Synthesis of Some New Dimers as Constructive of Nano Machines

ABDOL GHAFFAR EBADI[1,*] and SOMAYE ALAMI[2]

[1]Department of Biological Sciences, Jouybar Branch, Islamic Azad University, Jouybar, Iran
[2]Young Research Club, Department of Applied Chemistry, Tabriz Branch, Islamic Azad University, P.O. Box 1655, Tabriz, I.R. Iran

*Corresponding author: E-mail: Dr_ebadi@iaujouybar.ac.ir, dr_ebadi2000@yahoo.com

In this research work, a part of nano machines is synthesized, based on interlocked macrocycle named rotaxanes, pseudorotaxanes, knots and catenanes which constitute any passive or active structure capable of actuation, mesoscale molecular electronic devices, sensing, signaling, information processing, intelligence, swarm behaviour at the nano scale. The dibenzosulfide (**1**) was obtained by *p*-cresol and sulfur dicholorie in dry petroleum ether in 50 % yield. Treatment of compound (**1**) with methyl choloroacetate in presence of K_2CO_3 and KI at refluxed dry acetone gave diester (**2**) in 98 % yield. For synthesis of macrocycle (**3**), diester (**2**) and diethylene triamine was refluxed in dry methanol and gave dibenzosulfide 16-crown-6 in 75 % yields. Bis azacrown (**4**) was synthesized by macrocycle (**3**) and decanocoyl dicholoride in dry CH_2Cl_2 and was refluxed in presence of Et_3N in good yield and then purified by column chromatography.

Key Words: Nano machine, Rotaxane, Catenne, Bisazacrown.

INTRODUCTION

With the advent in the 1970s and 1980s of supra-molecular chemistry a discipline which exploits fundamental concepts such as self-assembly, self-organization and self-replication, that are central to nature's forms and functions sit becoming feasible to construct large and intricate, yet highly ordered, functioning molecular and supramolecular entities by recognizing the importance of mechanical as well as noncovalent and, ofcourse, covalent bonds[1,2].

The term 'nano machine' refers complex macromolecules (or bio macromolecules) that consume energy in order to perform certain specific cations. Nano machines could play a major role in the future of electronics, medicine and communications. Designed artificial nano machines and motors are based on interlocked macrocycles named rotaxanes and catenanes, which can made of macrocycles such as azacrown ethers. Catenanes can be defined as interlocked molecular compounds in which two or more rings are joined together by a mechanical bond (Fig. 1) rotaxanes are minimally composed of an axel-like molecule surrounded by a macrocyclic compound and terminated by bulky groups that prevent disassembly (Fig. 2)[3,4].

Like macroscopic machines, nanomachines are characterized by (i) the kind of energy input supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and
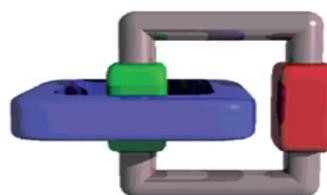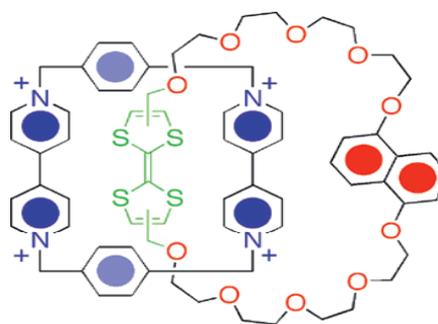
Catenanes

Fig. 1. Catenanes

manitored, (iv) the possibiling to repeat the operation at will and establish a cyclic process, (v) the time scale needed to complete a cycle of operation and (vi) the function performed. Chemical, photochemical or electro chemical stimuli can be used to feed nano machines[5-7].
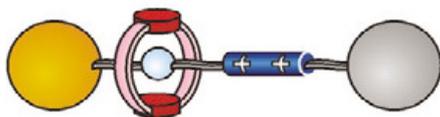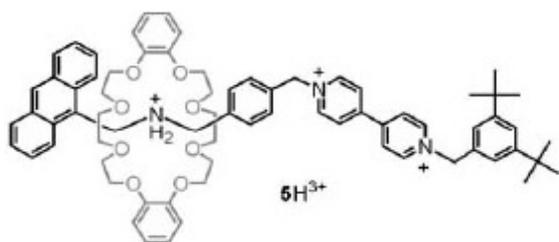
Rotaxane

Fig. 2. Rotaxane

The assembly of mechanically bonded molecules such as rotaxanes and catenanes is of great interest to the supramolecular chemists, not only for the challenge of their synthesis but also for the potential uses these systems may have such as molecular switches, sensors and machines[8-10].

The purpose of present study is to prepare a part of nano machines that would constitute any passive or active structure capable of actuation, mesoscale molecular electronic devices, sensing, signaling, information processing, intelligence, swarm behaviour at the nano scale.

