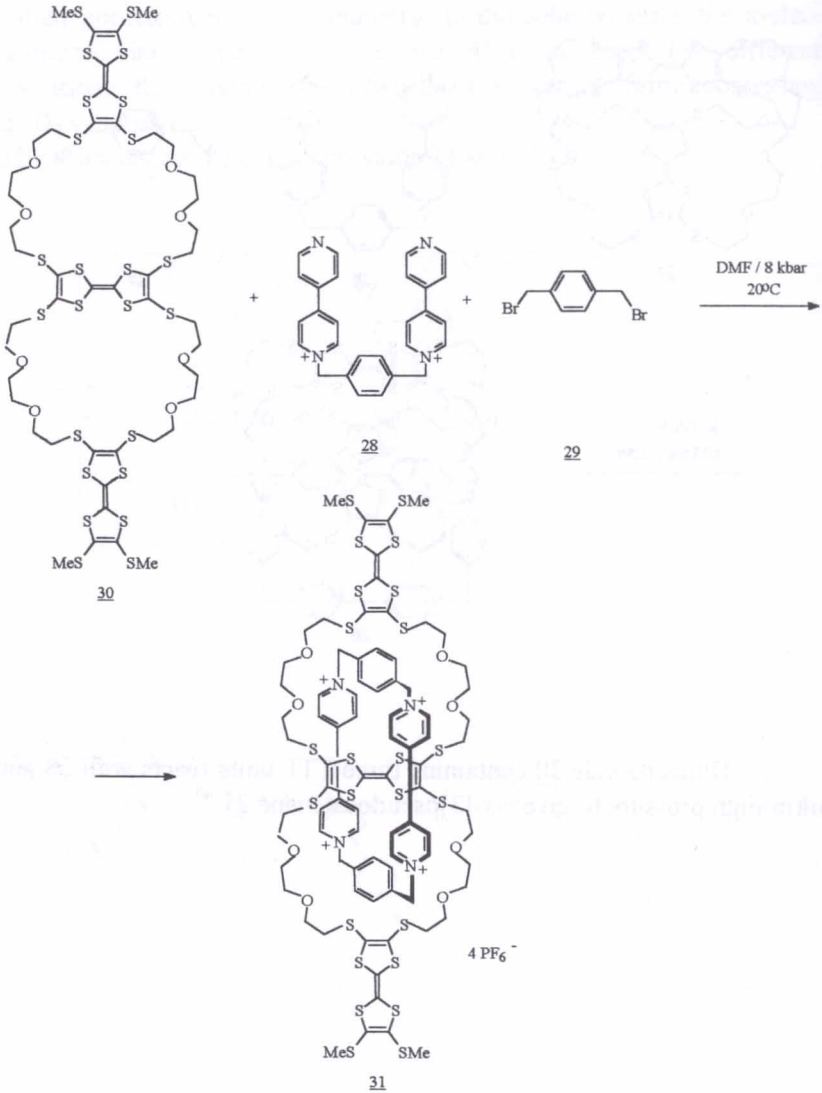
24



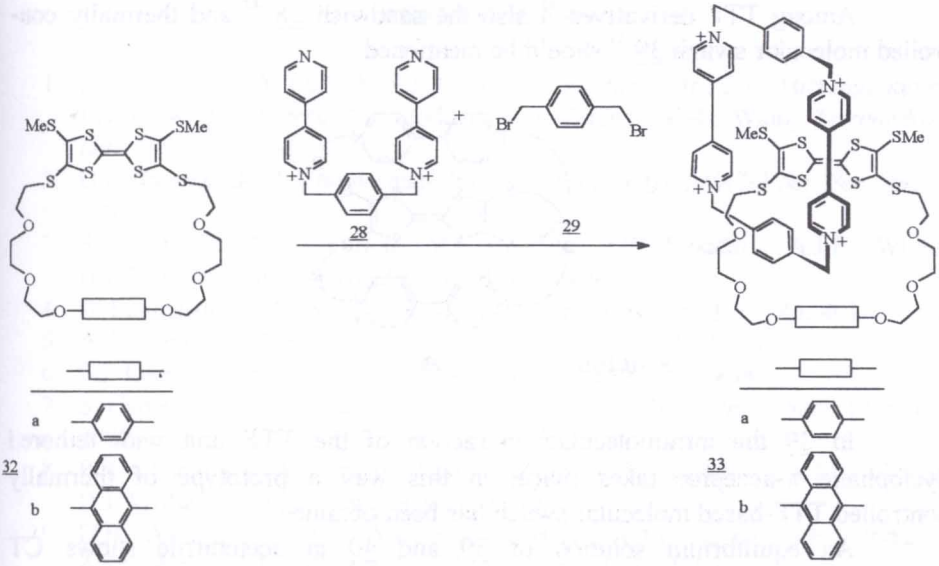
Many works deal with catenanes incorporating tetrathiafulvalene (TTF) units, some examples will be described here. The [2]catenane 26 has been synthesized from criss-cross cyclophane 27, dication 28 and 1,4-bis-(bromomethyl)benzene 29 under ultra-high pressure [39].

