Electronic Supplementary Information for

Chemically controlled self-assembly of [2]pseudorotaxanes based on 1,2-bis(benzimidazolium)ethane cations and 24-crown-8 macrocycles

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Computational Details

Kohn-Sham calculations within the linear combination of gausian type orbitals (LCGTO-KS), and using the variational fitting of the electron density as implemented in the suite of programs deMon2k,[1] were done to estimate the interaction energies between the dibenzo-24-crown-8 ether and bis(benzimidazole)ethane with different number of protons attached. The calculations were done with the GGA exchange-correlation functional of Perdew, Ernzerhof and Burke (PBE),[2] using a double-zeta with polarization orbital basis set, and with an automatically generated auxiliary basis set containing s, p, d, f, and g Hermite Gaussian functions. All the structures were fully optimized without symmetry restrictions. Several conformations of the crown ether and the pseudorotaxanes were tested. In Figure 1 the behaviour of the interaction energy of the pseudorotaxane with respect to the charge is depicted. As it can be seen there is a clear increase of the pseudorotaxane stability as one increases the number of protons in the system. One could expect that hydrogen bonding is the main factor contributing to the stability. However, this idea is not fully supported by the calculations done in the present work, since for the neutral and the monocation the number of hydrogen contacts found after the geometry optimization is two, while for the dication there are three hydrogen contacts. We believe that this result indicates that the binding energy between the crown ether and the bis(benzimidazolium)ethane has other important contributions, like electrostatic. It is also worth to note that in the present theoretical study, van der Waals interactions (non-bonded) were not included. Nevertheless, the results clearly support the observed experimental fact regarding the feasibility of obtaining the pseudorotaxane with the doubly protonated bis(benzimidazole)ethane. The frequency analyses for the full pseudorotaxanes were not done since they are highly demanding computational tasks. Thus, no zero point energy (ZPE) correction and basis set superstition error (BSSE) were included in the reported interaction energies. One can anticipate that these corrections can make an important difference in the neutral pseudorotaxane, probably even making it energetically unfeasible. But this will not be the case for the dication. In summary, the calculations reported in this work support the existence of the dicationic pseudorotaxane and that its stability is due to an increase in the positive charge and also to the number of hydrogen contacts prevailing in this species.

References

1. A. M. Köster, P. Calaminici, M. E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J. M. d. Campo, S. Patchkovskii, J. U. Reveles, D. R. Salahub and A. Vela, deMon developers, 2006.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.

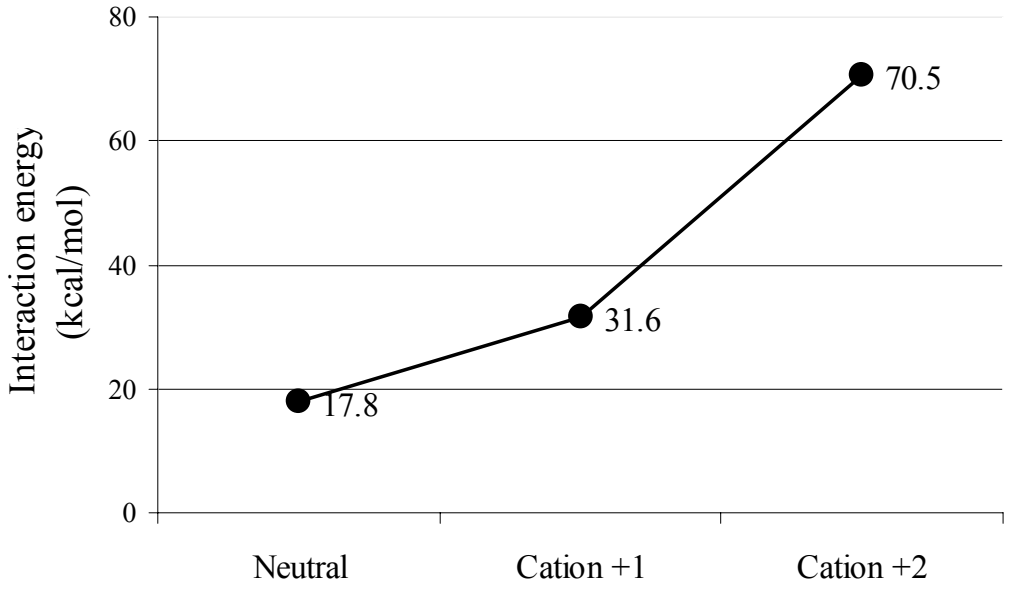
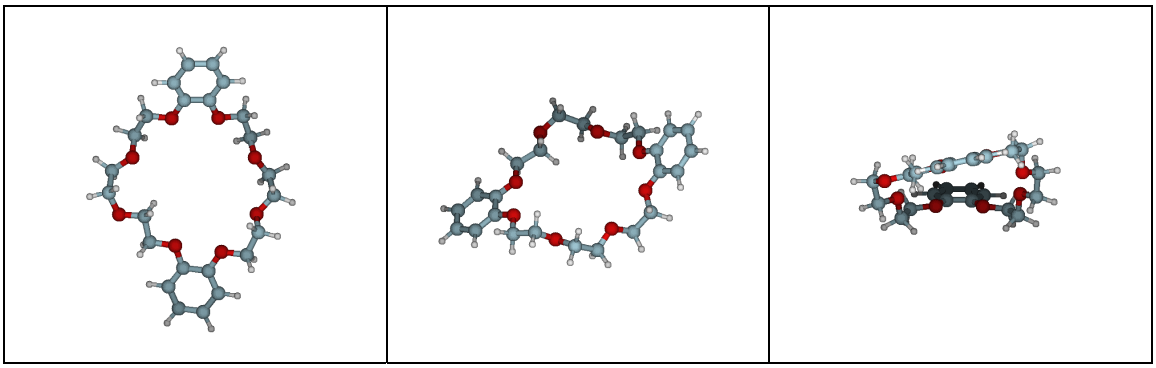


Figure 1. Interaction energy (kcal/mol) between **DB24C8** wheel and 1,2-bis(benzimidazolium)ethane axle with different number of protons added.

Figure 2. Three views of the optimized structure of the free dibenzo-24-crown-8 and the corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, oxygen atoms as red spheres, and hydrogen as white spheres.



64
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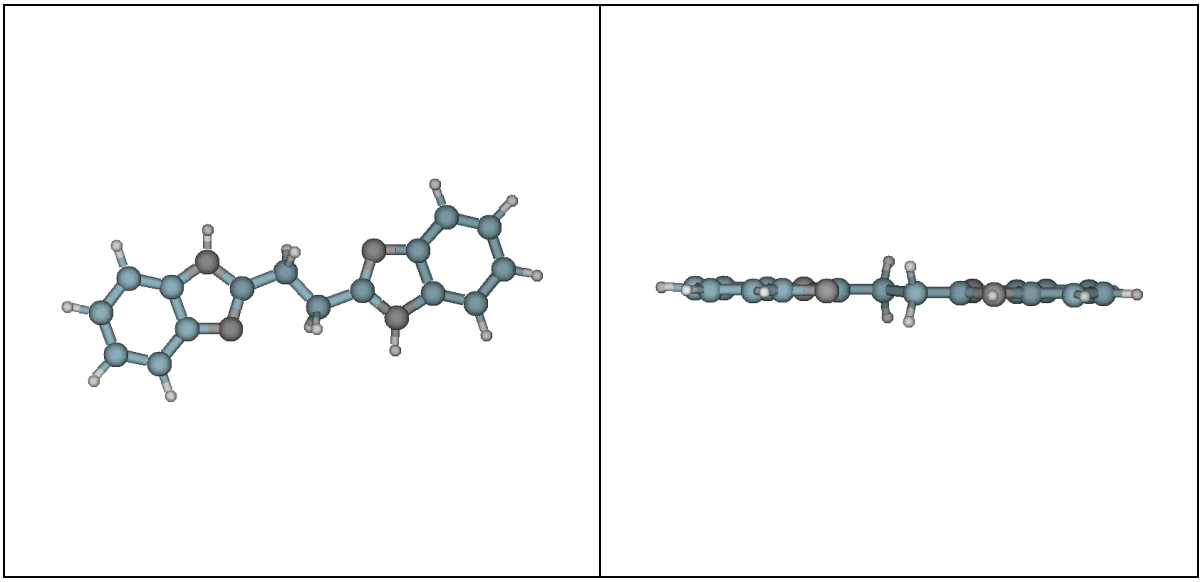
C	-1.212430	-0.001843	2.121657	H	5.634474	-1.534710	-11.317387
C	-2.428599	-0.006385	1.435287	H	3.432163	-0.939238	-12.364541
C	-2.442170	-0.011105	0.026108	H	-3.374970	-0.007161	1.981617
C	-1.242036	-0.010112	-0.701405	H	-1.190468	-0.000710	3.214216
O	-1.153677	-0.020011	-2.072212	H	-4.426233	0.202943	-6.575694
C	-2.395350	-0.058428	-2.785469	H	5.522261	-2.376299	-6.841971
C	2.380762	-0.009563	-0.089553	H	-1.475931	-0.985344	-4.530977
C	3.516548	-0.030372	-1.092571	H	-1.533528	0.801414	-4.592665
O	3.580489	-1.303676	-1.733124	H	-0.223189	-0.955395	-9.523412
C	4.858892	-1.521648	-2.335725	H	-0.067270	-2.670047	-10.036992
C	4.823477	-2.790801	-3.173744	H	-3.003238	0.836973	-2.561571
O	4.544841	-2.449199	-4.534930	H	-2.978628	-0.954237	-2.504299
C	4.543969	-3.597747	-5.382264	H	2.452459	-0.899911	0.562115
C	4.751905	-3.168618	-6.822386	H	-2.743892	0.807717	-6.657882
O	3.516518	-2.691322	-7.374972	H	3.602408	-4.172488	-5.279670
C	3.568606	-2.241285	-8.672104	H	5.112582	-4.029924	-7.416534
C	4.745877	-2.104222	-9.425624	H	5.385526	-4.269515	-5.110852
C	4.704213	-1.634829	-10.752945	H	2.474848	0.898172	0.537131
C	3.479417	-1.304914	-11.335997	H	5.145610	-0.676257	-2.991757
C	2.289413	-1.448023	-10.596077	H	4.057213	-3.475840	-2.760700
C	2.315417	-1.913452	-9.271592	H	-0.919821	-3.242216	-7.618909
O	1.200310	-2.102116	-8.488351	H	3.388400	0.778239	-1.839315
C	-0.060240	-1.988390	-9.165175	H	-3.218564	-2.186683	-6.464081
C	-1.199873	-2.366729	-8.235535	H	5.806399	-3.304365	-3.116921
O	-1.579216	-1.256602	-7.413000	H	-2.055942	-2.661171	-8.875457
C	-2.972067	-1.298398	-7.080398	H	4.452980	0.168755	-0.529987
C	-3.381039	-0.034019	-6.321829	H	5.630349	-1.614048	-1.542371
O	-3.381674	-0.150968	-4.899383	H	-3.567554	-1.365861	-8.016088
C	-2.090167	-0.102134	-4.278901				
H	5.709253	-2.364002	-8.985555				

