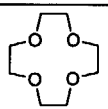
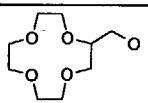
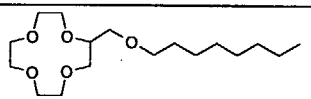
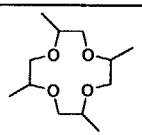
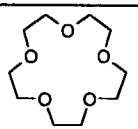
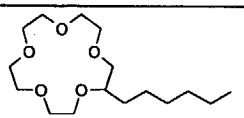
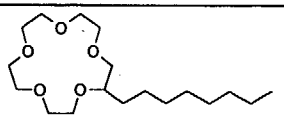
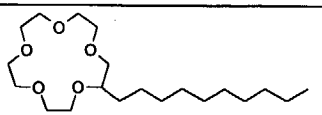
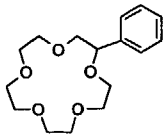
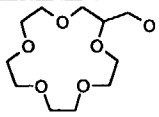
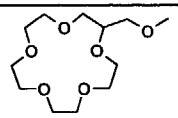
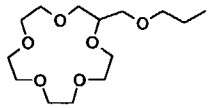
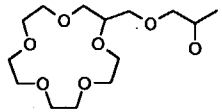
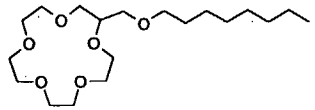
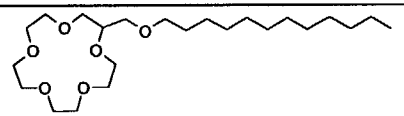
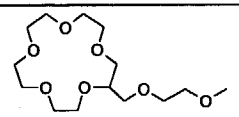
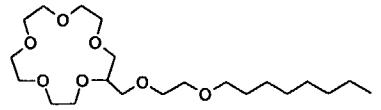
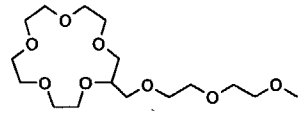
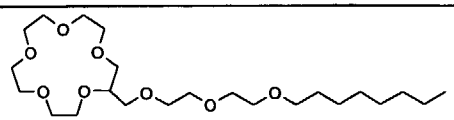
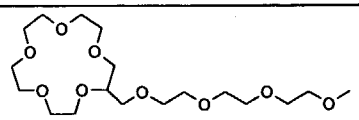
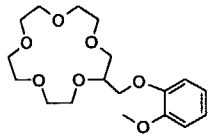
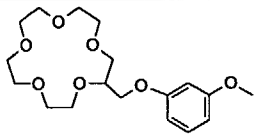
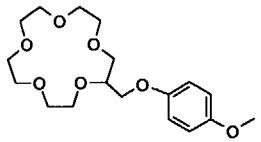
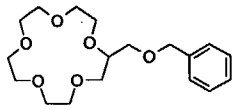
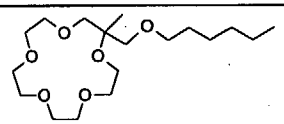
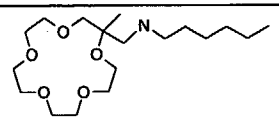
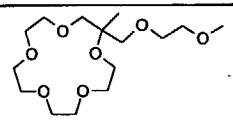
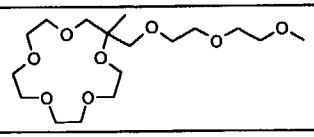
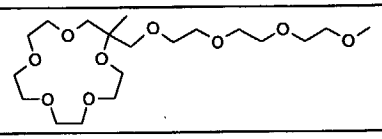
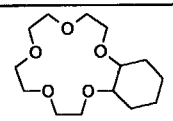
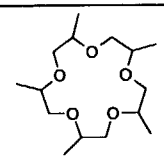
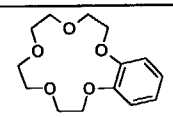
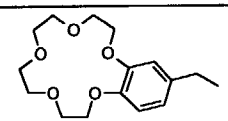
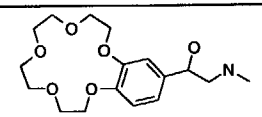
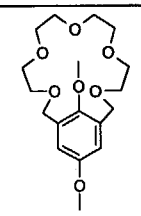
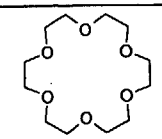
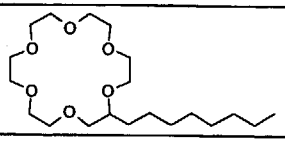
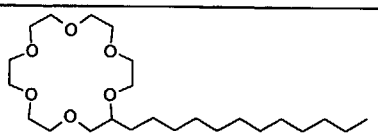
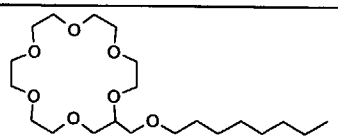
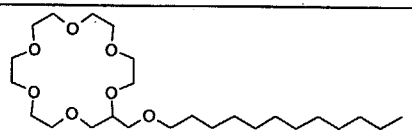
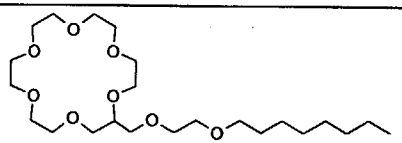
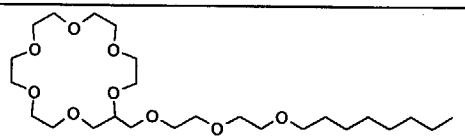
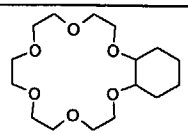
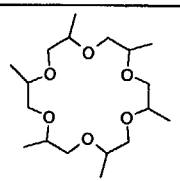
Table SM1. The 1:1 (M:L) complexation of crown ethers with Na^+ cation in MeOH at 298 K. Experimental and calculated stability constants (Log*K*) for learning set using **I(A**, 3-6), **II(B)**, **II(AB)**, **I(AB**, 2-4), **I(AB**, 3-4) and **I(AB**, 2-3) fragments sets. Crown ethers 61-69 were used for validation[a].

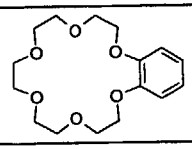
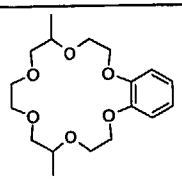
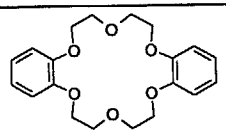
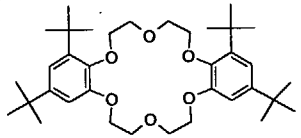
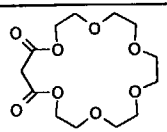
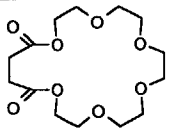
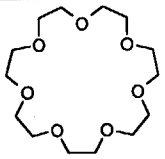
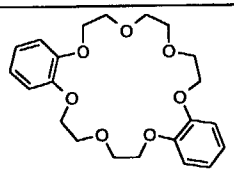
no.	ligand	Log*K*						
		exp	calculated					
			I(A, 3-6)	**II(B)**[b]	**II(AB)**	**I(AB**, 2-4)	**I(AB**, 3-4)	**I(AB**, 2-3)[b]
1		1.41	1.64	1.72	1.67	1.68	1.67	1.63
2		1.37	1.35	1.38	1.45	1.37	1.36	1.31
3		1.32	1.44	1.50	1.55	1.53	1.68	1.57
4		1.41	1.26	1.30	1.24	1.37	1.37	1.47
5		3.30	3.25	3.29	3.27	3.25	3.26	3.24
6		3.20	3.19	3.15	3.12	2.92	2.92	3.28
7		3.18	3.20	3.14	3.10	3.03	2.95	3.26
8		3.18	3.21	3.14	3.09	3.14	2.98	3.22

