Theoretical investigation of the complexation of crown ethers and crown ethers of fulleropyrrolidine with $(CH_3)_x NH_{4-x}^+$, $x = 0 - 4$‡

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Supplementary material

Table 1s

Table 2s

Figure 1s

Figure 2s

Figure 3s

Figure 4s

Figure 5s

Figure 6s

Geometries and harmonic frequencies are available upon request.

Table 1s Absolute energies E (hartree), Complexation energy without BSSE correction CE^{*} (eV), Complexation Energies CE (eV), with respect to the ZPE CE_0 (eV), Complexation enthalpy[a] CH (eV), Complexation Gibbs free energy[a] CG (eV), vdW R (Å) in the gas phase, absolute energies in $CHCl_3$ solvent E_{solv} (hartree), Complexation Energies CE_{solv} (eV), vdW R_{solv} (Å) in $CHCl_3$ solvent at the B3LYP/6-31G(dp) level of theory.

Structure	E	CE^{*}	CE[b]	CE_0[b]	CH[b]	CG[b]	R(NH…O)	R(NH···cph)	R(CH···O)	E_{solv}	CE_{solv}[b]	R_{solv}(NH…O)	R_{solv}(NH···cph)	R_{solv} (CH···O)
NH_4^+	56.905869									56.998291				
$MeNH_3^+$	96.227521									96.310684				
$Me_2NH_2^+$	135.547725									135.623500				
Me_3NH^+	174.865959									174.935964				
Me_4N^+	214.181275									214.246382				
12a	920.198759									920.206106				
12b	920.198121									920.203892				
12c	920.197512													
12d	920.196391													
12e	920.194099													
12-NH_4^+-1	977.183140		2.00	1.91	1.94	1.50	1.744, 1.764			977.2378736	0.77			
12-NH_4^+-2	977.181720		1.97	1.88	1.91	1.47	1.724, 1794							
12-NH_4^+-3	977.169727		1.67	1.59	1.62	1.18	1.844, 1.844	2.266						
12-NH_4^+-4	977.167370		1.60	1.51	1.54	1.07	1.891, 1.740	2.343						
12-NH_4^+-5	977.161868		1.46	1.41	1.43	1.02	1.733, 1.676							
12-$MeNH_3^+$-1	1016.497702		1.78	1.71	1.75	1.23	1.817, 1.796		2.585, 2.663	1016.549010	0.72			
12-$MeNH_3^+$-2	1016.484674		1.48	1.42	1.42	0.96	1.889, 1.889	2.283						
12-$MeNH_3^+$-3	1016.482215		1.41	1.34	1.34	0.85	1.782, 1.946	2.367						
12-$MeNH_3^+$-4	1016.476645		1.27	1.23	1.23	0.79	1.788, 1.741							
12-$Me_2NH_2^+$-1	1055.810986		1.58	1.51	1.51	0.98	1.910, 1.882		2.373, 2.370	1055.859756	0.64			
12-$Me_2NH_2^+$-2	1055.796103		1.21	1.17	1.15	0.69	1.848	2.249	2.462					
12-$Me_2NH_2^+$-3	1055.791813		1.13	1.10	1.08	0.63	1.840, 1.787							
12-$Me_2NH_2^+$-4	1055.776635		0.71	0.68	0.67	0.16		2.491, 2.496						
12-Me_3NH^+-1	1095.117197		1.23	1.17	1.16	0.65	2.041		2.393, 2.389, 2.817	1095.165375	0.44			
12-Me_3NH^+-2	1095.116610		1.21	1.15	1.14	0.64	2.198		2.547, 2.564, 2.627	1095.164844	0.42			
12-Me_3NH^+-3	1095.105225		0.95	0.91	0.89	0.42	1.853		2.584					
12-Me_3NH^+-4	1095.102767		0.90	0.88	0.85	0.39	1.765		2.622,[c] 2.673[c]					
12-Me_4N^+-1	1134.412534		0.73	0.69	0.66	0.23			2.168, 2.315, 2.357,[d] 2.505[d]	1134.463058	0.13			
12-Me_4N^+-2	1134.412383		0.71	0.66	0.64	0.19			2.280,[c] 2.201, 2.542,[c,d] 2.522[d]	1134.463418	0.13			
12-Me_4N^+-3	1134.411281		0.70	0.66	0.66	0.16			2.270, 2.435, 2.257, 2.577	1134.462377	0.12			
12-Me_4N^+-4	1134.403389		0.51	0.47	0.44	0.01		2.736	2.274, 2.838					
12-Me_4N^+-5	1134.402430		0.50	0.45	0.43	0.02			2.215, 2.323,[c] 2.467[c]					
12-Me_4N^+-6	1134.399339		0.41	0.37	0.35	-0.12		2.683	2.758					
18a	1227.877696													
18b	1227.871978													
18c	1227.864776													
18-NH_4^+-1	1284.894219		2.82	2.69	2.73	2.24	1.826, 1.835, 1.826			1284.943136	1.29			
18-NH_4^+-2	1284.888637		2.66	2.52	2.57	2.06	1.844, 1.722, 1.891							
18-NH_4^+-3	1284.887029		2.62	2.50	2.54	2.07	1.822, 1.762, 1.937							
18-$MeNH_3^+$-1	1324.207017		2.55	2.44	2.45	1.93	1.853, 1.859, 1.853			1324.253391	1.21			
18-$MeNH_3^+$-2	1324.201058		2.39	2.26	2.28	1.74	1.973, 1.753, 1.888							
18-$MeNH_3^+$-3	1324.199758		2.35	2.25	2.26	1.75	1.845, 1.797, 1.951							
18-$Me_2NH_2^+$-1	1363.510775		2.08	2.01	2.01	1.45	1.847, 1.847		2.269	1363.555493	0.90			
18-$Me_2NH_2^+$-2	1363.509886		2.04	1.96	1.96	1.42	1.999, 2.005		2.579, 2.814, 2.579, 2.814	1363.554487	0.85			
18-$Me_2NH_2^+$-3	1363.505821		1.95	1.84	1.85	1.28	1.887, 1.887		2.480, 2.480, 2.617, 2.617					
18-Me_3NH^+-1	1402.808943		1.53	1.46	1.45	0.91	1.810		2.294, 2.382, 2.596,[d] 2.627[d]	1402.854159	0.52			
18-Me_3NH^+-2	1402.804811		1.42	1.34	1.33	0.79	1.787		2.478, 2.200,[d] 2.641,[d] 2.294,	1402.852904	0.48			