EXPERIMENTAL

The reactions were carried out in an efficient hood. All the materials purchased from Merck and Fluka chemical companies and applied without further purification. IR spectra were measured on a Perkin-Elmer model 543, the ^{1}H NMR spectra were obtained using Bruker Avance DRX 500, 400 and 60 apparatus and ^{13}C NMR spectra were obtaine using Bruker Avance DRX 500 and 400 apparatus. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. The melting points were measured with an electrothermal engineering LTD 9100 apparatus. CH_2Cl_2 was dried over P_2O_5 and then distilled from CaH_2. MeOH was dried over CaH_2 and then distilled.

Preparation of 2,2'-sulfinyl-*bis*[(4-methyl)phenol] or dibenzosulfide (1): *p*-Cresol (10.8 g, 0.1 mol) was dissolved in 50 mL of petroleum ether. A solution of 3.39 mL (0.053 mol) of sulfur dichloride in 6 mL of petroleum ether was dropped in during 1 h. The mixture was allowed to stand overnight. The petroleum ether layer was then poured off from the brown, semi-solid mass which was crystallized from toluene/ glacial acetic acid yielded colourless crystals of sulfide (1) (45 %). m.p. 113.5-114 ℃.

Preparation of 2,2'-sulfinyl-*bis* methyl[(4-methyl phenoxy acetate)] or methyl diester (2): A mixture of 7.5 g (0.03 mol) of dibenzo sulfide (1), 6.45 mL of the methyl chloroacetate, 15 g K_2CO_3 and 0.5 g KI was refluxed in 100 mL of dry acetone for 24 h. The solvent was evaporated and dissolved in 50 mL NaOH 10 % then organic phase was separated, evaporated to give 98 % methyl diester (2). The crude product was recrystallized in methanol m.p. 98-100 ℃.

Preparation of 7,10,13-triaza-thia-4,16-dioxa-2,3,17,18-dibenzo-20,24-dimethyl cyclooctadecane-6,14-dione or macrocyclic diamides (3): Compound (3) was prepared by the cyclization reaction of diester (2) (3 g, 0.00769 mol) with diethylen triamine (0.84 mL, 0.0073 mol) in refluxing dry methanol (60 mL) for 24 h. The solution was cooled, filtered and washed with water. The white solid (48 %) was recrystallized in methanol. m.p. 220-222 ℃.

Preparation of 1,10-dioxo-1,4-*bis*(7,10,13-triaza-thia-4,16-dioxa-2,3,17,18-dibenzo-20,24-dimethyl cyclooctadecane-6,14-dione)octane or *bis* crown (4): A mixture of macrocyclic diamides (0.24 g, 0.56 mmol) and decanoyl dichloride (0.08 mL) and triethyl amine (0.8 mL, 5.6 mmol) in dry dichloromethane (25 mL) was refluxed for 24 h. This compound was purified by column chromatography on silica gel using ethyl acetate/methanol (2:1) as eluent and then recrystallized from C_6H_{13}/CHCl$_3$ to afford *bis* crown (4) (52 %). m.p. 260-263 ℃ (**Scheme-I**).
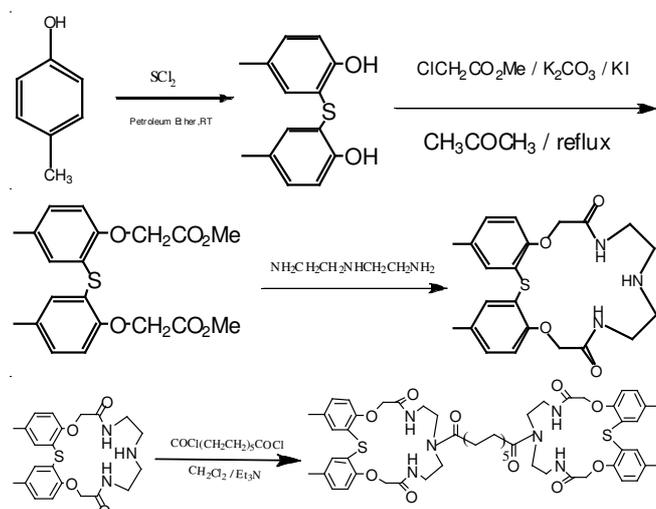
Scheme-I: Steps of reactions

RESULTS AND DISCUSSION

In this work, the synthesis of some new constructive component of rotaxanes and catenanes are discussed. Several synthetic methods have been developed for the synthesis of macrocycle diamides. Among these methods we used the diester technique in good yield.

Bisphenol (1): IR (KBr, ν_{max}, cm^{-1}): 3400, 3200, 3040, 2920, 1900, 1880, 1760, 1580, 1500, 1480, 1400, 1360, 1280, 1230, 1140, 1060, 940, 880, 820, 760; ^{1}H NMR (60 MHz, CDCl$_3$): δ 204 (s, 6H), 6.1 (b, 2H), 6.82 (s, 2H), 6.82 (s, 2H), 7.07 (s, 2H) ppm.

Methyl diester (2): IR (KBr, ν_{max}, cm^{-1}): 2960, 2940, 1760, 1480, 1280, 1250, 1200, 1150, 1080, 990; ^{1}H NMR (60 MHz, CDCl$_3$) δ 2.2 (s, 6H), 3.7 (s, 6H), 4.65 (s, 4H), 6.8 (s, 6H) ppm.