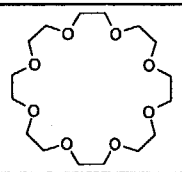
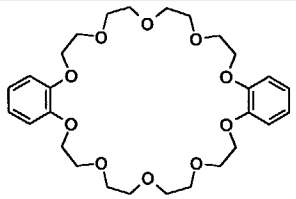
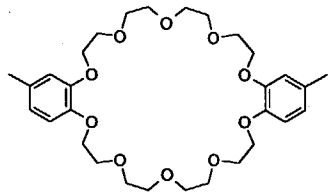
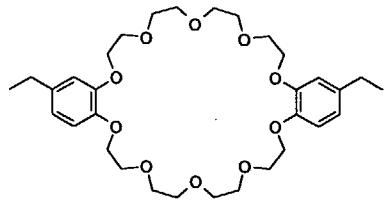
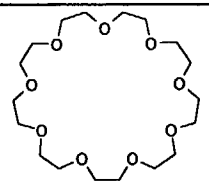
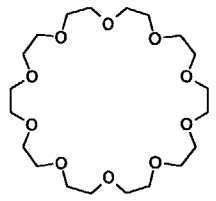
9		3.34	3.39	3.23	3.19	3.36	3.29	3.24
10		2.94	2.96	2.95	3.04	2.94	2.95	3.06
11		3.03	3.08	3.16	3.06	3.28	3.26	3.43
12		3.05	2.98	3.14	3.19	2.83	3.19	3.15
13		3.14	3.14	3.14	2.97	3.14	3.14	3.08
14		3.18	3.06	3.12	3.15	3.11	3.27	3.18
15		3.14	3.07	3.11	3.12	3.32	3.33	3.09
16		3.05	3.17	3.15	3.10	3.31	3.30	3.43
17		3.22	3.10	3.12	3.18	3.14	3.30	3.13
18		3.13	3.21	3.18	3.13	3.34	3.33	3.46

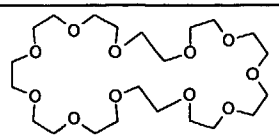
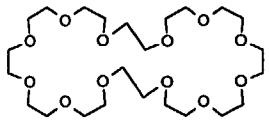
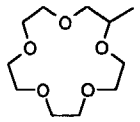
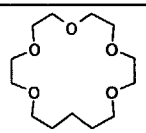
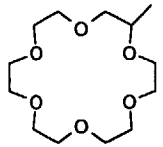
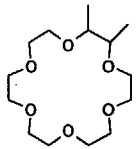
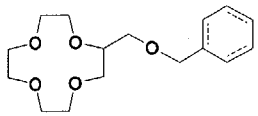
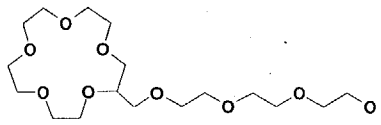
19		3.23	3.14	3.17	3.22	3.17	3.33	3.13
20		3.09	3.26	3.25	3.17	3.38	3.36	3.54
21		3.24	3.24	3.07	3.14	3.39	3.38	3.26
22		2.89	2.89	3.07	3.14	2.90	2.90	3.26
23		2.90	2.90	3.07	3.14	2.90	2.90	3.26
24		3.07	3.12	3.18	3.22	3.05	3.12	3.17
25		3.57	3.66	3.74	3.82	3.44	3.47	3.32
26		3.08	f	3.10	f	3.08	3.08	3.08
27		3.87	3.79	3.77	3.76	3.75	3.54	3.58

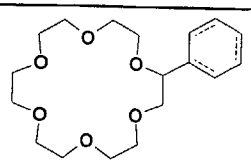
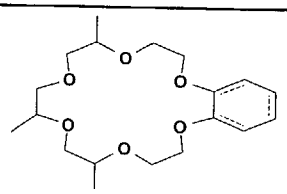
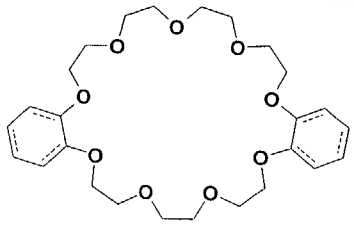
28		3.89	3.83	3.80	3.79	3.79	3.57	3.60
29		3.87	3.88	3.87	3.83	3.82	3.60	3.66
30		3.71	3.34	3.51	3.49	3.25	3.13	3.42
31		3.34	2.78	2.74	2.72	2.86	2.87	2.89
32		3.06	3.34	3.21	3.31	3.33	3.34	2.99
33		3.89	3.86	3.91	3.70	3.88	3.90	3.87
34		2.94	*f*	2.92	*f*	2.94	2.94	2.94
35		2.51	2.51	2.51	2.36	2.51	2.51	2.38
36		4.36	4.07	4.07	4.08	4.05	4.06	4.04

37		3.91	4.03	3.94	3.92	3.83	3.76	4.02
38		3.93	4.05	3.94	3.89	4.05	3.82	3.90
39		3.97	3.88	3.95	3.96	3.91	4.07	3.98
40		3.83	3.90	3.95	3.93	4.13	4.14	3.88
41		4.00	3.93	3.99	4.00	3.94	4.11	3.98
42		3.97	3.97	4.07	4.03	3.98	4.14	4.02
43		4.09	4.17	4.29	4.31	4.06	3.93	4.17
44		2.94	3.51	3.38	3.43	3.59	3.60	3.45

45		4.35	4.17	3.99	4.13	4.13	4.14	3.83
46		3.76	3.89	3.79	3.91	3.98	3.99	3.74
47		4.36	4.27	4.37	4.17	4.21	4.22	4.21
48		2.60	2.56	2.60		2.60	2.60	2.60
49		1.80	1.80	1.75	1.75	1.72	1.74	1.74
50		1.70	1.70	1.75	1.75	1.78	1.76	1.76
51		2.54	2.55	2.42	2.56	2.55	2.54	2.33
52		2.40	2.74	2.71	2.65	2.71	2.70	2.58

53		2.35	2.20	2.04	2.20	2.20	2.19	1.94
54		2.80	2.48	2.49	2.37	2.42	2.41	2.62
55		2.52	2.60	3.03	3.16	2.53	2.50	3.08
56		3.53	3.52	3.02	3.14	3.52	3.55	3.11
57		2.14	2.25	2.11	2.24	2.23	2.22	2.02
58		2.14	2.29	2.22	2.27	2.26	2.25	2.15

59		1.96	1.94	1.96	1.92	1.91	1.90	1.89
60		2.06	1.99	2.14	1.95	1.94	1.93	2.10
61		3.05[d]	**3.10**[c]	**3.19**[c]	**3.16**[c]	**3.17**[c]	**3.18**[c]	**3.20**[c]
62		2.46[e]	**4.62**[c]	**2.44**[c]	**2.46**[c]	**3.28**[c]	**2.22**[c]	**2.47**[c]
63		3.90[d]	**3.93**[c]	**3.97**[c]	**3.97**[c]	**3.98**[c]	**3.99**[c]	**3.98**[c]
64		3.77[d]	**3.58**[c]	**3.87**[c]	**3.86**[c]	**3.28**[c]	**3.27**[c]	**3.90**[c]
65		1.35	**1.51**[c]	**1.58**[c]	**1.63**[c]	**1.48**[c]	**1.53**[c]	**1.54**[c]
66		3.04	**2.37**[c]	**2.94**[c]	**3.14**[c]	**3.04**[c]	**3.04**[c]	**3.49**[c]

67		4.17	**4.22** [c]	**4.01** [c]	**4.00** [c]	**4.16** [c]	**4.10** [c]	**4.02** [c]
68		3.53	**3.79** [c]	**3.68** [c]	**3.80** [c]	**3.90** [c]	**3.91** [c]	**3.67** [c]
69		2.41	**2.44** [c]	**2.38** [c]	**2.33** [c]	**2.39** [c]	**2.38** [c]	**2.42** [c]

[a] Experimental data was selected from the THECOMAC database [2]. See text for fragments definitions. Unless specified, there was used fitting equation 1. [b] There was used fitting equation 2. [c] In bold: predicted log*K* value for the validation set. [d] Experimental stability constant has been estimated in this work by ISE method. [e] Experimental data from the work. [43] [f] Molecule containing fragments of "rare" occurrence (i.e., found in less than two molecules) is excluded from the learning set.