							2.690		
18-Me_3NH^+-3	1402.804396	1.42	1.34	1.34	0.78	1.937	2.446, 2.446, 2.230, 2.230	1402.852233	0.48
18-Me_3NH^+-4	1402.803095	1.37	1.29	1.28	0.73	1.768	2.426, 2.215,[d] 2.705,[d] 2.338		
18-Me_4N^+-1	1442.104057	0.99	0.94	0.92	0.41		2.308, 2.220, 2.392, 2.685, 2.719,2.837	1442.153854	0.24
18-Me_4N^+-2	1442.102050	0.93	0.86	0.85	0.33		2.487, 2.348,[d] 2.354,[d] 2.759, 2.556, 2.516, 2.356, 2.643		
18-Me_4N^+-3	1442.098744	0.85	0.78	0.77	0.25		2.451, 2.456, 2.323, 2.623, 2.447, 2.458, 2.675, 2.627		
24a	1535.546392								
24b	1535.539450								
24c	1535.534326								
24-NH_4^+-1	1592.582009	3.29	3.15	3.20	1.90	1.916, 1.849, 1.890, 1.945		1592.625934	1.56
24-NH_4^+-2	1592.579381	3.23	3.07	3.13	2.56	1.906, 1.879, 1.943, 1.885		1592.624330	1.53
24-NH_4^+-3	1592.578246	3.19	3.04	3.09	2.55	1.914, 1.836, 1.933, 1.919		1592.622675	1.47
24-NH_4^+-4	1592.569924	2.98	2.89	2.96	2.36	2.048, 1.942, 1.920, 2.488[d]			
24-NH_4^+-5	1592.567824	2.94	2.83	2.87	2.38	1.800, 1.877, 1.877, 2.567[d]			
24-NH_4^+-6	1592.552270	2.54	2.41	2.45	1.95	1.754, 1.824, 1.727			
24-$MeNH_3^+$-1	1631.880474	2.63	2.52	2.53	1.68	1.806, 1.980, 1.918	2.344	1631.925806	1.20
24-$MeNH_3^+$-2	1631.880412	2.62	2.50	2.52	1.96	1.867, 1.932, 1.992	2.434, 2.207	1631.924537	1.15
24-$MeNH_3^+$-3	1631.879780	2.60	2.48	2.50	1.96	1.992, 2.007, 1.961	2.342, 2.435, 2.622	1631.924146	1.14
24-$MeNH_3^+$-4	1631.878201	2.59	2.48	2.49	1.94	1.986, 1.941, 1.861	2.492	1631.924379	1.18
24-$MeNH_3^+$-5	1631.877148	2.56	2.45	2.46	1.93	2.003, 1.941, 1.828	2.355		
24-$MeNH_3^+$-6	1631.868709	2.33	2.20	2.21	1.69	1.902, 2.102, 2.013	2.641, 2.447		
24-$Me_2NH_2^+$-1	1671.187884	2.22	2.11	2.11	1.52	1.951, 1.948	2.238, 2.686, 2.280, 2.543	1671.231506	0.94
24-$Me_2NH_2^+$-2	1671.187025	2.22	2.11	2.12	1.52	1.897, 1.910	2.626, 2.784, 2.352, 2.261	1671.231324	0.95
24-$Me_2NH_2^+$-3	1671.185225	2.18	2.07	2.08	1.47	1.856, 1.811	2.509, 2.369, 2.253		
24-$Me_2NH_2^+$-4	1671.182826	2.12	2.02	2.02	1.41	1.839, 1.809	2.391, 2.420, 2.514		
24-$Me_2NH_2^+$-5	1671.172631	1.85	1.75	1.75	1.16	1.979, 1.801	2.554, 2.734, 2.377, 2.340		
24-Me_3NH^+-1	1710.492019	1.78	1.65	1.66	1.01	1.898	2.385, 2.460, 2.543, 2.444,[d] 2.498,[d] 2.602, 2.456, 2.522	1710.536150	0.67
24-Me_3NH^+-2	1710.490183	1.75	1.64	1.64	1.03	1.942	2.322, 2.615, 2.365, 2.748, 2.488, 2.325, 2.585	1710.533691	0.62
24-Me_3NH^+-3	1710.480483	1.55	1.47	1.45	0.90	1.921	2.734, 2.379,[d] 2.600,[d] 2.407, 2.263, 2.358		
24-Me_3NH^+-4	1710.478489	1.52	1.43	1.42	0.84	1.887	2.461, 2.676, 2.578, 2.310, 2.389		
24-Me_3NH^+-5	1710.479021	1.46	1.34	1.35	0.72	1.767	2.541,[d] 1.418,[d] 2.583, 2.532, 2.442, 2.571,[d] 2.509,[d] 2.459		
24-Me_4N^+-1	1749.788562	1.29	1.19	1.18	0.63		2.371, 2.373, 2.542, 2.533, 2.351, 2746, 2.775, 2.506, 2.602	1749.832413	0.30
24-Me_4N^+-2	1749.788129	1.28	1.18	1.17	0.61		2.321, 2.470, 2.525, 2.414,[d] 2.575,[d] 2.391, 2.544, 2.543, 2.390	1749.832095	0.29
24-Me_4N^+-3	1749.785478	1.22	1.12	1.11	0.54		2.269, 2.393, 2.661, 2.324, 2.205, 2.356, 2.676	1749.830433	0.26
24-Me_4N^+-4	1749.782458	1.14	1.04	1.05	0.42		2.191, 2.534, 2.676, 2.434, 2.677, 2.706, 2.450,[d] 2.386,[d] 2.793, 2.391,[d] 2.631[d]		
24-Me_4N^+-5	1749.780795	1.09	0.99	0.98	0.39		2.668, 2.304, 2.557, 2.432, 2.625, 2.495, 2.382		