Figure 3. Two views of the optimized structure of the neutral bis(benzimidazole)ethane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and hydrogen as white spheres.



34
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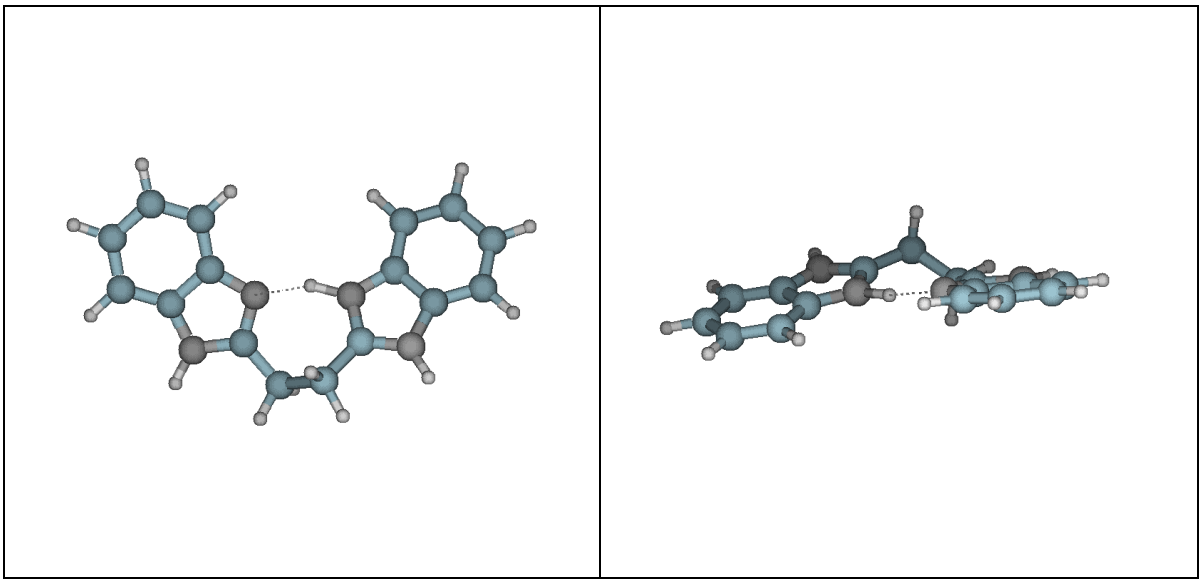
C	1.249552	0.000736	2.021950
C	2.436388	0.001046	-0.119205
C	2.446514	0.001400	1.276158
N	-1.018463	-0.001068	-0.943460
N	0.893378	-0.001419	-2.131195
C	-0.427326	-0.001562	-2.197722
H	-2.016599	0.000027	-0.756103
C	-1.250210	-0.006091	-3.446367
C	-0.390381	0.015660	-4.710794
C	-1.224991	0.022225	-5.952185
N	-2.546032	0.034565	-5.998599
C	-2.868500	0.039524	-7.354568
C	-4.121986	0.052870	-7.981840
C	-4.158296	0.054749	-9.376319
C	-2.974868	0.043623	-10.143172
C	-1.714429	0.030419	-9.540283
C	-1.686689	0.028810	-8.143529
N	-0.653090	0.017062	-7.215771
H	0.342010	0.008623	-7.418569
H	-0.922784	-0.000581	1.978865
H	-0.802733	0.021856	-10.139851
H	3.360609	0.001058	-0.698322
H	-5.035015	0.061922	-7.385260
H	-3.044534	0.045264	-11.232025
H	1.299861	0.000677	3.111730
H	3.400545	0.001870	1.805354
H	-5.122054	0.065289	-9.887660
H	0.287208	-0.854057	-4.713125
H	-1.906185	-0.892291	-3.462977
H	0.270397	0.898266	-4.692454
H	-1.934255	0.858548	-3.452900

Figure 4. Two views of the optimized structure of the singly protonated bis(benzimidazole)ethane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and hydrogen as white spheres.



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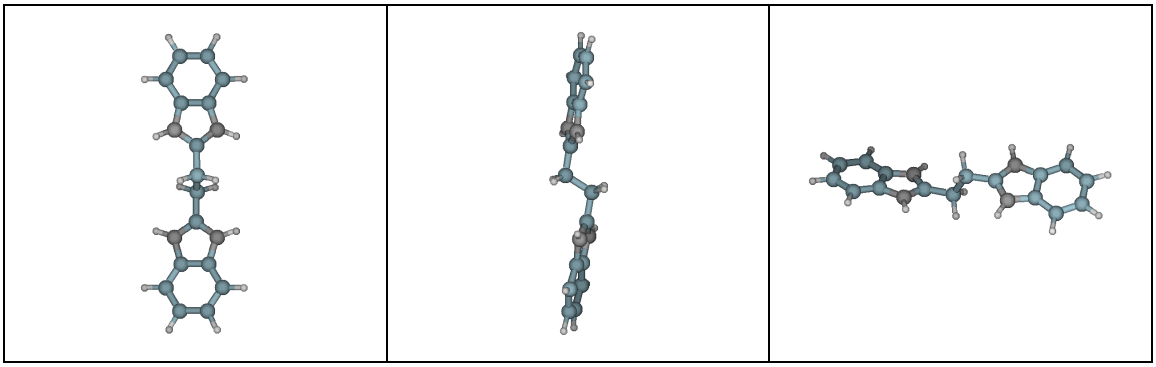
C	1.316907	-0.001371	1.798389
C	1.853893	0.002487	3.089563
C	3.243290	-0.000499	3.189856
C	4.071687	-0.004768	2.047641
C	3.544264	-0.005645	0.757455
C	2.151309	-0.005249	0.658040
H	1.562259	-0.001824	-1.418503
C	-1.217500	-0.041440	-0.867476
H	1.216421	0.007378	3.973082
H	4.188301	-0.008179	-0.121585
H	5.153775	-0.006621	2.178081
H	3.704377	0.000874	4.177468
H	-0.922087	0.241855	-1.888611
C	-2.384160	0.876951	-0.424480
C	-3.109303	0.446927	0.818146
N	-2.536685	0.037340	1.948277
N	-4.474848	0.469394	0.934703
C	-4.809143	0.052749	2.221639
C	-6.034063	-0.111700	2.873325
C	-5.979210	-0.563441	4.190897
C	-4.751918	-0.842345	4.829245
C	-3.533956	-0.678836	4.174025
C	-3.570035	-0.222551	2.849534
H	-5.128533	0.752262	0.209313
H	-6.908523	-0.706107	4.742521
H	-2.588120	-0.896312	4.670457
H	-6.985369	0.101824	2.385611
H	-4.761089	-1.194274	5.861019
H	-3.103168	0.917324	-1.255874
H	-1.570676	-1.085588	-0.923410
H	-2.011285	1.906818	-0.291277
H	-0.990323	-0.013390	1.852327

Figure 5. Three views of the optimized structure of the doubly protonated bis(benzimidazole)ethane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and hydrogen as white spheres.