Table SM2. The 1:1 (M:L) complexation of crown ethers with Na^+ cation in MeOH at 298 K. Fragment contributions (a_i) to stability constants log$K$ with the atom/bond sequences **I(AB**, 3-4) [a] and for additive fitting equation 1 [b].

no.	fragment	contribution a_i
1	C-C-O [c]	-0.155
2	C-O-C	0.555
3	C-C-O-C	-0.238
4	O-C-C-O	0.263
5	C-C-C	0.656
6	C-C-C-O	-0.340
7	C-C-C-C	-0.640
8	C-C.C; C-C.C.C [d]	0.021
9	C.C.C; C.C.C.C [d]	-1.363
10	C-C-C.C	-0.065
11	C.C-C-O	4.192
12	C.C-O; C-O-C.C; C.C.C-O [d]	1.814
13	O-C.C-O	0.482
14	C-C-N; C-C-N-C [d]	-3.012
15	C-N-C; N-C-C-O [d]	-11.356
16	C-C-C-N	5.333
17	C-C.C-O	-7.984
18	O-C=O; C-C=O; C-O-C=O; C-C-C=O [d]	0.146
19	a_{cycl} [e]	0.388
20	a_0 [f]	1.543

[a] See text for fragments definition.
[b] The learning set contains stability constants (log$K$) of (Na^+)L complexes of 60 crown ethers (L) including standard macrocycles (-CH2-CH2-O-)$_n$, where n = 4-12, 18-crown-5, 19-crown-6, 20-crown-6 and their benzo, dibenzo- cyclohexyl, dicyclohehyl, and lariate derivatives, which have been critically selected from the THECOMAC database [2].
[c] C-C-O, O-C=O and C.C.C are molecular fragments with single, double and aromatic bond accordingly.
[d] Linearly dependent fragments in learning set form one group as an extended fragment.
[e] "Cyclicity" descriptor a_{cycl} has been used for taking into account of "macrocyclic effect".
[f] The a_o term is fragment independent.

Table SM3. The 1:1 (M:L) complexation of crown ethers with Na^+ cation in MeOH at 298 K. Fragment contributions (a_i) to stability constants log*K* with augmented atoms fragments **II(AB)** [a] and for additive fitting equation 1 [b].

no.	Fragment	contribution a_i
1	C(-C'-O')[c]	-0.126
2	O(-C'-C')	0.287
3	C(-C'-C'-O')	0.003
4	O(-C')	-0.230
5	C(-C'-C')	-0.008
6	C(-C')	-0.237
7	C(.C'.C') [c]	-0.140
8	C(-C'.C'.C')	0.493
9	C(-O')	-0.493
10	C(.C'.C'-O')	0.178
11	C(-C'-C'-C'-O')	0.900
12	C(-C'-O'=O'); O(=C') [c, d]	-0.116
13	a_{cycl} [e]	0.390
14	a_0 [f]	1.532

[a] See text for fragments definition.

[b] The learning set contains stability constants (log*K*) of $(Na^+)L$ complexes of 60 crown ethers (L) including standard macrocycles $(-CH_2-CH_2-O-)_n$, where n = 4-12, 18-crown-5, 19-crown-6, 20-crown-6 and their benzo, dibenzo- cyclohexyl, dicyclohehyl, and lariate derivatives, which have been selected from the THECOMAC database [2].

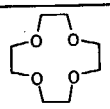
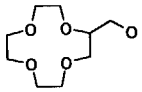
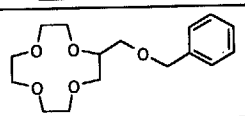
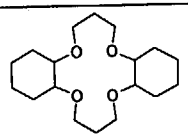
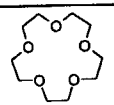
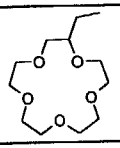
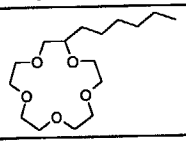
[c] C(-C'-O'), C(-C'-O'=O'), C(.C'.C') are molecular fragments with sp^3, sp^2 carbon and sp^2 aromatic carbon accordingly.

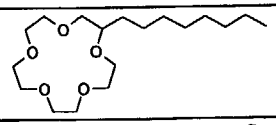
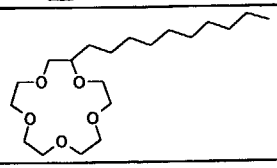
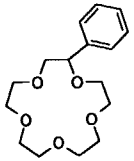
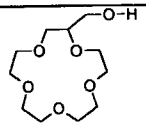
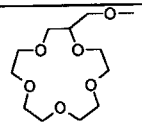
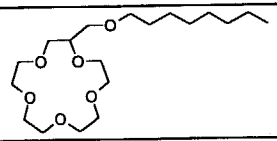
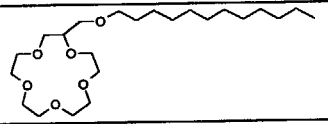
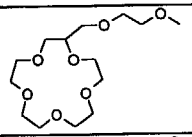
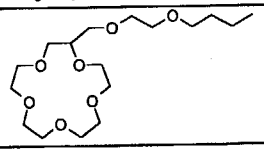
[d] Linearly dependent fragments in learning set form one group as an extended fragment.

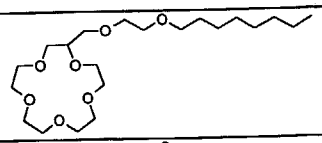
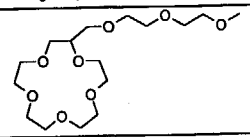
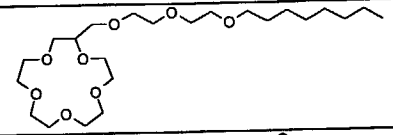
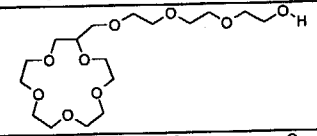
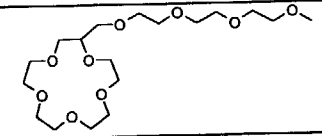
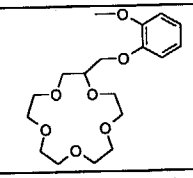
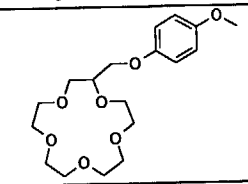
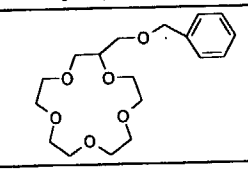
[e] "Cyclicity" descriptor a_{cycl} has been used for taking into account of "macrocyclic effect".