[a] T = 298.15 K, P = 1 atm. [b] BSSE corrected values.

Table 2s Absolute energies E(hartree), Complexation energy without BSSE correction CE* (eV), Complexation Energies CE (eV), absolute energies in $CHCl_3$ solvent E_{solv} (hartree) and Complexation Energies CE_{solv}(eV) in $CHCl_3$ solvent at the B3LYP/6-31G(dp) level of theory.

Structure	E	CE*	CE[a]	C_{SOLV}	CE_{solv}[a]
18A	3686.143418			3686.156622	
18A-NH_4^+	3743.158851	2.981	2.788	3743.208246	1.258
18A-$MeNH_3^+$	3782.471667	2.741	2.516	3782.518539	1.169
18A-$Me_2NH_2^+$-1	3821.774910	2.279	2.040	3821.820174	0.851
18A-$Me_2NH_2^+$-2	3821.760925	1.899	1.658	3821.808602	0.533
18A-Me_3NH^+-1	3861.072387	1.715	1.465	3861.119116	0.472
18A-Me_3NH^+-2	3861.057302	1.304	1.074	3861.107522	0.176
18A-Me_4N^+	3900.368193	1.184	0.945	3900.416857	0.138
18B	3686.143040			3686.156280	
18B-NH_4^+	3743.159816	3.018	2.824	3743.208540	1.274
18B-$MeNH_3^+$	3782.473380	2.798	2.564	3782.519042	1.184
18B-$Me_2NH_2^+$-1	3821.774383	2.275	2.018	3821.820083	0.839
18B-$Me_2NH_2^+$-2	3821.765326	2.029	1.791	3821.811295	0.620
18B-Me_3NH^+-1	3861.077127	1.854	1.570	3861.120336	0.481
18B-Me_3NH^+-2	3861.073703	1.761	1.480	3861.119224	0.453
18B-Me_4N^+	3900.373548	1.340	1.078	3900.420575	0.226
18C	3686.142581			3686.155811	
18C-NH_4^+	3743.157586	2.970	2.775	3743.207347	1.254
18C-$MeNH_3^+$	3782.470333	2.727	2.503	3782.517632	1.167
18C-$Me_2NH_2^+$-1	3821.774087	2.280	2.039	3821.819513	0.853
18C-$Me_2NH_2^+$-2	3821.774058	2.279	2.014	3821.819168	0.820
18C-$Me_2NH_2^+$-3	3821.771300	2.204	1.960	3821.818597	0.825
18C-Me_3NH^+-1	3861.071872	1.723	1.475	3861.118814	0.488
18C-Me_3NH^+-2	3861.067383	1.601	1.371	3861.115774	0.423
18C-Me_4N^+	3900.366759	1.167	0.930	3900.418064	0.195
18D	3686.1421279			3686.155513	
18D-NH_4^+	3743.158255	3.000	2.806	3743.207569	1.269
18D-$MeNH_3^+$	3782.471723	2.778	2.535	3782.517878	1.164
18D-$Me_2NH_2^+$-1	3821.776612	2.361	2.101	3821.820319	0.864
18D-$Me_2NH_2^+$-2	3821.773467	2.275	2.009	3821.819024	0.822
18D-Me_3NH^+-1	3861.076471	1.861	1.571	3861.119368	0.469
18D-Me_3NH^+-2	3861.071008	1.712	1.458	3861.117294	0.448
18D-Me_4N^+	3900.371427	1.307	1.045	3900.419227	0.210
18E	3686.134240			3686.147723	
18E-NH_4^+	3743.147870	2.932	2.736	3743.198979	1.245
18E-$MeNH_3^+$	3782.460567	2.689	2.463	3782.509193	1.156
18E-$Me_2NH_2^+$-1	3821.764463	2.245	2.006	3821.811272	0.850
18E-$Me_2NH_2^+$-2	3821.761030	2.151	1.908	3821.809992	0.812
18E-Me_3NH^+-1	3861.062579	1.697	1.449	3861.110419	0.478
18E-Me_3NH^+-2	3861.058693	1.592	1.358	3861.107515	0.415
18E-Me_4N^+-1	3900.357243	1.136	0.900	3900.409667	0.188
18E-Me_4N^+-2	3900.354486	1.060	0.852	3900.407827	0.164
18E-Me_4N^+-3	3900.352504	1.007	0.787	3900.401532	0.018

[a] BSSE corrected values.