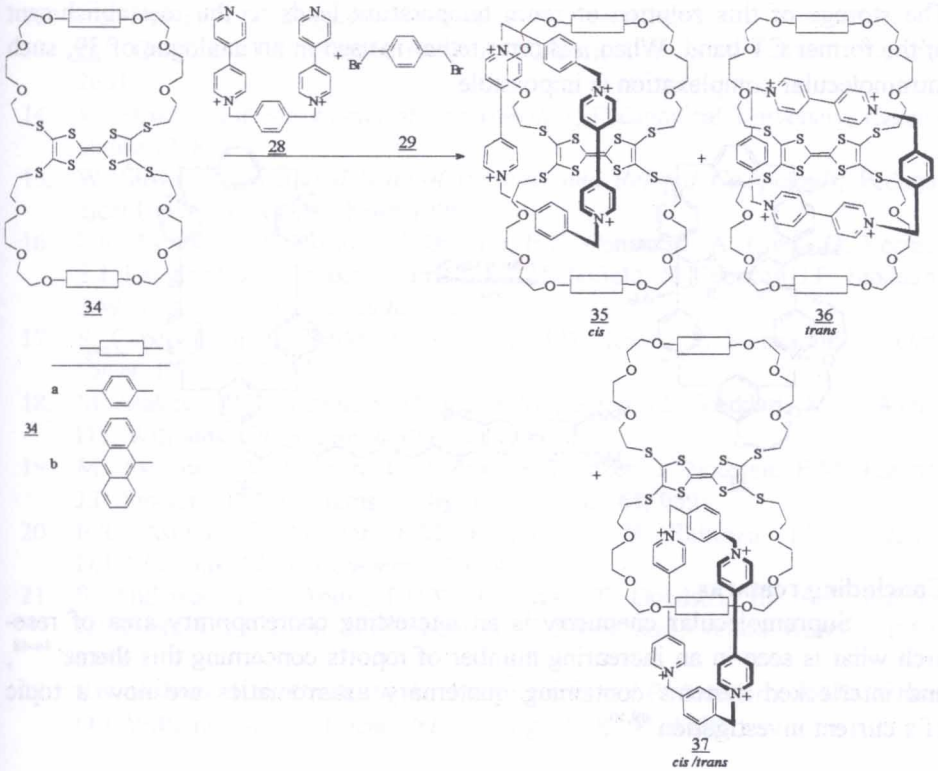


Dimacrocycle 30 containing three TTF units reacts with 28 and 29 under ultra-high pressure to give *cis*-[3]pseudocatenane 31 [40].

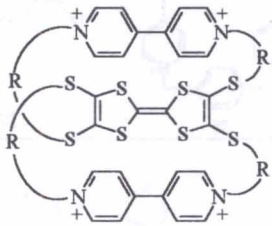


Following reactions of the macrocycle 32 leading to [2]catenane 33 and of the dimacrocycle 34 affording *cis*-, *trans*- and *cis/trans*- [3]pseudo-catenanes 35 , 36 and 37, respectively, have been made [26].


MeS
SMe
28
29
a
32
b
33


28
29
34
a
b
35
cis
36
trans
37
cis /trans

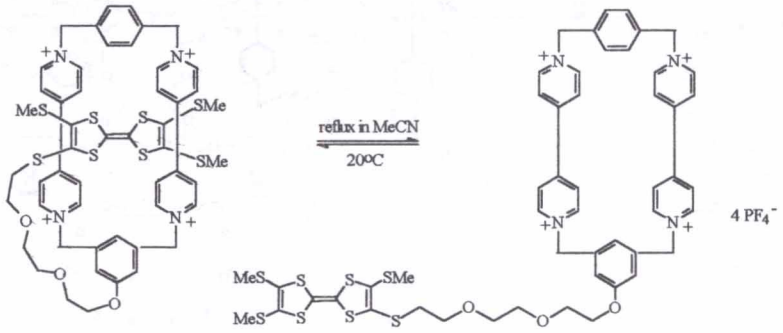
Among TTF derivatives [41] also the sandwich 38 [42] and thermally controlled molecular switch 39 [43] should be mentioned.



R = $(CH_2)_4$ 38

In 39 the intramolecular interaction of the TTF unit with tethered cyclophane π-acceptor takes place; in this way a prototype of thermally controlled TTF-based molecular switch has been obtained.