36
TOTAL ENERGY = -836.929842918

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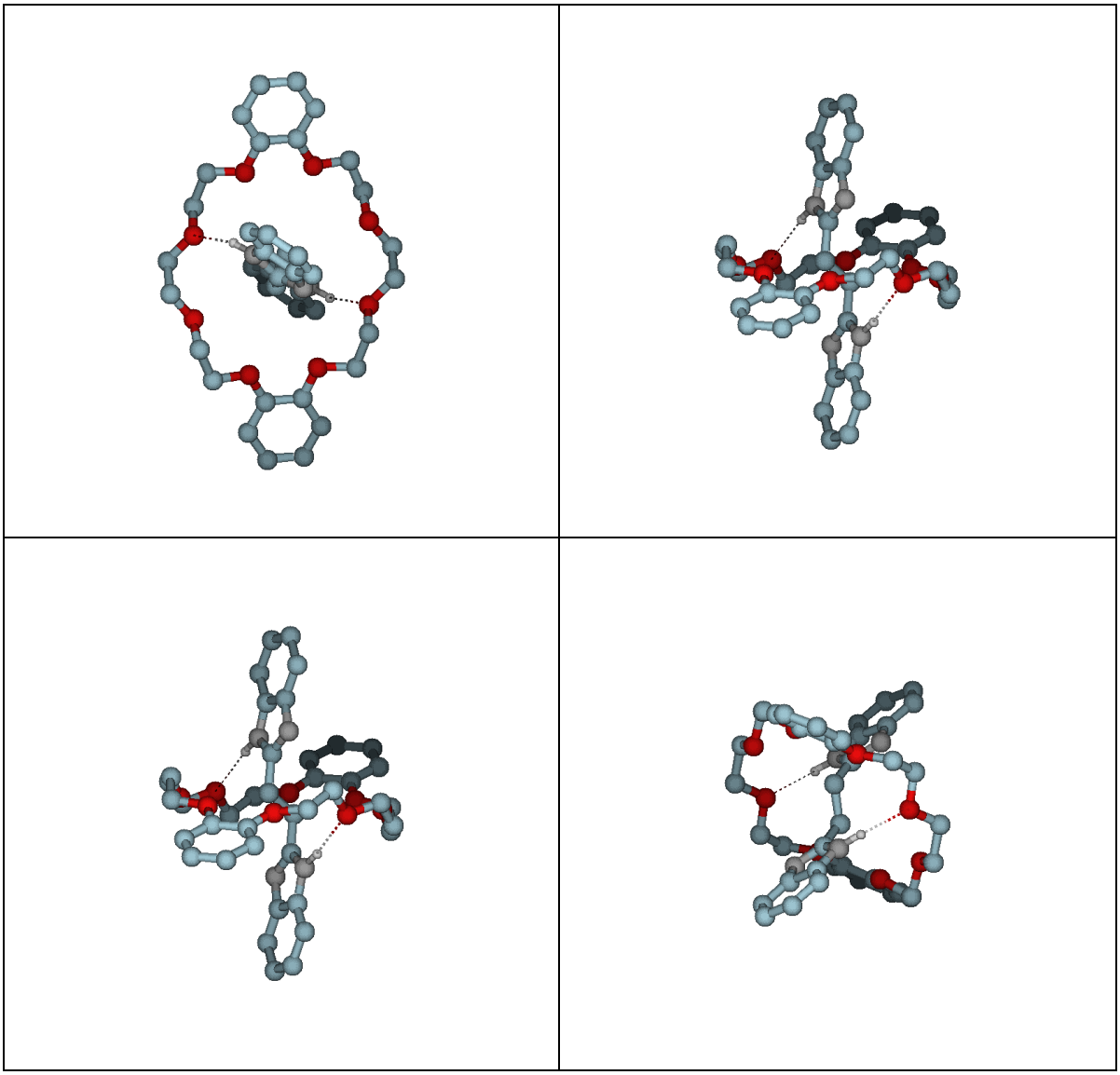
N	2.691518	-1.105190	0.079221
C	4.016762	0.696729	0.254845
C	5.187974	1.458284	0.248300
C	6.359618	0.774582	-0.066701
C	4.022596	-0.685154	-0.035626
C	5.199185	-1.369934	-0.349048
C	6.364789	-0.607723	-0.359809
H	2.373047	-2.066668	-0.033749
H	2.351734	1.948679	0.798185
C	0.415501	-0.110064	0.637070
H	5.191463	2.524248	0.475161
H	5.212364	-2.436985	-0.570606
H	7.302056	1.322059	-0.085009
H	7.311416	-1.091176	-0.601496
H	0.134100	0.748410	1.265149
H	0.173623	-1.009009	1.225686
C	-0.422395	-0.095942	-0.685798
C	-1.898622	-0.060672	-0.452277
N	-2.692189	1.029517	-0.543738
N	-2.687343	-1.100306	-0.099215
C	-4.020675	0.697713	-0.251875
C	-5.193717	1.455542	-0.224909
C	-6.358339	0.768265	0.107804
C	-4.017653	-0.684315	0.037784
C	-5.186954	-1.372134	0.371111
C	-6.355010	-0.614575	0.399100
H	-2.365420	-2.061399	0.005927
H	-2.367603	1.953626	-0.827796
H	-5.192073	-2.438631	0.594302
H	-5.206546	2.521303	-0.451044
H	-7.296173	-1.102597	0.651166
H	-7.301935	1.312652	0.141584
H	-0.146411	0.778008	-1.294391
H	-0.181430	-0.980780	-1.296050

Figure 6. Four views of the optimized structure of the neutral pseudorotaxane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and oxygen atoms as red spheres. Hydrogen atoms are deleted, keeping only those involved in hydrogen contacts, which are shown as white spheres. The dashed lines indicate the hydrogen contacts where the H…O distance is smaller than the sum of its van der Waals radii.



98
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N	1.276700	0.000000	-0.536696	H	3.835786	0.004717	4.014587
C	2.172484	-0.008979	0.521709	H	-2.074650	0.256513	-0.263278
C	3.573884	-0.010306	0.587797	H	-1.112238	0.738256	-1.665290
C	4.148803	-0.005990	1.868206	C	-1.419703	-1.415392	-1.529554
C	1.348124	-0.003423	1.688787	C	-2.647840	-1.443941	-2.379095
C	1.947702	0.003360	2.962354	N	-2.683782	-1.459980	-3.710042
C	3.347746	0.001482	3.036023	N	-3.910309	-1.423049	-1.809062
C	-1.209079	-0.024173	-0.876597	C	-4.833521	-1.419448	-2.843096
H	1.475586	-0.021574	-1.541947	C	-6.236173	-1.404622	-2.872082
H	1.329192	0.009842	3.863636	C	-6.844863	-1.419258	-4.136621