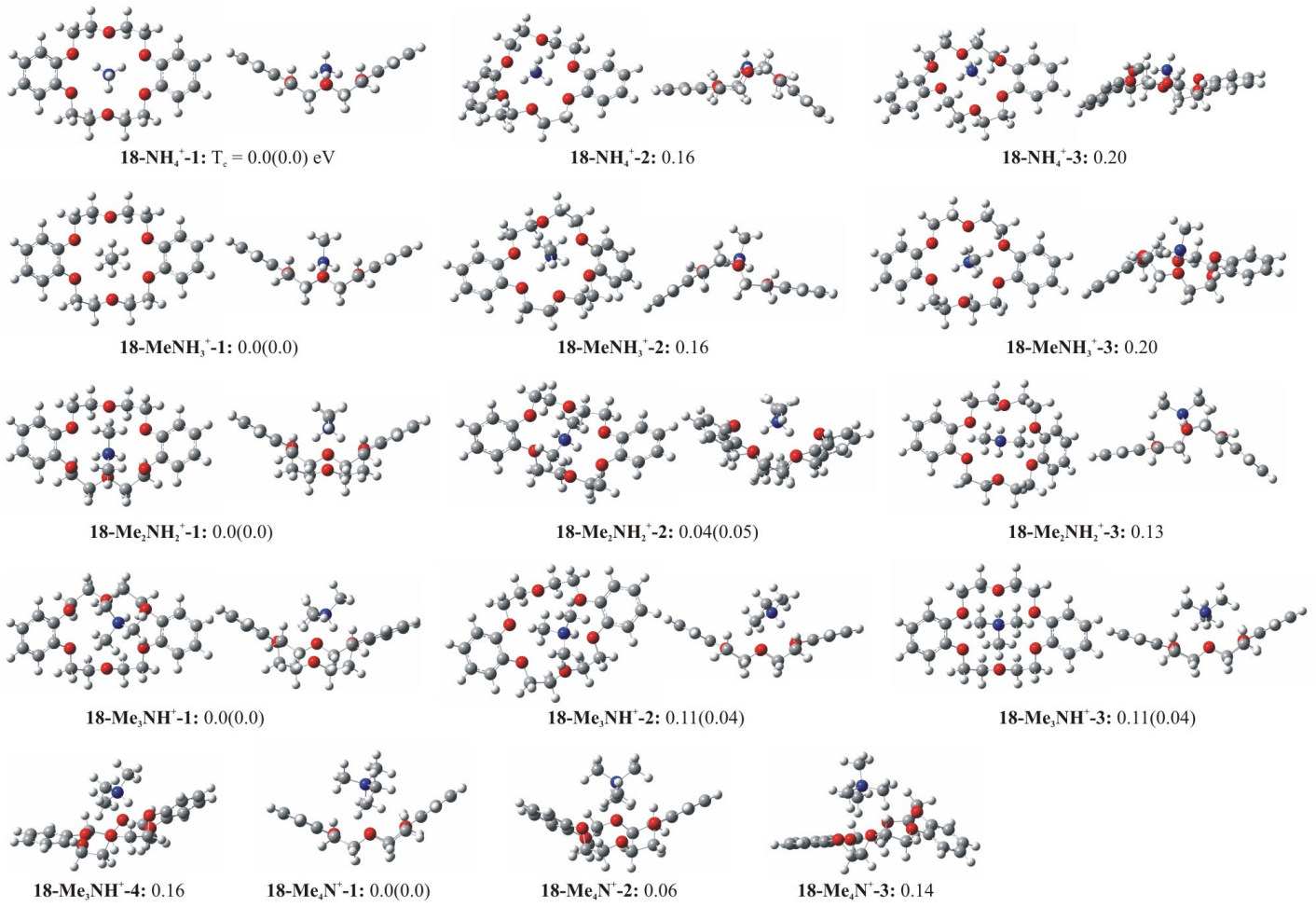


Fig. 1s Different minima and BSSE corrected relative energies with respect to the lowest minimum of dibenzo-18-crown-6 ether with $(CH_3)_xNH_{4-x}^+$, x = 0-4 in the gas phase (in $CHCl_3$ solvent). Some structures are shown from two different viewing angles. (Grey spheres = C atoms, red spheres = O atoms, white spheres = H atoms, and blue spheres = N atoms).