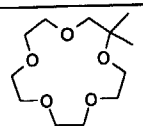
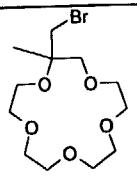
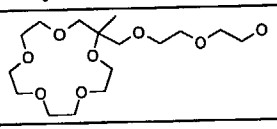
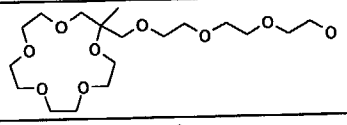
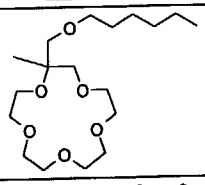
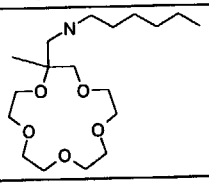
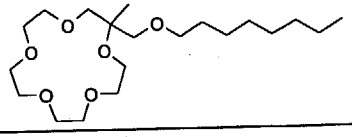
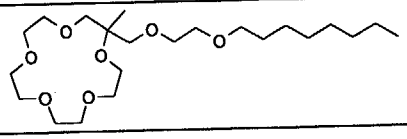
[f] The a_o term is fragment independent.

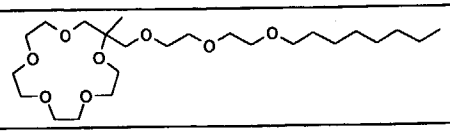
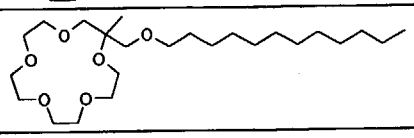
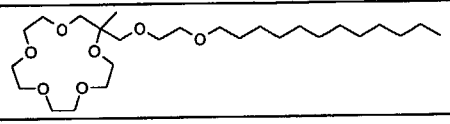
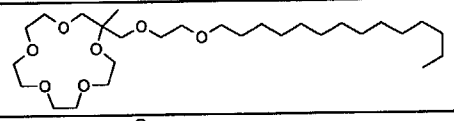
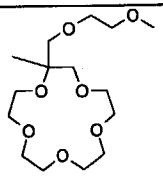
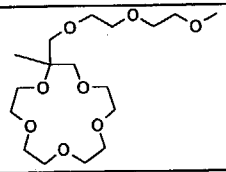
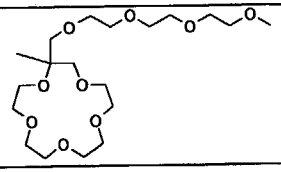
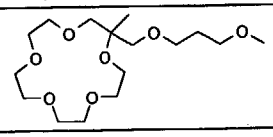
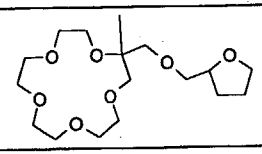
Table SM4. The 1:1 (M:L) complexation of crown ethers with K^+ cation in MeOH at 298 K. Experimental and calculated stability constants (Log*K*) for learning set using **II(Hy)**, **I(AB**, 2-6), **I(AB**, 3-5), **I(AB**, 2-5) and **I(AB**, 2-4) fragments sets. Crown ethers 114-123 were used as test (validation) compounds[a].

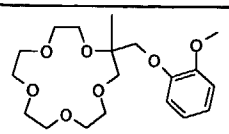
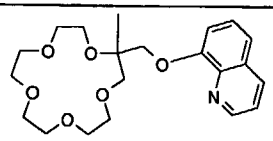
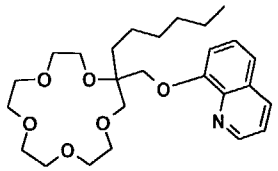
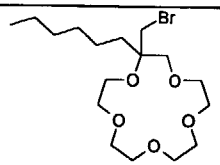
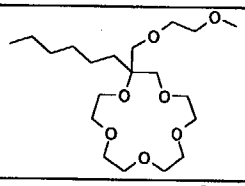
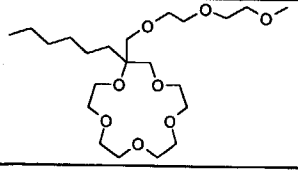
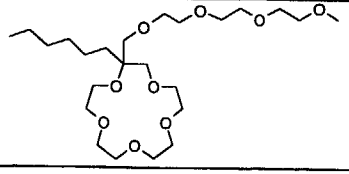
		Log*K*					
		exp	calculated				
no.	Ligand		**II(Hy)**[b]	**I(AB**, 2-6)	**I(AB**, 3-5)	**I(AB**, 2-5)	**II(Hy)**	**I(AB**, 2-4)
1		1.58	1.70	1.68	1.67	1.67	1.72	1.69
2		1.43	1.46	1.48	1.61	1.57	1.62	1.66
3		1.42	1.48	1.54	1.54	1.55	1.52	1.89
4		1.30	1.49	1.31	1.35	1.32	1.65	0.87
5		3.35	3.36	3.18	3.16	3.16	3.26	3.16
6		3.29	2.93	3.33	3.06	3.13	2.99	2.96
7		3.13	2.88	3.12	3.11	3.13	2.96	3.07

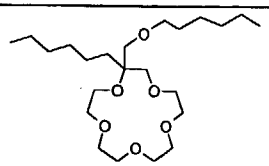
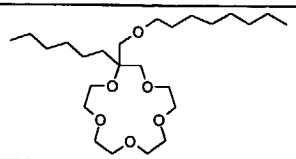
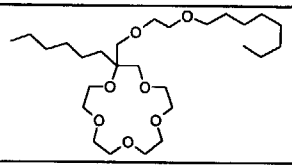
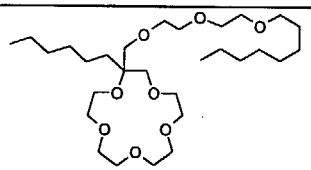
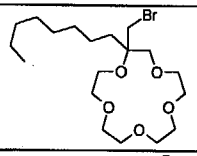
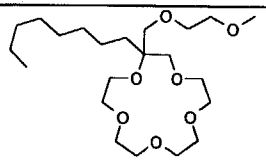
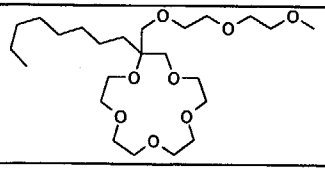
8		3.05	2.86	3.14	3.14	3.14	2.95	3.13
9		3.15	2.85	3.17	3.18	3.16	2.94	3.19
10		3.38	3.34	3.39	3.39	3.39	3.35	3.07
11		3.09	3.12	2.98	3.10	3.06	3.16	3.13
12		3.27	3.21	3.02	3.19	3.17	3.15	3.32
13		3.09	3.14	3.10	3.07	3.10	3.11	3.17
14		3.09	3.12	3.15	3.13	3.12	3.09	3.29
15		3.20	3.42	3.36	3.34	3.33	3.30	3.47
16		3.37	3.38	3.34	3.17	3.23	3.29	3.20

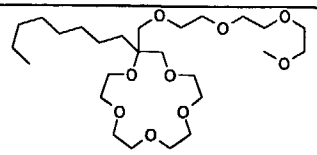
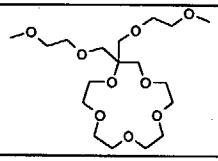
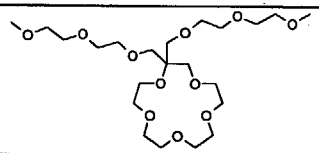
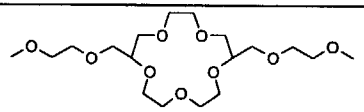
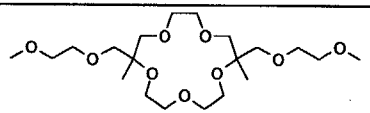
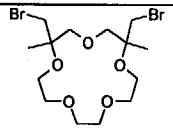
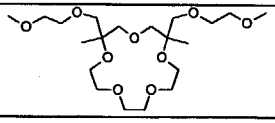
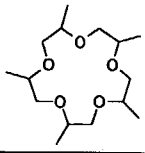
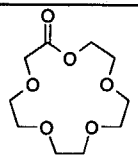
17		3.14	3.34	3.24	3.23	3.26	3.26	3.32
18		3.50	3.56	3.51	3.50	3.49	3.45	3.61
19		3.28	3.47	3.39	3.39	3.41	3.42	3.46
20		3.45	3.69	3.73	3.64	3.66	3.62	3.57
21		3.52	3.62	3.66	3.66	3.65	3.61	3.76
22		3.32	3.16	3.26	3.34	3.34	2.89	3.05
23		3.17	3.16	[c]	3.17	3.17	2.89	3.17
24		3.16	3.10	3.04	3.04	3.03	3.06	3.36