C	-4.040788	-1.448565	-4.031561
C	-4.673977	-1.465513	-5.288717
C	-6.075460	-1.449970	-5.325225
H	-4.081878	-1.390837	-0.798531
H	-6.833329	-1.374507	-1.956713
H	-4.079516	-1.489592	-6.205769
H	-7.935952	-1.403802	-4.204846
H	-6.589699	-1.460271	-6.290270
H	-0.563711	-1.689206	-2.158764
H	-1.498431	-2.179332	-0.740204
O	-3.814510	-1.671169	1.241223
C	-3.451031	-2.932644	1.832594
C	-3.641932	-0.593633	2.188586
C	-4.572403	0.557945	1.857755
O	-4.015243	1.361566	0.805191
C	-4.726024	2.492603	0.464264
C	-6.036752	2.762879	0.887058
C	-6.695247	3.942354	0.489449
C	-6.039429	4.860295	-0.333001
C	-4.720400	4.607846	-0.755403
C	-4.049904	3.437438	-0.364270
O	-2.755691	3.127200	-0.709576
C	-2.024957	4.152878	-1.399052
C	-0.586617	3.717719	-1.605542
O	-0.517690	2.745675	-2.653220
C	0.804258	2.612769	-3.183653
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O	-2.123608	-4.173649	0.257382
C	-2.057408	-5.138720	-0.796979
C	-0.621190	-5.584251	-0.996303
O	0.123624	-4.557894	-1.669911
C	1.423439	-4.867444	-1.993444
C	2.087209	-6.039000	-1.594546
C	3.414373	-6.288666	-1.992736
C	4.085053	-5.366889	-2.798896
C	3.432628	-4.187065	-3.205550
C	2.113630	-3.920245	-2.807431
O	1.406736	-2.790397	-3.160637
C	1.979774	-1.985323	-4.203102
C	1.048229	-0.841330	-4.556635
O	1.193824	0.241537	-3.612003
C	0.817478	1.494375	-4.214291
H	3.967366	-3.476162	-3.836643
H	1.574321	-6.771211	-0.969814
H	-6.560020	2.054972	1.530989
H	-4.218901	5.337193	-1.392688
H	5.113179	-5.551373	-3.119403
H	3.908915	-7.207533	-1.668629
H	-7.716664	4.129321	0.829581
H	-6.539241	5.778532	-0.650972
H	-2.483589	4.361636	-2.382557
H	-0.173078	-5.805684	-0.010559
H	-0.187986	1.422069	-4.667968
H	-2.446304	-2.873303	2.289710
H	2.138207	-2.611292	-5.100855
H	-4.707970	1.183537	2.759368
H	-5.556962	0.149271	1.562662
H	-0.616437	-6.507218	-1.606357
H	2.955437	-1.568884	-3.889392
H	-2.031938	5.081226	-0.797542
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H	-3.924246	-0.955287	3.196338
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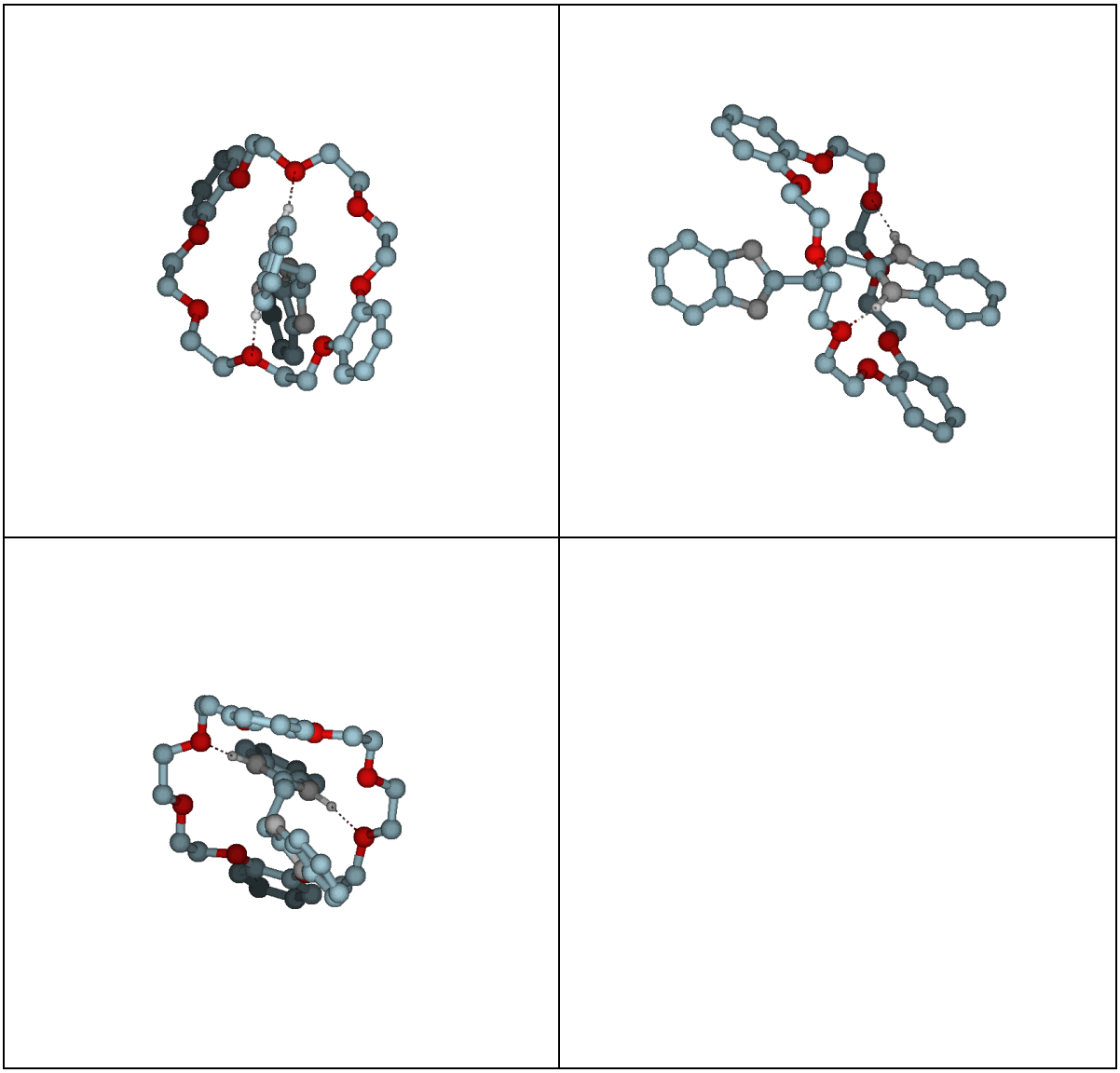
H	1.346867	-0.481964	-5.560681
H	1.542502	2.398553	-2.385437
H	-4.183829	-3.818907	-0.002444
H	1.544512	1.734571	-5.015499
H	-4.182694	-3.174343	2.629256
H	-0.007122	4.620574	-1.887655
H	1.104838	3.563759	-3.669518
H	-2.646039	-6.038619	-0.524740
H	-3.745890	-4.995838	1.271186

Figure 7. Three views of the optimized structure of the singly protonated pseudorotaxane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and oxygen atoms as red spheres. Hydrogen atoms are deleted, keeping only those involved in hydrogen contacts, which are shown as white spheres. The dashed lines indicate the hydrogen contacts where the H…O distance is smaller than the sum of its van der Waals radii.



99
FINAL HEAT OF FORMATION = -2370.628755

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N	1.278707	0.000000	-0.433305	H	5.160141	0.165878	2.177699
C	1.313895	0.041800	1.813819	H	3.715715	0.151972	4.191639
C	1.853749	0.077828	3.107053	H	-2.006195	-0.542383	-0.412306
C	3.250460	0.120080	3.203855	H	-0.927811	-0.508651	-1.812820
C	2.140694	0.045825	0.662263	C	-1.653031	1.472169	-1.237497
C	3.538125	0.086304	0.761885	C	-2.432284	1.489398	-2.516144
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C	-1.190803	0.023567	-0.885944	N	-3.666886	0.877506	-2.653768
H	-0.880833	0.060756	1.899151	C	-4.053727	1.014843	-3.982074
H	1.509769	0.094630	-1.443394	C	-5.189328	0.592799	-4.689453