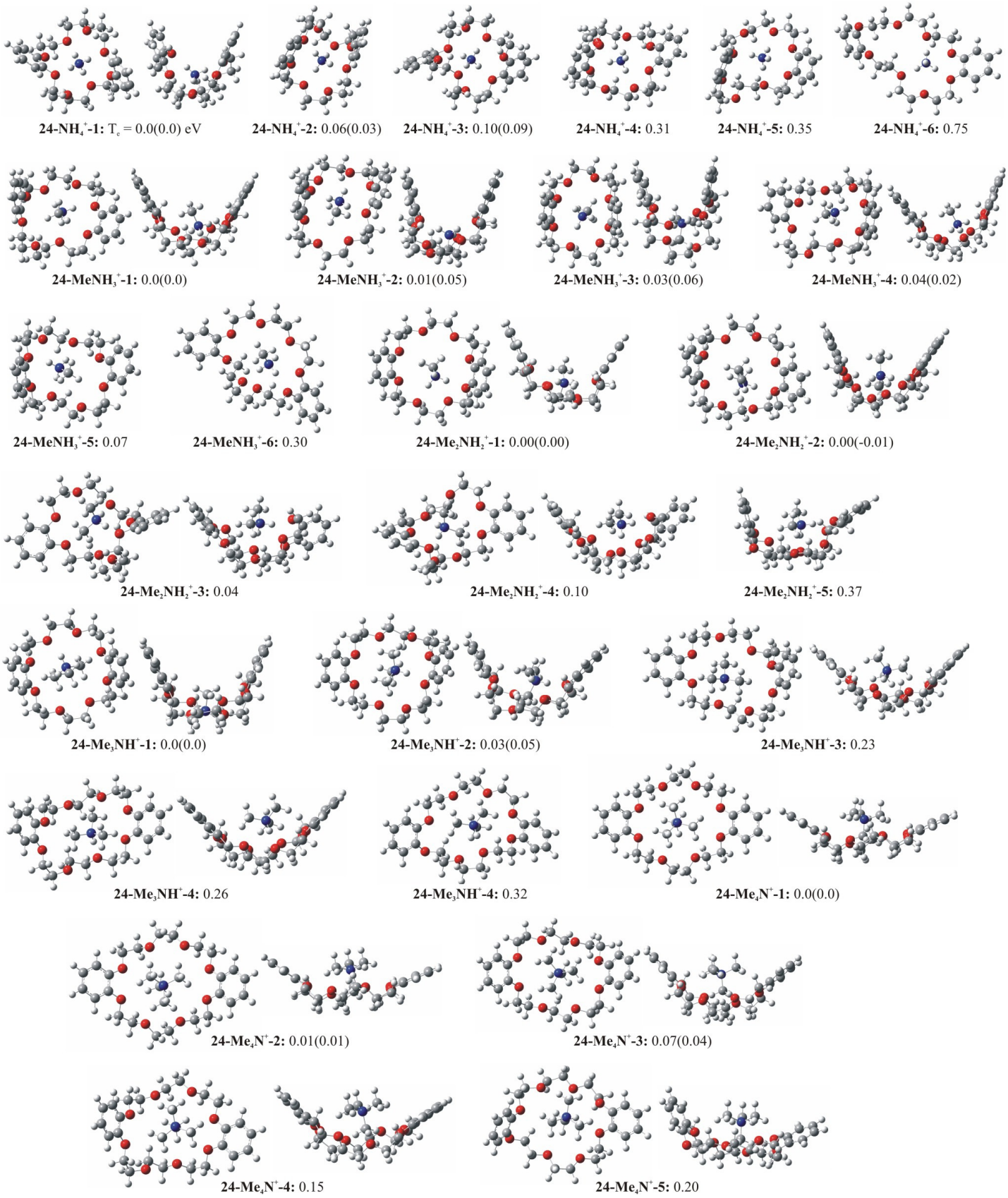


Fig. 2s Different minima and BSSE corrected relative energies with respect to the lowest minimum of dibenzo-24-crown-8 ether with $(CH_3)_xNH_{4-x}^+$, x = 0-4 in the gas phase (in $CHCl_3$ solvent). Some structures are shown from two different viewing angles. (Grey spheres = C atoms, red spheres = O atoms, white spheres = H atoms, and blue spheres = N atoms).