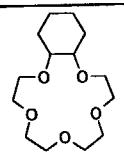
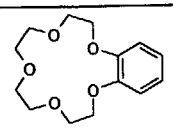
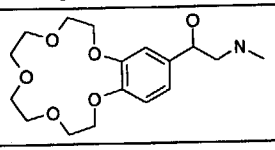
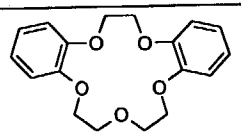
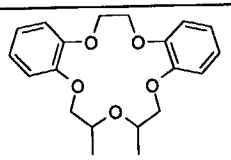
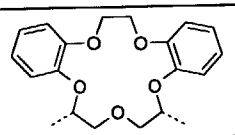
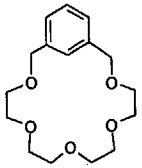
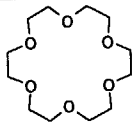
25		2.85	3.04	2.92	3.03	2.93	3.14	3.11
26		2.70	2.67	2.66	2.66	2.66	2.67	2.62
27		3.82	3.70	3.72	3.64	3.67	3.61	3.40
28		3.99	3.82	3.87	3.79	3.83	3.76	3.55
29		3.35	3.26	3.21	3.20	3.26	3.27	3.10
30		2.94	*c*	*c*	*c*	*c*	*c*	2.94
31		3.15	3.24	3.23	3.23	3.27	3.25	3.16
32		3.47	3.44	3.38	3.39	3.43	3.41	3.30

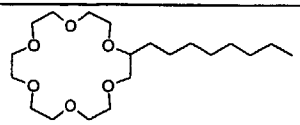
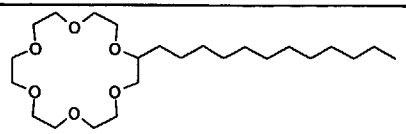
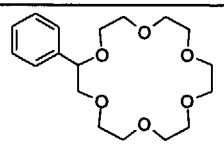
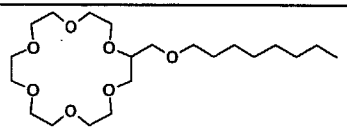
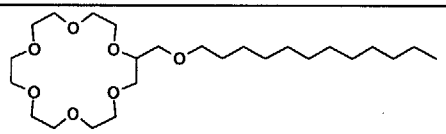
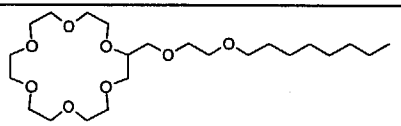
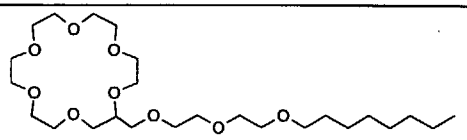
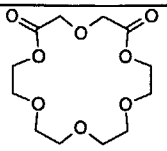
33		3.79	3.57	3.53	3.55	3.58	3.56	3.45
34		3.09	3.23	3.29	3.29	3.29	3.23	3.27
35		3.42	3.43	3.44	3.45	3.45	3.38	3.42
36		3.78	3.43	3.47	3.48	3.46	3.37	3.48
37		3.42	3.55	3.50	3.50	3.50	3.45	3.45
38		3.98	3.68	3.65	3.66	3.66	3.60	3.60
39		4.00	3.75	3.79	3.82	3.82	3.75	3.74
40		3.14	3.53	3.10	3.20	3.19	3.44	3.20
41		3.49	3.60	3.48	3.54	3.52	3.69	3.62

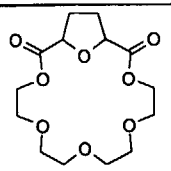
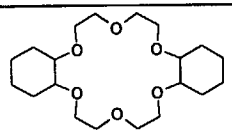
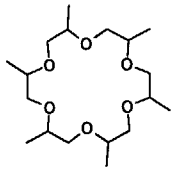
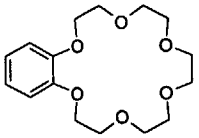
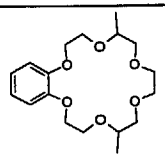
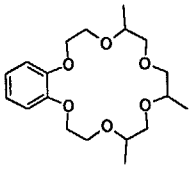
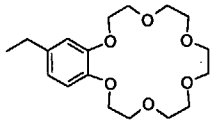
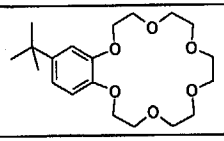
42		3.35	3.29	3.41	3.50	3.51	3.03	3.03
43		3.56	3.52	3.55	3.55	3.56	3.50	3.48
44		3.41	3.45	3.42	3.42	3.41	3.47	3.49
45		2.55	2.60	2.57	2.56	2.57	2.64	2.64
46		3.29	3.48	3.37	3.37	3.36	3.42	3.47
47		3.84	3.62	3.52	3.53	3.52	3.57	3.62
48		3.72	3.68	3.67	3.69	3.67	3.72	3.76

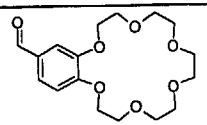
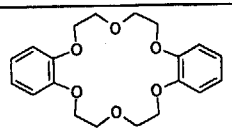
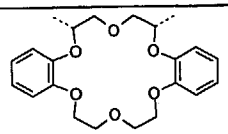
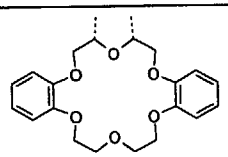
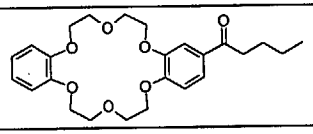
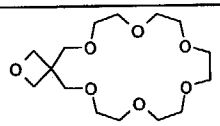
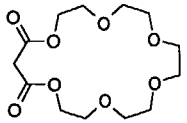
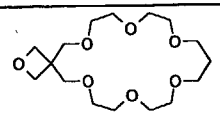
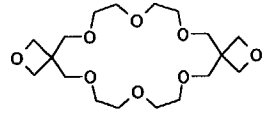
49		2.93	3.23	3.08	3.07	3.11	3.24	3.12
50		2.97	3.23	3.11	3.10	3.12	3.22	3.18
51		3.25	3.42	3.25	3.26	3.28	3.38	3.32
52		3.56	3.55	3.40	3.41	3.44	3.53	3.47
53		2.61	2.59	2.59	2.60	2.59	2.63	2.70
54		3.17	3.47	3.40	3.40	3.37	3.40	3.53
55		3.76	3.60	3.55	3.56	3.53	3.56	3.67