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C	-3.067325	2.079824	-5.955510
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H	-4.280481	1.905041	-7.733301
H	-6.101916	0.622353	-6.644379
H	-5.996121	0.030869	-4.211373
H	-0.785390	2.132564	-1.373657
H	-2.248404	1.878318	-0.403159
O	-2.614082	-0.072236	2.371086
C	-3.179557	0.957418	3.211849
C	-3.149165	-1.391656	2.622557
C	-2.888548	2.315687	2.604816
O	-1.475008	2.482916	2.495788
C	-1.132044	3.799614	2.033907
C	0.371172	3.989410	2.052575
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C	2.301230	3.719837	0.679916
C	3.118501	4.321035	1.650728
C	4.459564	4.640743	1.371235
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C	4.186887	3.754111	-0.869909
C	2.852108	3.412835	-0.597886
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C	1.571847	1.804015	-3.673401
O	1.542495	0.413693	-3.248440
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C	0.856461	-1.858250	-3.883248
O	-0.484440	-1.909791	-3.381363
C	-0.957302	-3.243351	-3.147713
C	-2.474345	-3.252001	-3.161091
O	-2.978324	-2.677571	-1.938528
C	-4.349803	-2.635185	-1.808327
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O	-3.897902	-1.868246	0.403816
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H	2.717785	4.550349	2.638711
H	-6.629591	-1.831430	0.639124
H	-8.210729	-2.443065	-1.166804
H	-7.336136	-3.193535	-3.394048
H	6.024131	4.626139	-0.128950
H	5.072078	5.113470	2.142275
H	-2.343854	-2.106827	2.395188
H	-3.416949	-1.500634	3.687853
H	-2.826226	-2.674192	-4.033807
H	0.588133	5.072326	2.072561
H	0.262907	-0.038040	-4.847697
H	-4.274867	0.835974	3.288510
H	-2.829347	-4.294583	-3.251671
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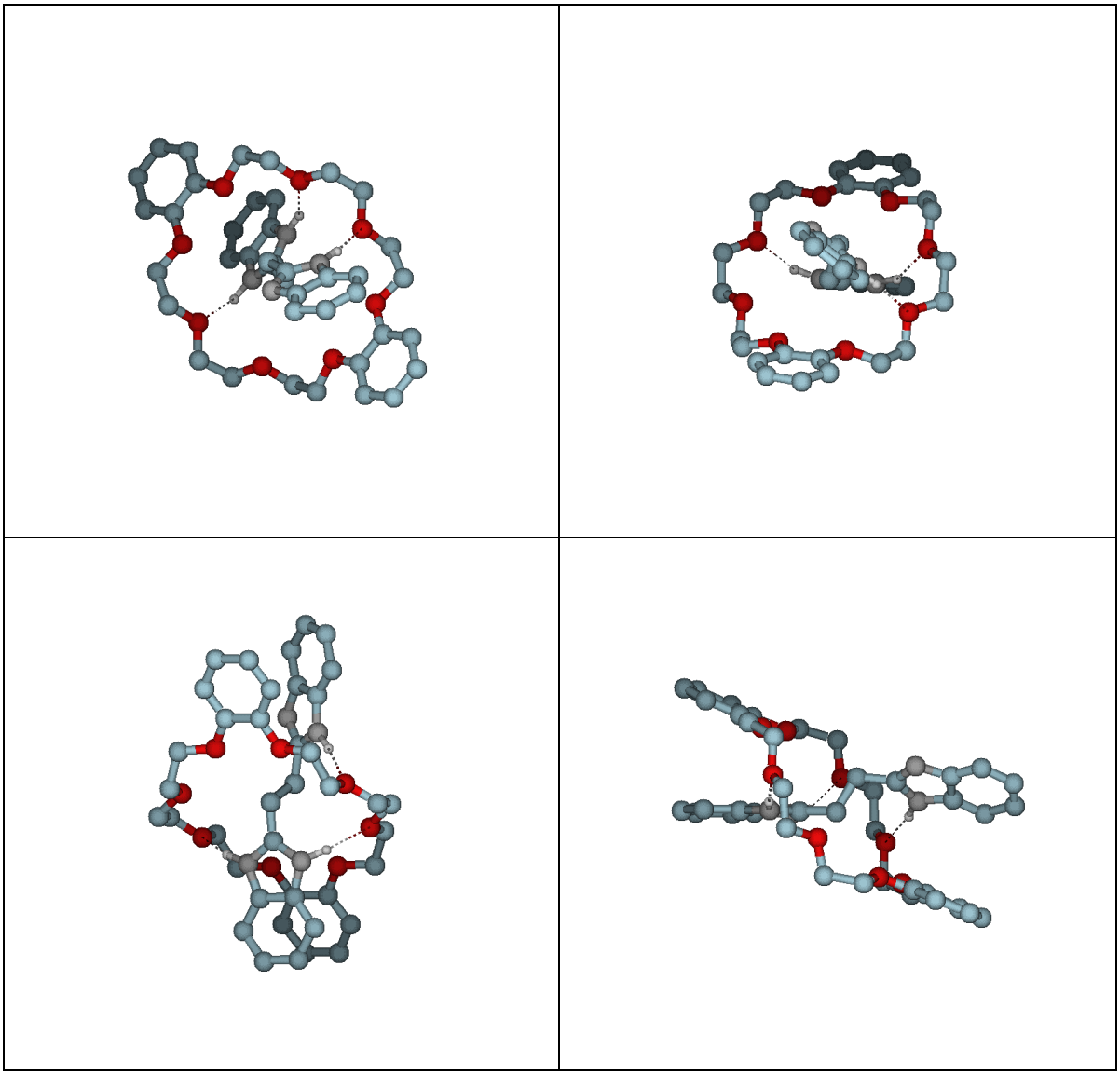
H	0.547639	2.219380	-3.651096
H	3.504277	2.041480	-2.776472
H	1.944908	1.849841	-4.712879
H	-4.846934	-2.623893	2.108242
H	1.991579	-0.474355	-5.076440
H	-5.093441	-0.872434	1.819784
H	-0.569676	-3.644357	-2.191434
H	-0.615673	-3.911548	-3.962393
H	-1.527094	3.976567	1.014997
H	0.954613	-2.533445	-4.756147
H	-1.580780	4.554058	2.710181
H	1.590817	-2.190039	-3.122000
H	-3.329954	3.092200	3.262261
H	-3.374265	2.401267	1.611220

Figure 8. Four views of the optimized structure of the doubly protonated pseudorotaxane and its corresponding Cartesian coordinates, in angstroms, and final energy, in atomic units. Carbon atoms are depicted by light blue spheres, and oxygen atoms as red spheres. Hydrogen atoms are deleted, keeping only those involved in hydrogen contacts, which are shown as white spheres. The dashed lines indicate the hydrogen contacts where the H…O distance is smaller than the sum of its van der Walls radii.



100
FINAL HEAT OF FORMATION = -2370.947815

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C	3.246343	-0.120477	3.207158	H	-1.090800	0.889242	-1.580479
C	2.143991	-0.050366	0.665790	C	-1.477287	-1.267038	-1.628410
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H	1.538841	-0.234812	-1.405877	C	-3.300425	-0.445198	-4.731661
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H	-1.847744	-2.041034	-0.940908
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O	-2.210798	-1.159346	2.593908
C	-2.274706	-2.605286	2.581802
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C	-3.433359	0.933747	2.771197
O	-3.443465	1.262406	1.374457
C	-3.554715	2.683650	1.149137
C	-0.924515	-3.226370	2.868438
O	-0.051585	-3.109545	1.729882
C	1.214416	-3.659841	1.909244
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C	-3.659409	3.699832	-4.806290
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H	-6.115189	3.524646	-1.796138
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H	1.138153	2.840146	-4.712095
H	0.689564	2.793142	-2.977914
H	-2.961610	-2.939251	3.379524
H	2.430412	-3.278168	-3.656942
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H	-5.281033	2.369156	-0.089952
H	-0.860685	4.145412	-4.465261
H	-4.280753	-0.981336	2.282346
H	-1.081011	-4.292909	3.111858
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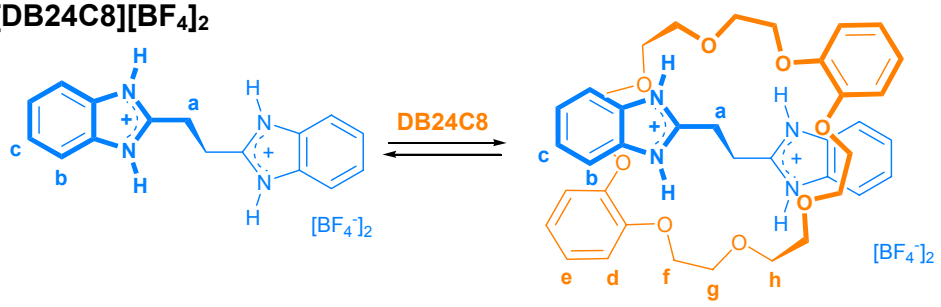
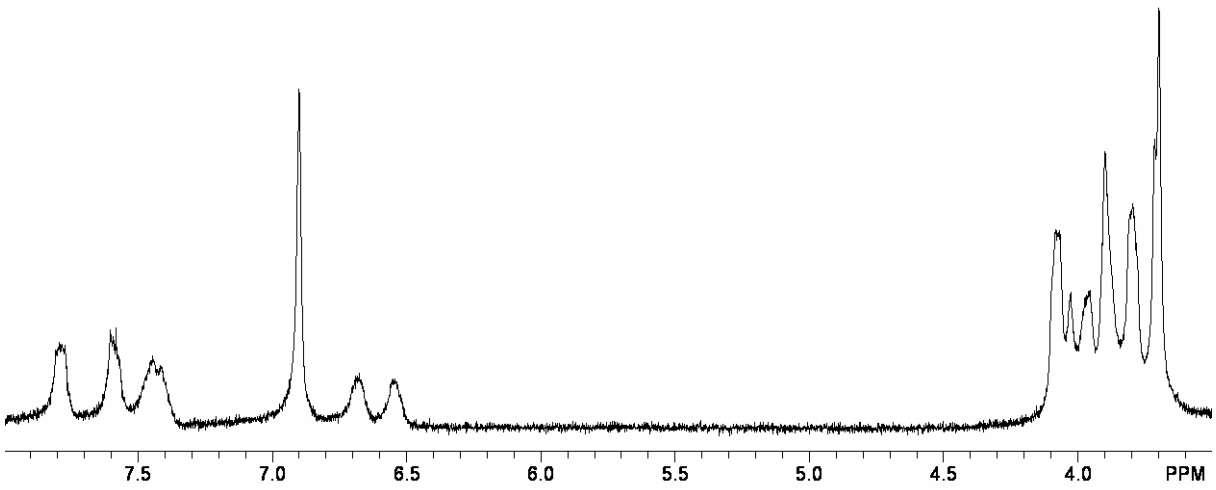
H	2.741806	-4.397519	-1.644689
H	-4.099553	3.152466	1.988741
H	-0.482823	-2.730673	3.752145
H	-2.552573	3.146852	1.093019
H	1.868445	0.752788	-5.453294
H	2.520922	-1.422385	-4.854054
H	2.425927	0.879782	-3.759578
H	0.803605	-3.372981	-2.924417
H	3.406379	-2.753432	-1.402687
H	-1.244377	2.646599	-5.365109
H	-2.678639	-2.959014	1.614433
H	-4.322559	1.363743	3.271013
H	0.736867	-1.465735	-4.811805
H	-2.537411	1.344878	3.277769