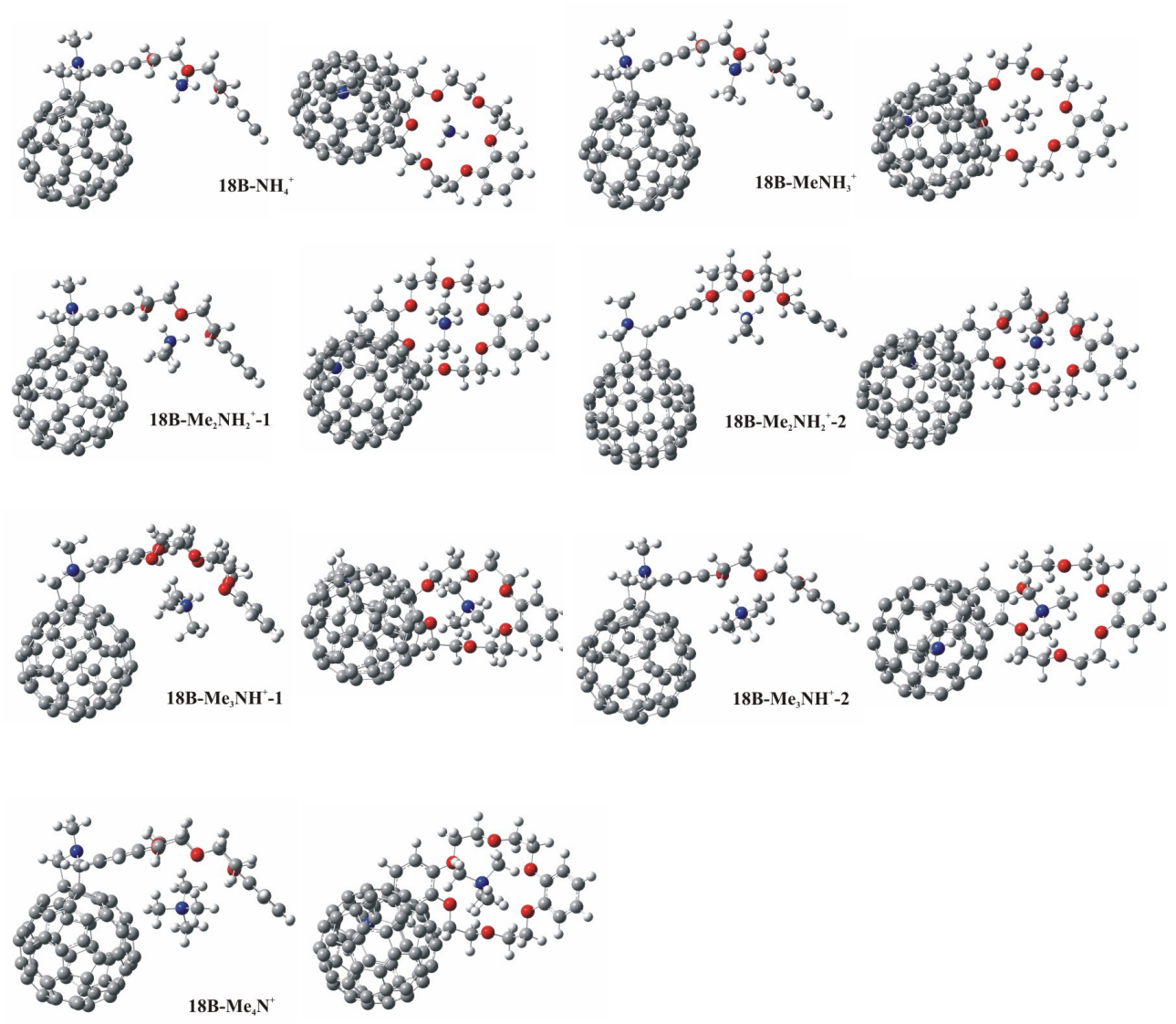


Fig. 3s Minima of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine (**18B** isomer) with $(CH_3)_x NH_{4-x}^+$. (Grey spheres = C atoms, red spheres = O atoms, white spheres = H atoms, and blue spheres = N atoms).

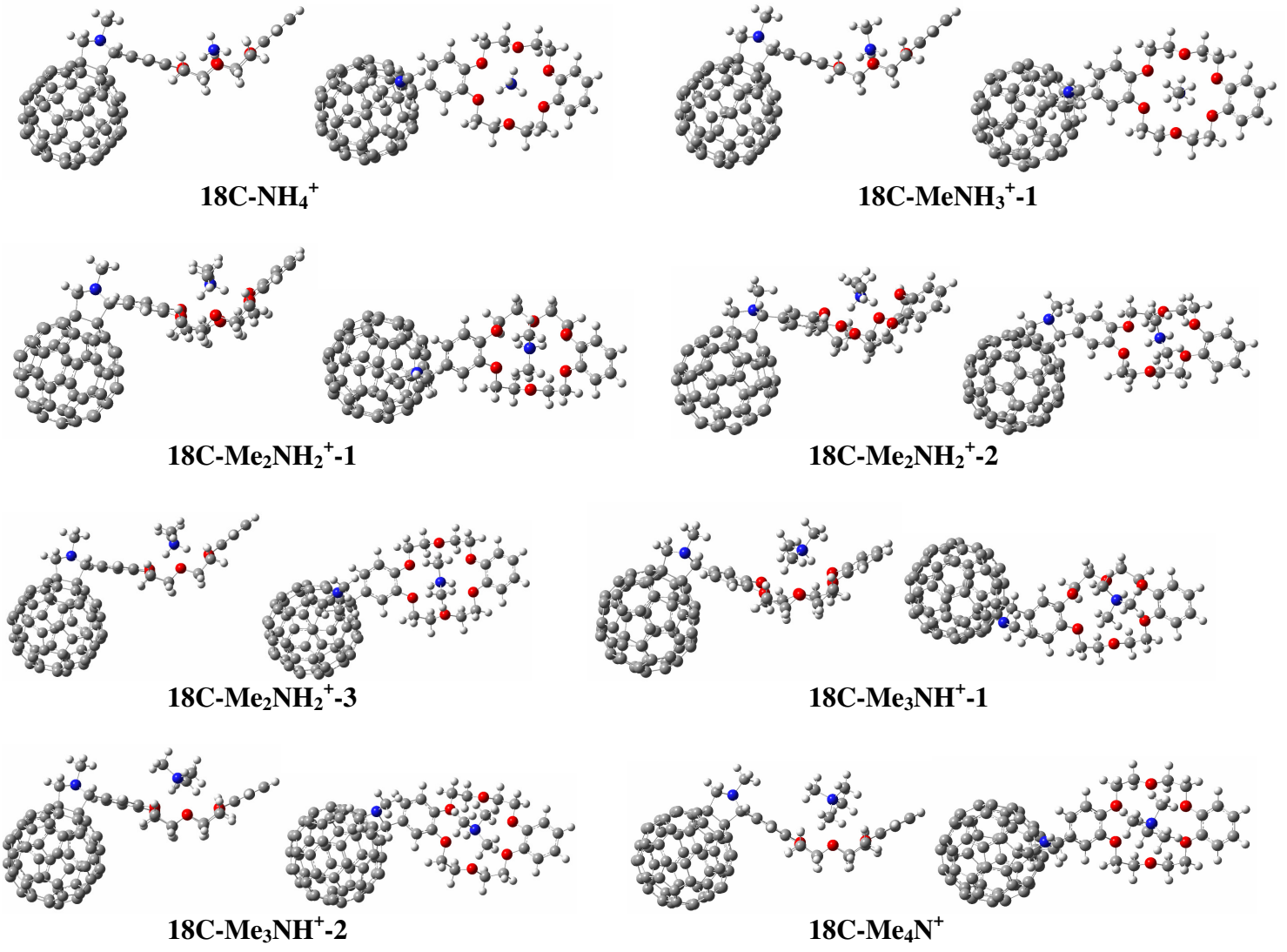
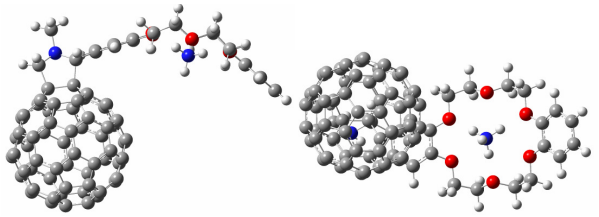
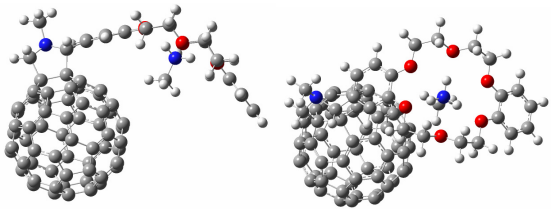