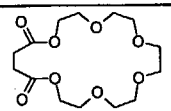
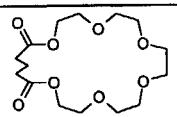
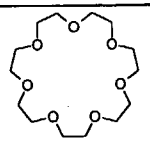
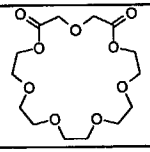
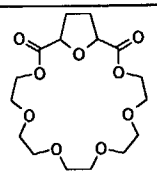
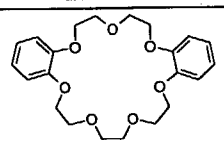
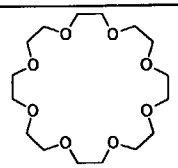
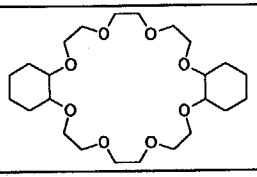
56		3.79	3.67	3.69	3.72	3.69	3.71	3.82
57		3.44	3.68	3.43	3.39	3.35	3.75	3.79
58		3.98	3.61	3.73	3.70	3.67	4.06	4.08
59		3.13	3.26	3.54	3.52	3.50	3.35	3.78
60		3.54	3.56	3.82	3.84	3.84	3.63	3.75
61		2.13	2.13	2.15	2.15	2.15	2.09	2.08
62		3.58	3.56	3.82	3.84	3.84	3.63	3.75
63		2.85	2.02	2.26	2.09	2.10	1.94	2.50
64		2.12	2.12	2.08	2.08	2.08	2.10	2.09

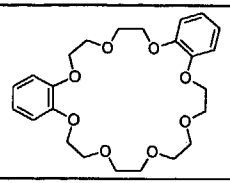
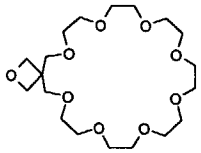
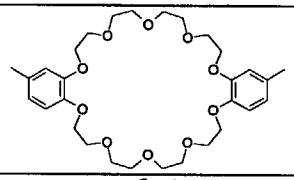
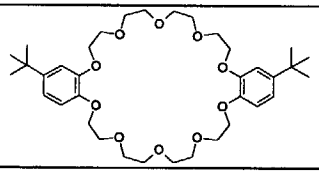
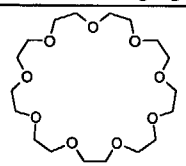
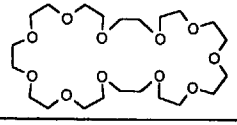
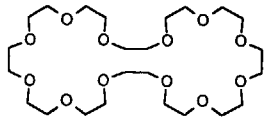
65		3.40	3.07	3.31	3.31	3.30	3.23	3.00
66		2.90	2.87	2.98	2.91	2.91	2.85	2.74
67		2.63	[c]	[c]	[c]	[c]	[c]	2.63
68		2.00	2.22	2.78	2.66	2.67	2.43	2.32
69		1.40	1.42	1.31	1.37	1.36	1.91	2.06
70		1.40	1.42	1.68	1.73	1.73	1.91	2.06
71		2.82	2.82	[c]	[c]	[c]	2.82	2.82
72		6.07	5.62	5.34	5.33	5.32	5.49	5.29

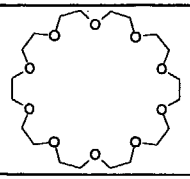
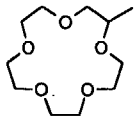
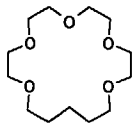
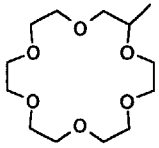
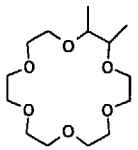
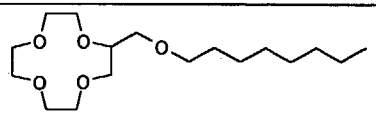
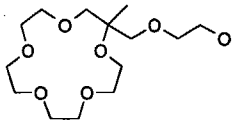
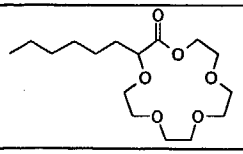
73		5.03	5.13	5.31	5.31	5.30	5.19	5.26
74		5.28	5.12	5.37	5.37	5.32	5.16	5.38
75		5.56	5.60	5.55	5.55	5.55	5.59	5.20
76		5.36	5.34	5.26	5.23	5.25	5.34	5.31
77		5.37	5.32	5.32	5.29	5.27	5.32	5.42
78		5.49	5.46	5.41	5.39	5.41	5.50	5.45
79		5.50	5.51	5.56	5.55	5.57	5.65	5.60
80		2.79	3.05	3.16	3.15	3.15	3.18	3.15

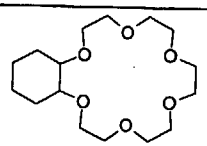
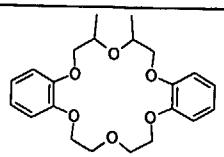
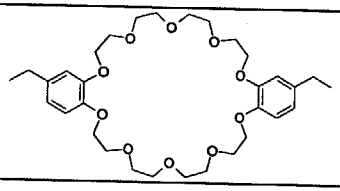
81		2.79	3.41	3.51	3.50	3.50	3.53	3.50
82		5.63	5.50	5.62	5.61	5.59	5.44	4.97
83		3.86	4.29	4.25	4.04	4.04	3.91	4.50
84		5.29	5.25	5.15	5.07	5.07	5.08	4.87
85		4.49	4.49	4.40	4.64	4.64	4.55	4.61
86		3.91	4.22	4.21	4.43	4.43	4.29	4.48
87		5.20	[c]	5.21	5.35	5.43	[c]	5.40
88		5.12	5.12	5.66	5.62	5.61	5.74	5.67

89		4.93	[c]	[c]	[c]	[c]	[c]	4.93
90		5.10	4.73	4.95	4.82	4.82	4.67	4.46
91		4.13	3.95	3.85	3.89	3.89	4.14	4.19
92		3.42	3.95	3.48	3.54	3.52	4.14	4.19
93		4.56	[c]	[c]	[c]	[c]	[c]	4.56
94		3.81	3.48	3.36	3.34	3.34	3.37	3.36
95		2.55	[c]	[c]	[c]	[c]	[c]	2.04
96		1.67	2.13	1.64	1.70	1.69	1.98	1.79
97		1.80	1.80	2.04	2.02	2.02	1.94	2.09

98		1.94	1.83	[c]	1.82	1.82	1.83	2.07
99		1.71	1.82	[c]	1.83	1.83	1.82	2.10
100		4.41	4.48	4.15	4.15	4.14	4.26	4.11
101		2.32	2.06	1.96	1.98	1.98	1.94	1.97
102		3.03	2.41	2.31	2.32	2.32	2.29	2.32
103		4.19	3.84	3.75	3.64	3.65	3.43	3.28
104		3.53	3.93	3.62	3.64	3.64	3.72	3.60
105		3.84	3.89	3.89	3.93	3.92	3.66	3.27

106		3.45	3.55	3.22	3.13	3.14	2.89	2.76
107		2.43	2.30	2.46	2.34	2.37	2.29	2.41
108		4.67	[c]	4.67	4.62	4.59	[c]	4.49
109		4.83	4.83	4.56	4.55	4.55	4.52	4.64
110		3.47	3.97	3.77	3.80	3.80	3.87	3.74
111		3.16	3.17	3.39	3.45	3.45	3.48	3.37
112		3.03	3.00	3.54	3.61	3.61	3.63	3.52

113		3.98	3.94	3.92	3.96	3.96	4.02	3.89
114		3.09[f]	**2.94**[d]	**2.80**[d]	**2.95**[d]	**2.95**[d]	**3.00**[d]	**3.03**[d]
115		2.79[g]	**2.65**[d]	**3.03**[d]	**2.82**[d]	**2.88**[d]	**2.55**[d]	**2.31**[d]
116		5.68[f]	**5.21**[d]	**4.97**[d]	**5.11**[d]	**5.10**[d]	**5.23**[d]	**5.16**[d]
117		5.49[f]	**4.88**[d]	**3.58**[d]	**4.65**[d]	**4.58**[d]	**4.96**[d]	**5.00**[d]
118		1.36	**1.54**[d]	**1.60**[d]	**1.58**	**1.61**[d]	**1.57**[d]	**1.70**[d]
119		3.36	**3.51**[d]	**3.57**[d]	**3.48**[d]	**3.51**[d]	**3.46**[d]	**3.26**[d]
120		1.90	**2.10**[d]	[e]	**2.12**[d]	**2.19**[d]	**1.99**[d]	**2.05**[d]