An equilibrium solution of 39 and 40 in acetonitrile shows CT absorption band at λ_{max}= 785 nm providing from the TTF unit inserted into the cyclophane cavity; however refluxing this solution for 45 min causes disappearance of this band, due to the conversion into the decomplexed form 40. The storage of this solution at room temperature leads to the reestablishment of the former CT band. When a shorter tether is used in an analogue of 39, such intramolecular complexation is impossible.



39 40

Concluding remarks

Supramolecular chemistry is an interesting contemporary area of research what is seen in an increaring number of reports concerning this theme [44-48], and interlocked systems containing quaternary azaaromatics are now a topic of a current investigation [49,50].

REFERENCES

1. P.R. Ashton, R.A. Bartsch, S.J. Cantrill, R.E. Hanes, Jr., S.K. Hickingbottom, J.N. Lowe, J.A. Preece, J.F. Stoddart, V.S. Talanov, Z.-H. Wang, *Tetrahedron Lett.* 1999, **40**, 3661
2. D.N. Reinhoudt, P. Timmerman, F.C.J.M. Van Veggel, *NATO Sci. Ser.,Ser. C* 1999, 51
3. S.J. Cantrill, D.A. Fulton, M.C.T. Fyfe, J.F. Stoddart, A.J.P. White, D.J. Williams, *Tetrahedron Lett.* 1999, **40**, 3669
4. B. Baumeister, A.C. de Dios, S. Matile, *Tetrahedron Lett.* 1999, **40**, 4623
5. A. Nangia, G.R. Desiraju, *NATO Sci. Ser., Ser. C* 1999, 193
6. S.J. Loeb, J.A. Wisner, *Angew. Chem., Int. Ed.* 1998, **37**, 2838
7. S. Capobianchi, G. Doddi, G. Ercolani, P. Mencarelli, *J. Org. Chem.* 1998, **63**, 8088
8. P.R. Ashton, J.A. Bravo, F.M. Raymo, J.F. Stoddart, A.J.P. White, D.J. Williams, *Eur. J. Org. Chem.* 1999, 899
9. D.B. Amabilino, P.R. Ashton, J.A. Bravo, F.M. Raymo, J.F. Stoddart, A.J.P. White, D.J. Williams, *Eur. J.Org. Chem.* 1999, 1295
10. J.-P. Sauvage, *Bull. Pol. Acad. Sci. Chem.* 1998, **46**, 289
11. B.J. Coe, S. Houbrechts, I. Asselberghs, A. Persoons, *Angew. Chem., Int. Ed.* 1999, **38**, 366.
12. C.S. Penkett, I.D. Simpson, *Tetrahedron* 1999, **55**, 6183.
13. D.L. Comins, J.T. Kuethe, H. Hong, F.J. Lakner, *J. Am. Chem. Soc.* 1999, **121**, 2651.
14. W. Śliwa, *Quaternary Salts of Azaaromatics*, Pedagogical University, Częstochowa 1998.
15. W. Śliwa, *N-Substituted Salts of Pyridine and Related Compounds*, Pedagogical University, Częstochowa 1996.
16. P.R. Ashton, R. Ballardini, V. Balzani, E.C. Constable, A. Credi, O. Kocian, S.J. Langford, J.A. Preece, L. Prodi, E.R. Schofield, N. Spencer, J.F. Stoddart, S.Wenger, *Chem. Eur. J.* 1998, **4**, 2413
17. S. Capobianchi, G. Doddi, G. Ercolani, J.W. Keyes, P. Mencarelli, *J. Org. Chem.* 1997, **62**, 7015
18. M. Asakawa, P.R. Ashton, S. Menzer, F.M. Raymo, J.F. Stoddart, A.J.P. White, D.J. Williams, *Chem. Eur. J.* 1996, **2**, 877
19. M. Asakawa, W. Dehaen, G. L'abbé, S. Menzer, J. Nouwen, F.M. Raymo, J.F. Stoddart, D.J. Williams, *J. Org. Chem.* 1996, **61**, 9591
20. P.R. Ashton, S. Menzer, F.M. Raymo, G.K.H. Shimizu, J.F. Stoddart, D.J. Williams, *Chem. Commun.* 1996, 487
21. S. Anderson, R.T. Aplin, T.D.W. Claridge, T. Goodson, III, A.C. Maciel, G. Rumbles, J.F. Ryan, H.L. Anderson, *J. Chem. Soc., Perkin Trans. 1* 1998, 2383
22. P.R. Ashton, P.T. Glink, M.-V. Martinez-Diaz, J.F. Stoddart, A.J.P. White, D.J. Williams, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 1930