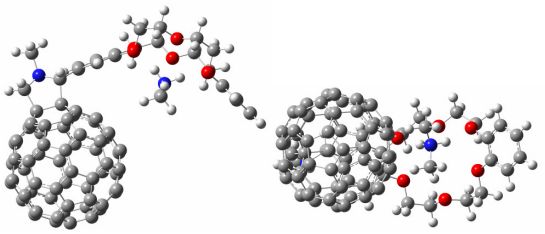
Fig. 4s: Minima of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine (**18C** isomer) with $(CH_3)_xNH_{4-x}^+$, x = 0-4.



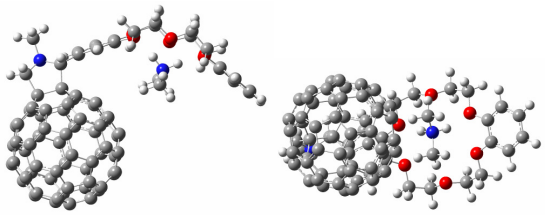
18D-NH_4^+



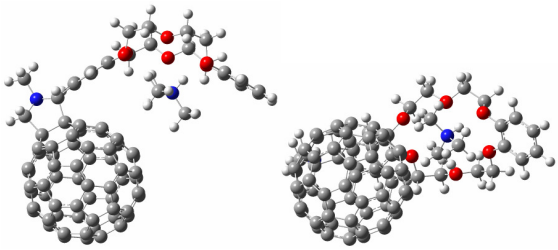
18D-$MeNH_3^+$



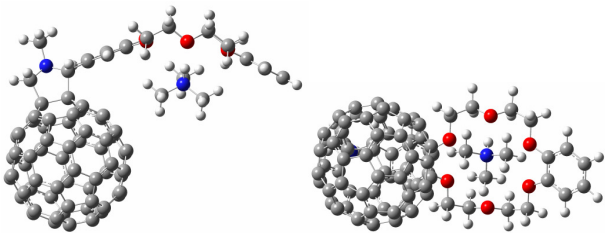
18D-$Me_2NH_2^+$-1



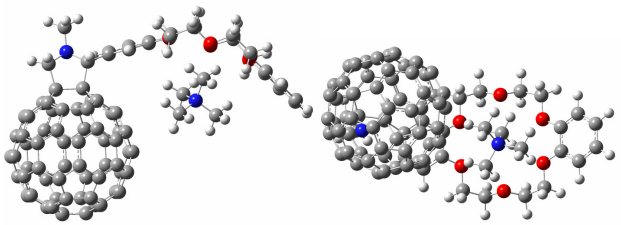
18D-$Me_2NH_2^+$-2



18D-Me_3NH^+-1

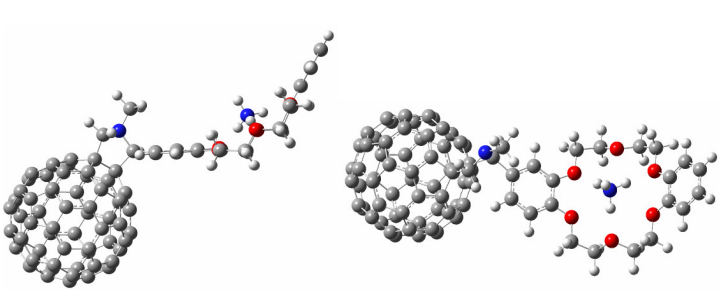


18D-Me_3NH^+-2

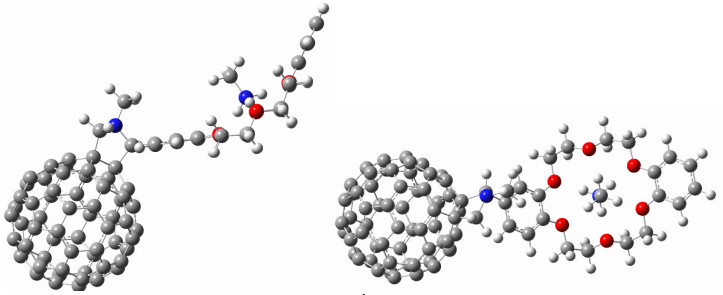


18D-Me_4N^+

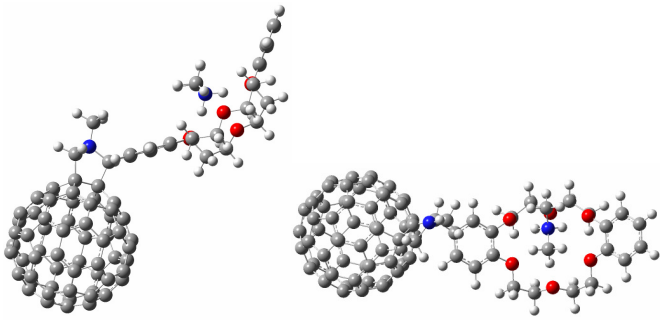
Fig. 5s: Minima of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine (**18D** isomer) with $(CH_3)_xNH_{4-x}^+$, x = 0-4.