121		5.89	**5.34** [d]	**5.48** [d]	**5.47** [d]	**5.45** [d]	**5.46** [d]	**5.13** [d]
122		4.04	**3.95** [d]	**3.48** [d]	**3.54** [d]	**3.52** [d]	**4.14** [d]	**4.19** [d]
123		4.44	[e]	**3.65** [d]	**4.01** [d]	**4.19** [d]	[e]	**4.10** [d]

[a] Experimental data was selected from the THECOMAC database [2]. See text for fragments definitions. Unless specified, there was used fitting equation 1. [b] There was used fitting equation 2. [c] Molecule containing fragments of "rare" occurrence (i.e., found in less than two molecules) is excluded from the learning set. [d] In bold: predicted log*K* value for the validation set. [e] Learning set does not have some fragment contributions for this compound. [f] Experimental stability constant has been estimated in this work by ISE method. [g] Experimental data from the work. [43]

Table SM5. The 1:1 (M:L) complexation of crown ethers with K^+ cation in MeOH at 298 K. Fragment contributions (a_i) to stability constants log$K$ with the atom/bond sequences **I(AB, 2-4)** [a] and for additive fitting equation 1 [b].

no.	fragment	contribution a_i
1	C-C [c]	-0.161
2	C-O	0.037
3	C-O-C	0.306
4	C-C-O	0.062
5	C-C-O-C	-0.150
6	O-C-C-O	0.103
7	C-C-C	0.217
8	C-C-C-O	-0.100
9	C.C [c]	-0.207
10	C-C.C; C-C.C.C [d]	0.440
11	C.C.C	-0.005
12	C.C-C-O	0.040
13	C.C.C.C	0.200
14	C-C-C-C	-0.027
15	C-C-C.C	-0.124
16	C.C-O; C-O-C.C; C.C.C-O [d]	0.035
17	O-C.C-O	-0.120
18	Br-C; Br-C-C; Br-C-C-C; Br-C-C-O [d]	-0.490
19	C-N; C-N-C; N-C-C-O [d]	-0.626
20	C-C-N; C-C-N-C [d]	0.020
21	C-C-C-N	0.353
22	C.N; C.N.C; C.C.N; C.C.N.C; C.C.C.N; N.C.C-O [d]	0.405
23	C=O [c]	-0.086
24	O-C=O; C-O-C=O	0.085
25	C-C=O	0.106
26	O-C-C=O	-1.176
27	C-C-C=O	0.046
28	C.C-C=O	-0.342
29	a_{cycl} [e]	0.662
30	a_0 [f]	1.105

[a] See text for fragments definition.
[b] The learning set contains stability constants (log$K$) of (K^+)L complexes of 113 crown ethers (L) including standard macrocycles (-CH2-CH2-O-)$_n$, where n = 4-12, 14-crown-4, 18-crown-5, 19-crown-6, 20-crown-6, 21-crown-6 25-crown-8 and their benzo, dibenzo- cyclohexyl, dicyclohehyl, and lariate derivatives, which have been critically selected from the THECOMAC database [2].
[c] C-C, C=O and C.C are molecular fragments with single, double and aromatic bond accordingly.
[d] Linearly dependent fragments in learning set form one group as an extended fragment.
[e] "Cyclicity" descriptor a_{cycl} has been used for taking into account of "macrocyclic effect".
[f] The a_o term is fragment independent.

Table SM6. The 1:1 (M:L) complexation of crown ethers with K^+ cation in MeOH at 298 K. Fragment contributions (a_i) to stability constants log*K* with the **II(Hy)** fragments [a] and for additive fitting equation 1 [b].

no.	fragment	contribution a_i
1	C(C'O') [c]	0.034
2	O(C'C')	0.084
3	C(C'C'O')	0.033
4	O(C')	-0.130
5	C(O'CB')	0.124
6	CB(CB'CB') [c]	-0.275
7	CB(C'CB'CB')	0.934
8	C(C'C')	-0.006
9	C(C')	-0.263
10	C(C'O'CB')	0.569
11	C(O')	-0.226
12	O(C'CB'); CB(O'CB'CB') [d]	0.462
13	C(C'C'C'O')	0.439
14	C(C'Br'); Br(C') [d]	-0.728
15	CB(CB'CB'CB'); CB(CB'CB'NI'); CB(CB'NI'); NI(CB'CB') [c, d]	0.977
16	O(C'CO'); CO(C'O'O'); O(CO') [d]	-0.452
17	C(O'CO')	-0.553
18	C(C'O'CO')	-0.372
19	C(C'C'C'CB')	0.241
20	C(C'C'C'C')	-0.195
21	C(C'CO')	0.472
22	a_{cycl} [e]	0.694
23	a_0 [f]	1.109

[a] See text for fragments definition.

[b] The learning set contains stability constants (log*K*) of (K^+)L complexes of 113 crown ethers (L) including standard macrocycles $(-CH_2-CH_2-O-)_n$, where n = 4-12, 14-crown-4, 18-crown-5, 19-crown-6, 20-crown-6, 21-crown-6 25-crown-8 and their benzo, dibenzo- cyclohexyl, dicyclohehyl, and lariate derivatives, which have been selected from the THECOMAC database [2].

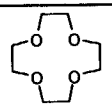
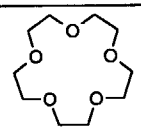
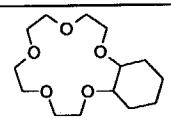
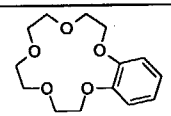
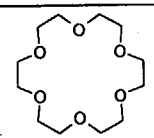
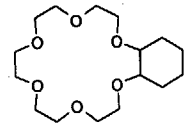
[c] C(C'O'), CB(C'CB'CB'), NI(CB'CB') are molecular fragments with sp^3 carbon, sp^2 carbon and sp^2 nitrogen accordingly.

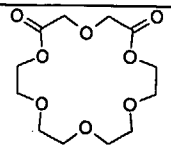
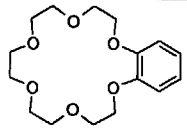
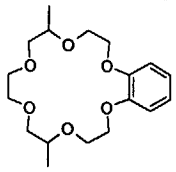
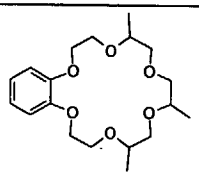
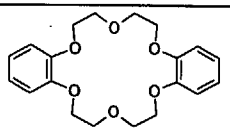
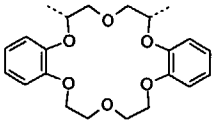
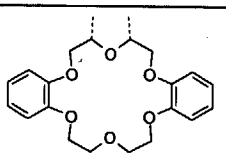
[d] Linearly dependent fragments in learning set form one group as an extended fragment.