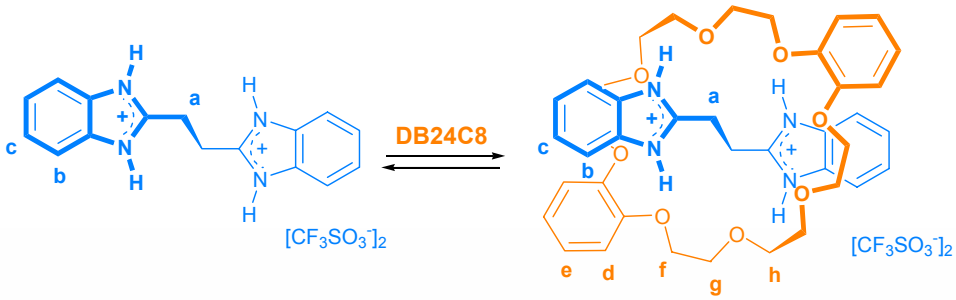
NMR Spectra of [2]Pseudorotaxanes

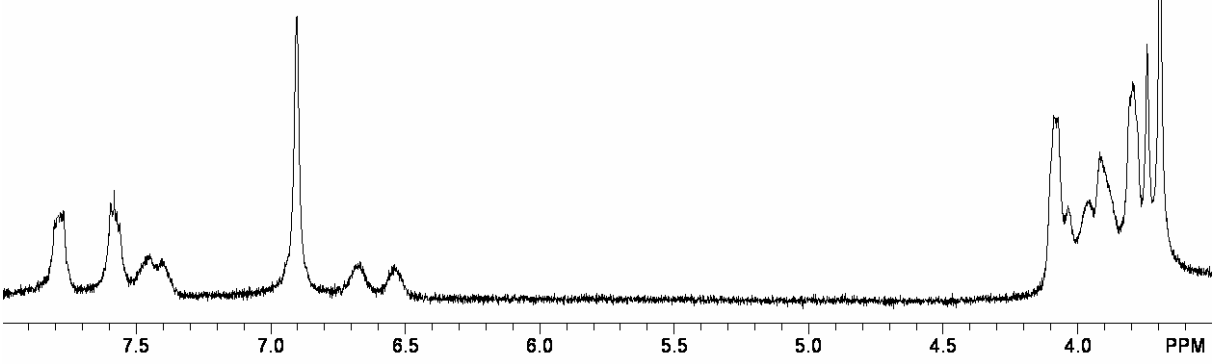
$[2\cdot H_2]^{2+}\subset[DB24C8][BF_4]_2$





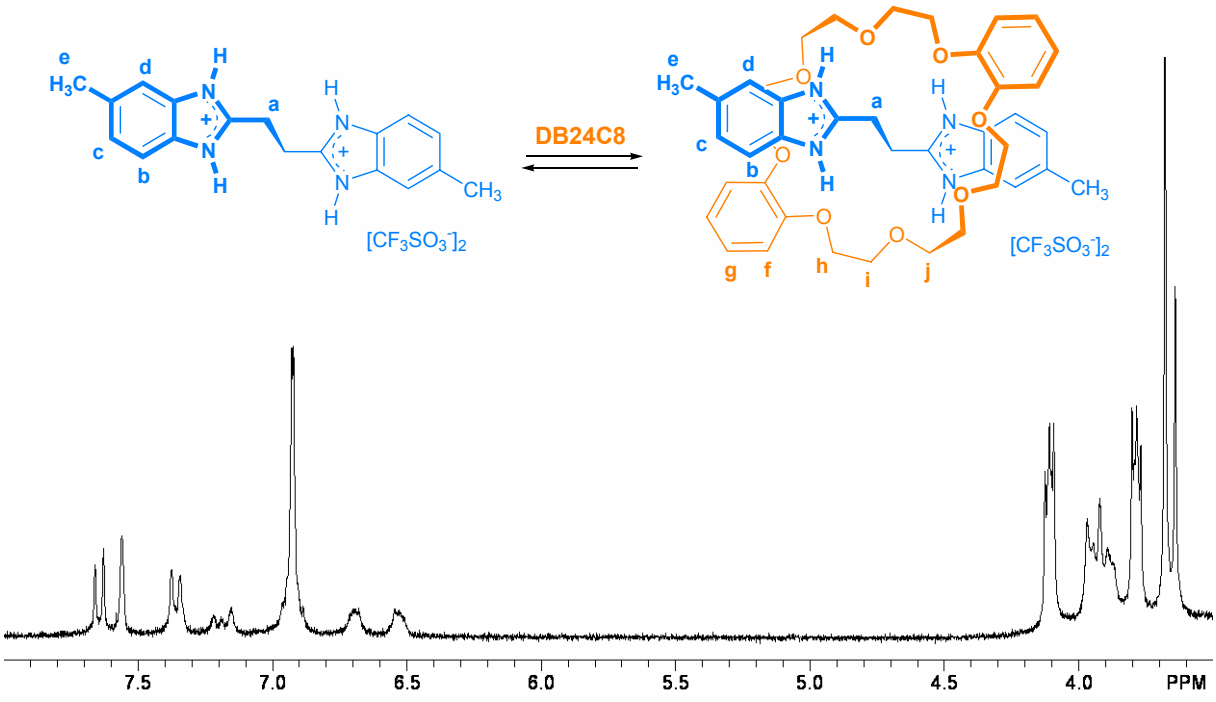
$[2\cdot H_2]^{2+}\subset[DB24C8][CF_3SO_3]_2$



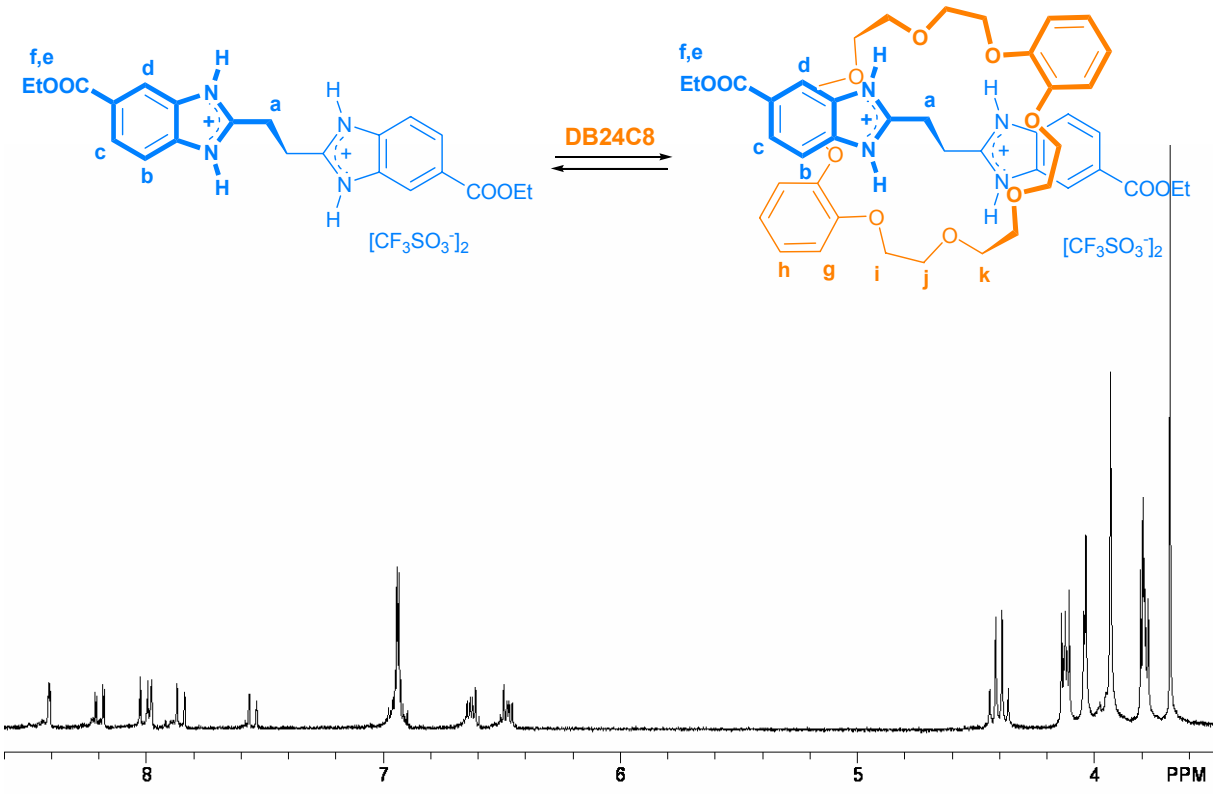


Note: Strictly, the following two spectra are the result of a mixture of two stereoisomers.