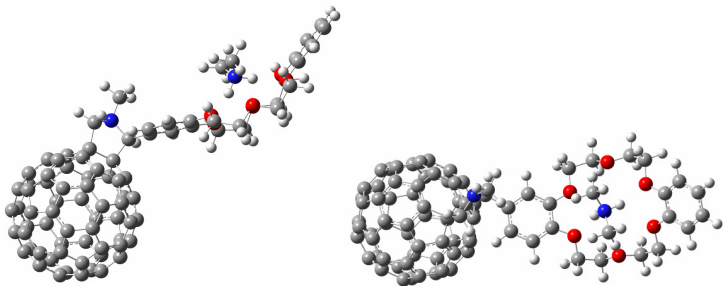
18E-NH_4^+-1



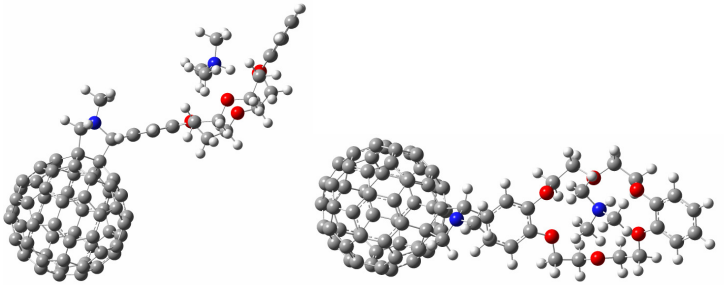
18E-$MeNH_3^+$



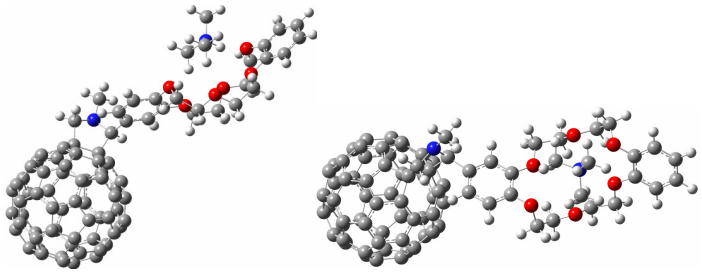
18E-$Me_2NH_2^+$-1



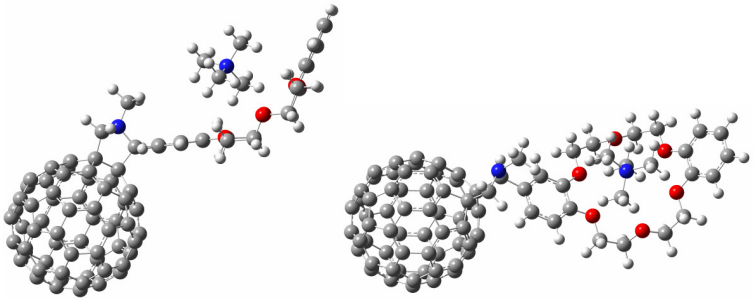
18E-$Me_2NH_2^+$-2



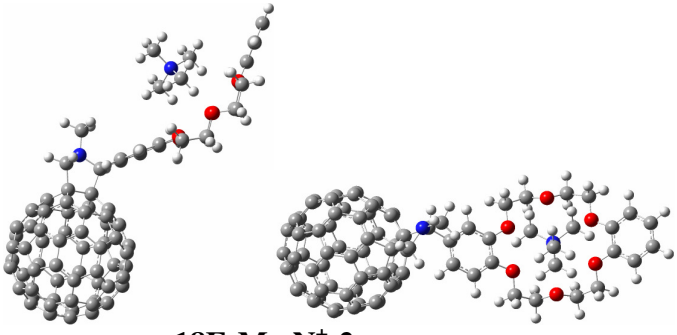
18E-Me_3NH^+-1



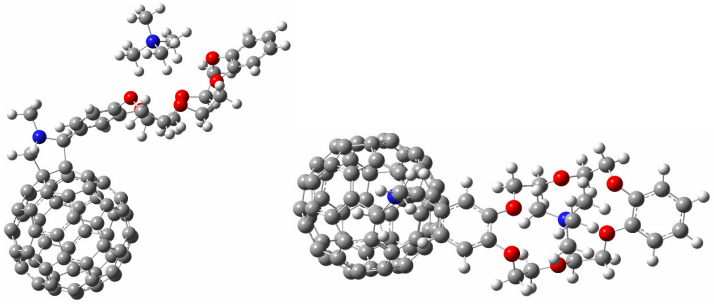
18E-Me_3NH^+-2



18E-Me_4N^+-1



18E-Me_4N^+-2



18E-Me_4N^+-3

Fig. 6s: Minima of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine (**18E** isomer) with $(CH_3)_xNH_{4-x}^+$, x = 0-4.