23. S.J. Loeb, J.A. Wisner, *Chem. Commun.* 1998, 2757
24. D. Whang, K.-M. Park, J. Heo, P. Ashton, K. Kim, *J. Am. Chem. Soc.* 1998, **120**, 4899
25. P.R. Ashton, R. Ballardini, V. Balzani, M.C.T. Fyfe, M.T. Gandolfi, M.-V. Martinez-Diaz, M. Morosini, C. Schiavo, K. Shibata, J.F. Stoddart, A.J.P. White, D.J. Williams, *Chem. Eur. J.* 1998, **4**, 2332
26. Z.-T. Li, P.C. Stein, J. Becher, D. Jensen, P. Mork, N. Svenstrup, *Chem.Eur. J.* 1996, **2**, 624
27. X. Grabuleda, C. Jaime, *J. Org. Chem.* 1998, **63**, 9635
28. P.R. Ashton, J. Huff, S. Menzer, I.W. Parsons, J.A. Preece, J.F. Stoddart, M.S. Tolley, A.J.P. White, D.J. Williams, *Chem. Eur. J.* 1996, **2**, 31
29. P.E. Mason, I.W. Parsons, M.S. Tolley, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 2238
30. N. Yamaguchi, D.S. Nagvekar, H.W. Gibson, *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 2361
31. P.R. Ashton, I. Baxter, S.J. Cantrill, M.C.T. Fyfe, P.T. Glink, J.F. Stoddart, A.J.P. White, D.J. Williams, *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 1294
32. P.R. Ashton, I.W. Parsons, F.M. Raymo, J.F. Stoddart, A.J.P. White, D.J. Williams, R. Wolf, *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 1913
33. S. Shimada, K. Ishikawa, N. Tamaoki, *Acta Chem. Scand.* 1998, **52**, 374
34. C. Hamers, F.M. Raymo, J.F. Stoddart, *Eur. J. Org. Chem.* 1998, 2109
35. M.P.L. Werts, M. van den Boogaard, G. Hadziioannou, G.M. Tsivgoulis, *Chem. Commun.* 1999, 623
36. F.M. Raymo, K.N. Houk, J.F. Stoddart, *J. Org. Chem.* 1998, **63**, 6523
37. P.R. Ashton, F. Diederich, M. Gómez-López, J.-F. Nierengarten, J.A. Preece, F.M. Raymo, J.F. Stoddart, *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 1448
38. P.R. Ashton, S.E. Boyd, C.G. Claessens, R.E. Gillard, S. Menzer, J.F. Stoddart, M.S. Tolley, A.J.P. White, D.J. Williams, *Chem. Eur. J.* 1997, **3**, 788
39. M.B. Nielsen, N. Thorup, J. Becher, *J. Chem. Soc., Perkin Trans. 1* 1998, 1305
40. Z.-T. Li, J. Becher, *Chem. Commun.* 1996, 639
41. M.R. Bryce, *Adv. Mater.* 1999, **11**, 11
42. K.B. Simonsen, N. Thorup, M.P. Cava, J. Becher, *Chem. Commun.* 1998, 901
43. M.B. Nielsen, S.B. Nielsen, J. Becher, *Chem. Commun.* 1998, 475
44. Ch. Heim, A. Affeld, M. Nieger, F. Vögtle, *Helv. Chim. Acta* 1999, **82**, 746
45. Ch. Seel, A. H. Parham, O. Safarowsky, G. M. Hübner, F. Vögtle, *J. Org. Chem.* 1999, **64**, 7236
46. F.M. Raymo, J.F. Stoddart, *Chem. Rev.* 1999, **99**, 1643.
47. T. Suzuki, T. Tsuji, T. Fukushima, S. Miyanari, T. Miyashi, Y. Sakata, T. Kouda, H. Kamiyama, *J. Org. Chem.* 1999, **64**, 7107.
48. D.G. Hamilton, L. Prodi, N. Feeder, J.K.M. Sanders , *J. Chem. Soc., Perkin Trans. 1* 1999, 1057.

49. Ch.J. Easton, S.F. Lincoln, A.G. Meyer, H. Onagi, *J. Chem. Soc., Perkin Trans. 1* 1999, 2501.
50. Z.-T. Li, G.-Z. Ji, Ch.-X. Zhao, S.-D. Yuan, H. Ding, Ch. Huang, A.-L. Du, M. Wei, *J.Org. Chem.* 1999, **64**, 3572.

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Supramolekularne układy o wbudowanych czwartorzędowych solach związków azaaromatycznych

Streszczenie: W artykule przedstawiono rotaksany i katenany zawierające układy czwartorzędowych soli związków azaaromatycznych; opisano ich syntezy i właściwości.