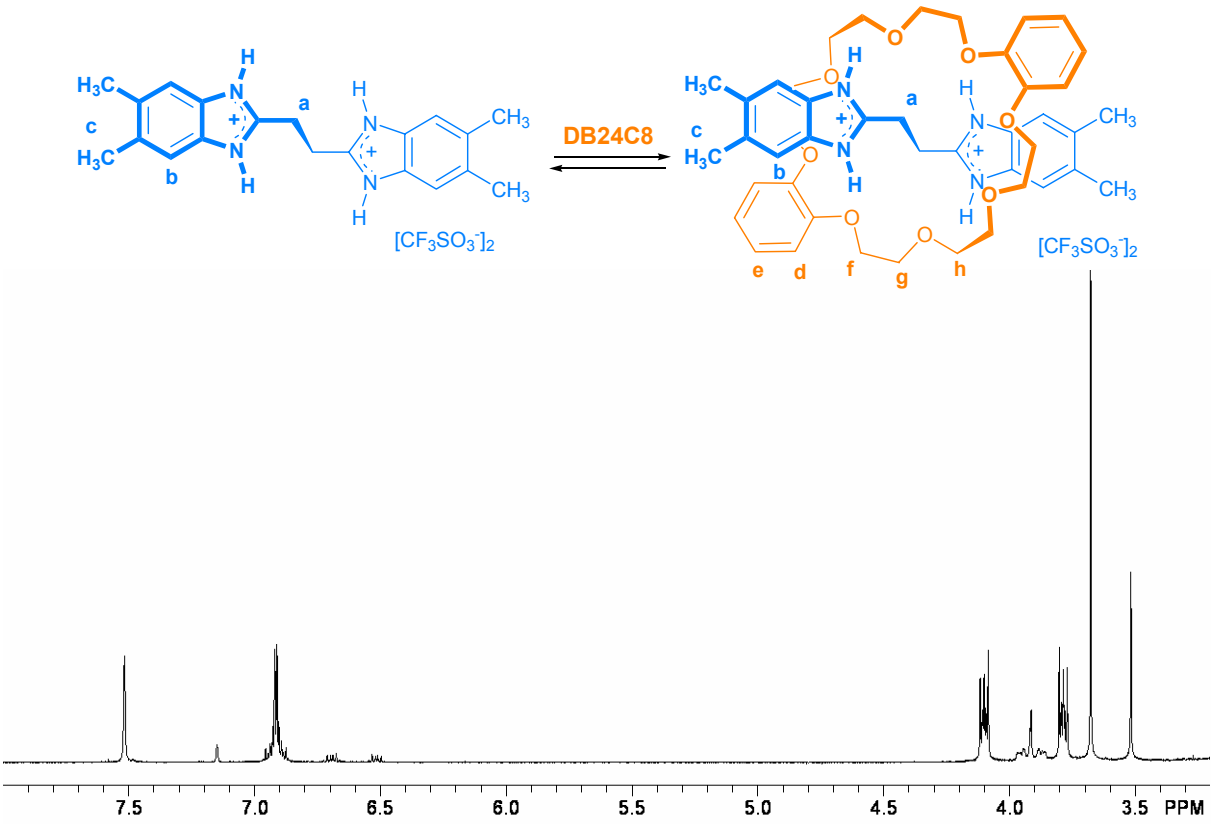
$[3\cdot H_2]^{2+}\subset[DB24C8][CF_3SO_3]_2$



$[4\cdot H_2]^{2+}\subset[DB24C8][CF_3SO_3]_2$

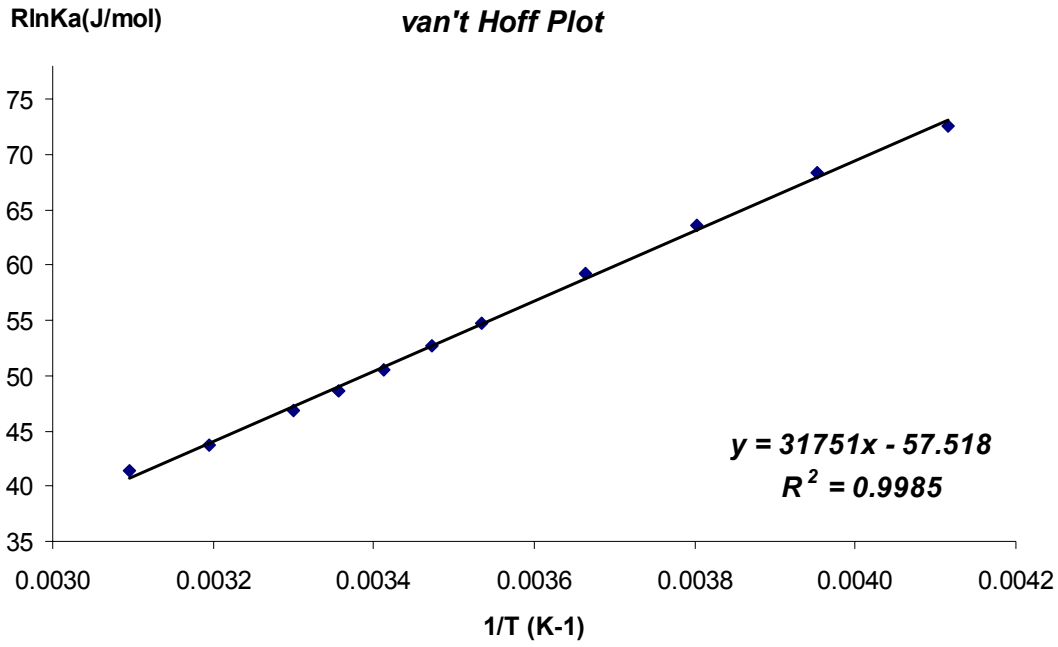


$[5{\cdot}H_2]^{2+}\subset[DB24C8][CF_3SO_3]_2$



^{1}H NMR Variable Temperature Study for $[2\cdot H_2][BF_4]_2\subset$[DB24C8] at 400 MHz and using 5×10^{-3} *M* concentrations

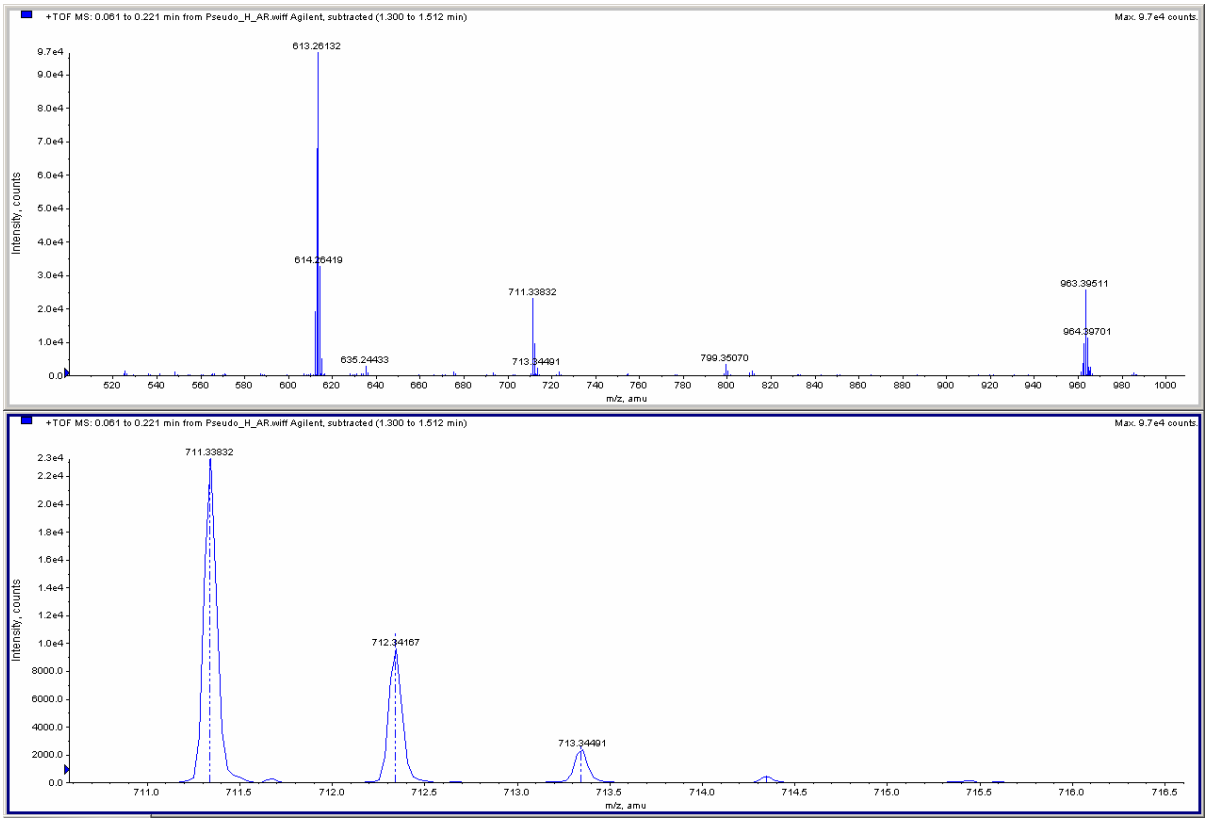
Temp (K)	C Uncomplex	C Complex	Ka	ΔG (kJ/mol)	1/T	RlnKa
323	8.92	4.36	146	-13.4	0.0031	41.4101
313	7.921	4.731	191	-13.7	0.0032	43.6588
303	5.274	4.147	281	-14.2	0.0033	46.8749
298	4.703	4.278	347	-14.5	0.0034	48.6412
293	3.93	4.17	438	-14.8	0.0034	50.5746
288	3.31	4.16	568	-15.2	0.0035	52.7216
283	2.81	4.14	729	-15.5	0.0035	54.7989
273	2.00	4.07	1236	-16.2	0.0037	59.1911
263	1.44	3.99	2079	-16.7	0.0038	63.5149
253	1.04	3.98	3723	-17.3	0.0040	68.3604
243	0.79	4.03	6216	-17.6	0.0041	72.6222