Macrocyclic diamide (3): IR (KBr, ν_{max}, cm^{-1}): 3420, 3360, 3010, 2940, 2880, 1680, 1570, 1490, 1280, 1250, 1210, 1080, 1050, 830, 800, 770, 680, 590, 560, 438; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.25 (s, 6H), 2.78-2.8 (m, 4H), 3.39-3.4 (m, 4H), 4.6 (s, 4H), 6.82 (d, J = 8.29 Hz, 2H), 7.1 (d, J = 8.17 Hz,

2H), 7.48 (s, 2H) ppm; ^{13}CNMR (125 MHz, CDCl$_3$) δ: 168.27, 153.58, 132.61, 132.51, 129.7, 122.19, 112.29, 67.88, 49.33, 39.25, 20.97 ppm; MS (EI) m/e 429 (M)$^+$, 430 (M+1)$^+$, 431 (M+2)$^+$, 386, 360, 316, 303, 257, 241, 228, 180, 178, 164, 151, 121, 108, 105, 91, 85, 84, 56, 49, 43, 30.

Bis azacrown (4): IR (KBr, ν$_{max}$, cm^{-1}): 3506(m), 3440(m), 2926 (w), 2854(m), 2093(w), 1737(vs), 1681(m), 1639(w), 1529(s), 1488(m), 1280(m), 1289(s), 1153(m), 1075(m), 1039(m), 878(m), 802(w), 750(w), 664(w), 555(w), 431(w); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.28 (m, 14H), 2.13 (s, 6H), 2.28 (s, 6H), 3.30 (s, 4H), 3.44-3.48 (s, 4H), 3.50-3.60 (d, 4H), 3.65-3.70 (d, 4H), 4.38 (s, 2H), 4.54 (s, 2H), 6.63 (s, 4H), 6.74 (m, 4H), 6.94-6.95 (d, 2H), 7.26-7.37 (d, 2H), 7.40 (b, 2H), 7.44-7.50 (b, 2H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$) δ: 175.00, 169.58, 169.47, 153.83, 152.26, 137.13, 133.07, 132.44, 132.03, 131.70, 128.97, 124.93, 121.23, 113.40, 113.03, 68.47, 49.81, 49.20, 39.21, 38.50, 33.14, 32.09, 25.00, 23.25, 21.01, 20.69, 19.12 ppm.

Conclusion

The *bis* macrocycle (**4**) is ditopic system that two azacrown ring in *bis* macrocycle can move in long of linear molecules, like shuttling (Fig. 3).
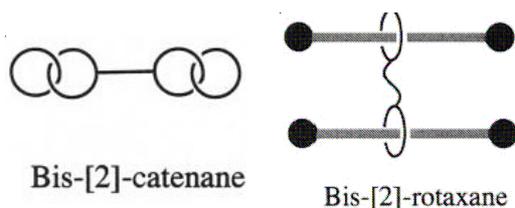
Fig. 3. Bisrotaxane and *bis* catenane

Macrocycle (**3**) can also interlock with the same macrocycle and made a catenane. Therefore this molecule can be used on structure of rotaxanes and catenanes in nano machines. The design, synthesis and investigation of chemical systems able to function as molecular machines and motors are interest not only for basic research, but also for the growth of nanoscience and the subsequent development of nanotechnology. Therefore can said nano machines depended on macrocyclic diamide and corresponding *bis* azacrown compound that move and can control chemical, photochemical and electrochemical switchings.

REFERENCES

1. V. Balzani, A. Credi and M. Venturi, *Nanotoday*, **2**, 18 (2007).
2. A. Shockravi and T.S. Bavili, *J. Incl. Phenom. Macrocycl. Chem.*, **52**, 223 (2005).
3. V. Balzani, M. Gome-Loapez and J.F. Stoddart, *Acc. Chem. Res.*, **31**, 405 (2008).
4. M. Clemente-Leon, F. Marchioni, S. Silvi and A. Credi, *Synth. Met.*, **139**, 773 (2003).
5. V. Balzani, M. Gomez-Lopez and J.F. Stoddart, *Acc. Chem. Res.*, **31**, 405 (1998).
6. P.R. Ashton, R.A. Bartsch, S.J Cantrill, R.E. Hanes, S.K. Hickingbottom, J.N. Lowe, J.A. Preece, J.F. Stoddart, V.S. Talanov and Z. Wang, *Tetrahedron Lett.*, **40**, 3661 (1999).
7. Y.L. Huang, C. Lin, P. Cheng, C. Lai and S. Chiu, **49**, 1665 (2008).
8. M.R. Sambrook, P.D. Beer, J.A. Wisner, R.L. Paul and A.R. Cowley, *J. Am. Chem. Soc.*, **126**, 15364 (2004).
9. A.G. Ebadi and S. Alami, *Appl. Mech. Mater.*, **110–116**, 3293 (2011).
10. A.G. Ebadi and S.Alami, *Appl. Mech. Mater.*, **110–116**, 3807 (2011).