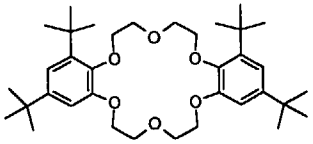
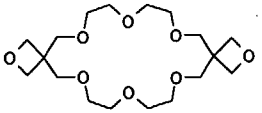
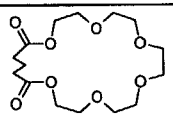
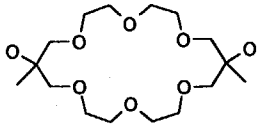
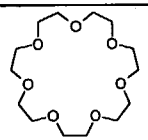
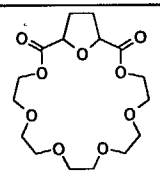
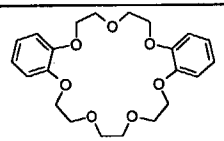
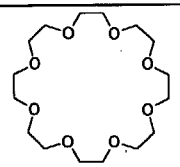
[e] "Cyclicity" descriptor a_{cycl} has been used for taking into account of "macrocyclic effect".

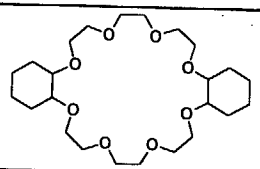
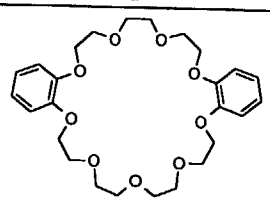
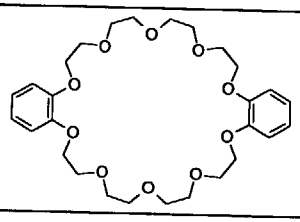
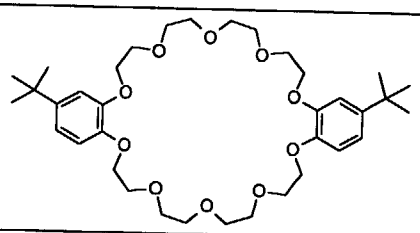
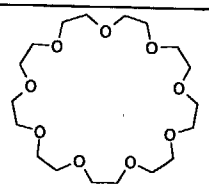
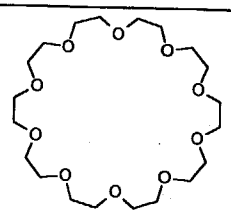
[f] The a_o term is fragment independent.

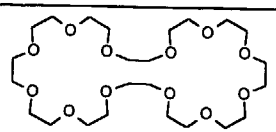
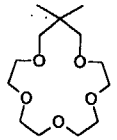
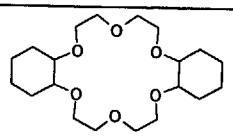
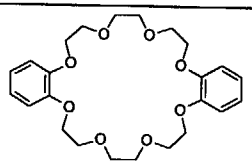
Table SM7. The 1:1 (M:L) complexation of crown ethers with Cs^+ cation in MeOH at 298 K. Experimental and calculated stability constants (Log*K*) for learning set using **I(A**, 4-5), **I(A**, 2-4), **I(A**, 3-5), **I(AB**, 2-4), **II(A)** and **II(B)** fragments sets. Crown ethers 29-31 were used as test (validation) compounds[a].

no.	ligand	Log*K*						
		exp	predicted					
			I(A, 4-5)	**I(A**, 2-4)	**I(A**, 3-5)	**I(AB**, 2-4)	**II(A)**[b]	**II(B)**
1		1.6	1.83	1.84	1.83	1.78	1.80	1.80
2		3.58	3.53	3.55	3.53	3.53	3.54	3.47
3		3.53	3.32	3.30	3.32	3.44	3.29	3.42
4		3.52	3.32	3.30	3.32	3.23	3.29	3.21
5		4.79	4.53	4.56	4.53	4.55	4.57	4.47
6		4.30	4.32	4.30	4.32	4.47	4.39	4.41

7		2.55	2.55	2.55	2.55	2.55	2.61	2.62
8		3.95	4.32	4.30	4.32	4.25	4.39	4.21
9		3.38	3.42	3.27	3.42	3.28	3.37	3.26
10		2.99	2.97	2.75	2.97	2.80	2.99	2.78
11		3.66	4.10	4.05	4.10	3.95	3.82	3.95
12		2.63	2.64	3.02	2.64	2.98	2.79	3.00
13		2.94	2.92	3.02	2.92	2.98	2.79	3.00

14		3.17	3.17	3.17	3.17	[c]	3.17	3.44
15		0.8	0.80	0.80	0.80	0.80	0.80	0.80
16		1.02	1.02	1.02	1.02	1.02	1.00	0.99
17		1.9	1.90	1.90	1.90	1.90	[c]	[c]
18		5.01	4.82	4.86	4.82	4.85	4.88	4.79
19		2.64	2.64	2.64	2.64	2.64	2.61	2.60
20		4.25	4.39	4.34	4.39	4.25	4.27	4.27
21		4.15	4.06	4.08	4.06	4.07	4.15	4.08

22		3.95	3.63	3.57	3.63	3.91	3.67	3.97
23		3.67	3.56	3.51	3.56	3.42	3.71	3.54
24		4.0	3.86	3.81	3.86	3.72	4.05	3.86
25		4.15	4.15	4.15	4.15	[c]	4.15	3.60
26		3.95	3.99	4.02	3.99	4.02	4.06	4.06
27		4.15	4.29	4.32	4.29	4.32	4.27	4.38

28		3.98	4.16	4.20	4.16	4.20	3.89	4.33
29		1.73	[e]	**2.51** [d]	**1.21** [d]	**1.07** [d]	**1.50** [d]	**0.64** [d]
30		4.25	**4.10** [d]	**4.05** [d]	**4.10** [d]	**4.38** [d]	**3.82** [d]	**4.36** [d]
31		3.85	**3.62** [d]	**3.57** [d]	**3.62** [d]	**3.47** [d]	**3.67** [d]	**3.56** [d]

[a] Experimental data was selected from the THECOMAC database [2]. See text for fragments definitions. Unless noted otherwise, there was used fitting equation 1. [b] There was used fitting equation 2. [c] Molecule containing fragments of "rare" occurrence (i.e., found in less than two molecules) is excluded from the learning set. [d] In bold: predicted log*K* value for the validation set. [e] Learning set does not have some fragment contributions for this compound.

Table SM8. The 1:1 (M:L) complexation of crown ethers with Cs^+ cation in MeOH at 298 K. Fragment contributions (a_i) to stability constants log$K$ with the atom/bond sequences **I**(**AB**, 2-4)[a] and for additive fitting equation 1 [b].

no.	fragment	contribution a_i
1	C-C [c]	-0.002
2	C-O	0.303
3	C-O-C	0.122
4	C-C-O	-0.122
5	C-C-O-C	-0.243
6	O-C-C-O	0.306
7	C-C-C	0.014
8	C-C-C-C	0.366
9	C-C-C-O	-0.131
10	C.C; C.C-O; C.C.C; O-C.C-O; C.C.C-O; C.C.C.C; C-O-C.C [c, d]	-0.121
11	C=O; O-C=O; C-C=O; C-O-C=O [c, d]	-0.539
12	O-C-C=O	-0.460
13	C-C-C=O	-0.244
14	a_{cycl} [e]	0.360
15	a_0 [f]	0.571

[a] See text for fragments definition.
[b] The learning set contains stability constants (log$K$) of (Cs^+)L complexes of 28 crown ethers (L) including: standard macrocycles (-CH2-CH2-O-)$_n$, where n = 5-10, 12; 20-crown-6, 21-crown-6, and some their benzo, dibenzo- cyclohexyl, dicyclohehyl, carbonyl and lariate derivatives, which have been critically selected from the THECOMAC database [2].
[c] C-C, C=O and C.C are molecular fragments with single, double and aromatic bond accordingly.
[d] Linearly dependent fragments in learning set form one group as an extended fragment.
[e] "Cyclicity" descriptor a_{cycl} has been used for taking into account of "macrocyclic effect".
[f] The a_o term is fragment independent.