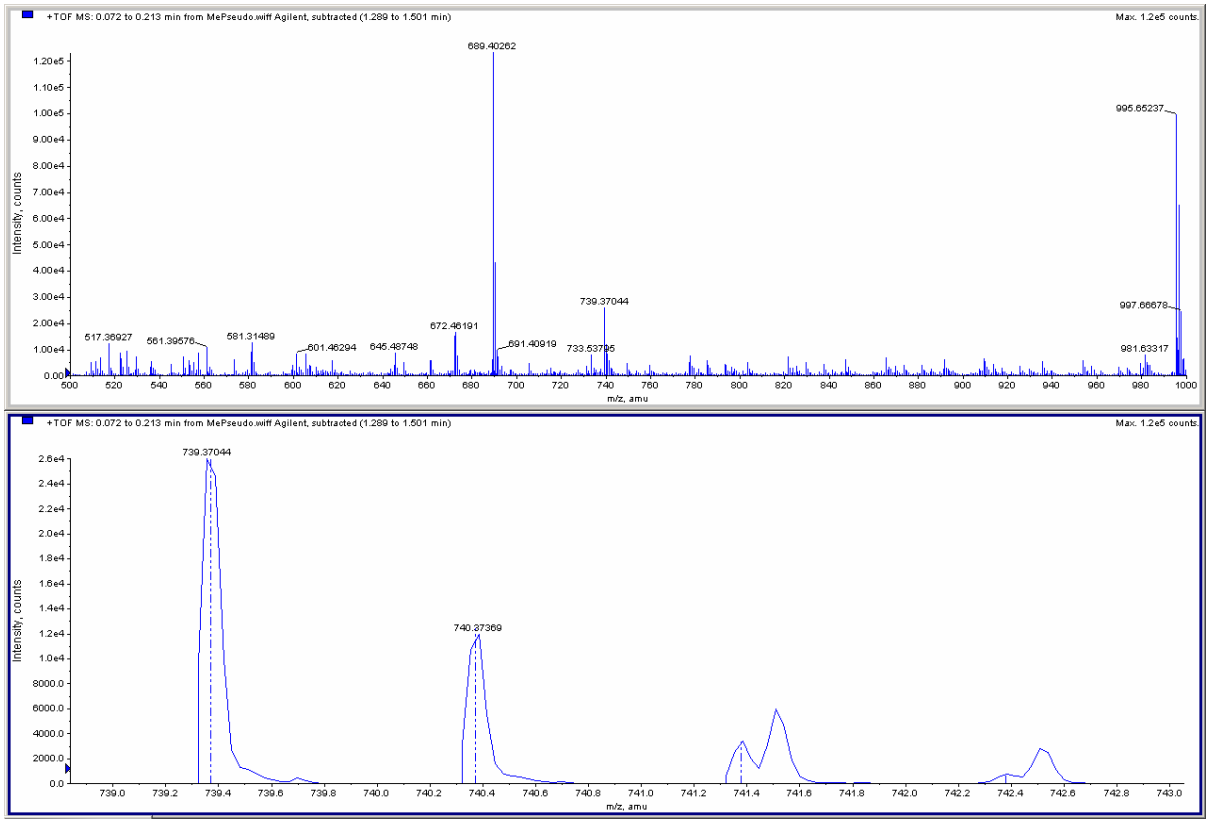
At 298 K: ΔH = -31.7 kJ/mol, ΔS = -57.5 J/mol

Mass Spectra of [2]Pseudorotaxanes

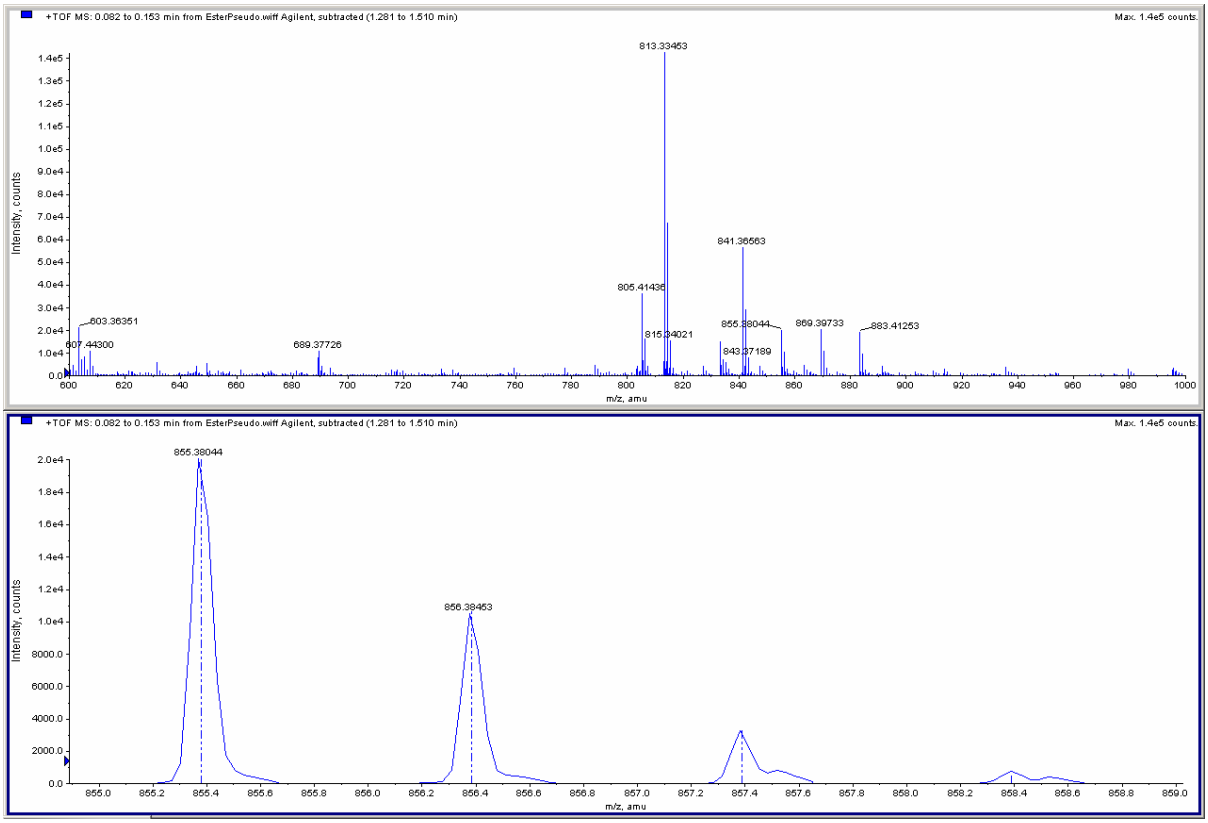
$[2\cdot H_2]^{2+}\subset[DB24C8][BF_4]_2$



$[3{\cdot}H_2]^{2+}\subset[DB24C8][BF_4]_2$



$[4 \cdot H_2]^{2+} \subset [DB24C8][BF_4]_2$



X-Ray Crystal Structures

Crystals were mounted on a short glass fibre attached to a tapered copper pin. A full hemisphere of data were collected with 30s frames on a Enraf-Nonius Kappa diffractometer fitted with a CCD based detector using MoK_{α} radiation (0.71073 Å). Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library. Ball-and-stick diagrams were prepared using DIAMOND 3.0 - Visual Crystal Structure Information System CRYSTAL IMPACT.

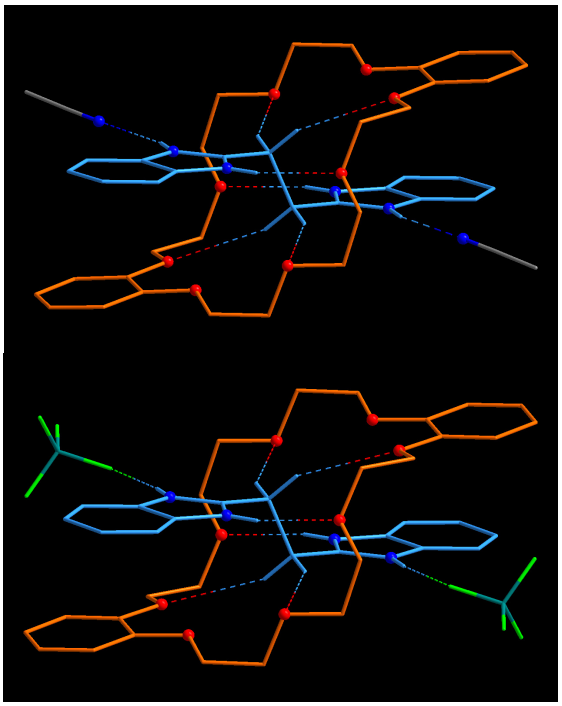


Figure 1. Hydrogen bonding pattern in [**2**·$\mathbf{H_2}$][BF_4]⊂ **DB24C8**.
Top: from acetonitrile, anions omitted. Bottom: from nitromethane.