

Supplementary material to Ms. “Azidocryptands – Synthesis, Structure, and Complexation Properties”

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Calculated geometry (B3LYP / 6-31G(d)) of cryptand **1** (azido group pointing towards larger bridge)

| | | | |
|---|-----------|-----------|-----------|
| H | -1.173207 | 0.062585 | -4.978581 |
| C | -0.887230 | -0.258675 | -3.981075 |
| C | -0.166248 | -1.179494 | -1.455028 |
| C | 0.460406 | -0.329567 | -3.621369 |
| C | -1.862893 | -0.516748 | -3.019447 |
| C | -1.529150 | -0.946052 | -1.729988 |
| C | 0.838230 | -0.758304 | -2.350633 |
| H | 1.230158 | -0.024974 | -4.327344 |
| H | -2.912512 | -0.355319 | -3.257062 |
| C | 2.259642 | -0.609869 | -1.830456 |
| H | 2.938818 | -0.380939 | -2.672858 |
| H | 2.605057 | -1.549132 | -1.389532 |
| C | -2.569945 | -0.933320 | -0.619393 |
| H | -3.566644 | -0.783067 | -1.073334 |
| H | -2.625869 | -1.889587 | -0.092176 |
| N | 2.287247 | 0.420689 | -0.787839 |
| N | -2.236507 | 0.108689 | 0.364733 |
| C | -2.471545 | 1.471716 | -0.116129 |
| H | -3.351636 | 1.919573 | 0.381392 |
| H | -2.707591 | 1.432004 | -1.184403 |
| C | -1.286206 | 2.427571 | 0.044897 |
| H | -0.937750 | 2.451691 | 1.082900 |
| O | -0.238015 | 2.005329 | -0.804389 |
| C | 2.096898 | 1.787528 | -1.262729 |
| H | 3.038232 | 2.366079 | -1.231193 |
| H | 1.781226 | 1.761712 | -2.310085 |
| C | 1.024690 | 2.548939 | -0.483430 |
| H | 1.071269 | 3.621475 | -0.749762 |
| H | 1.211023 | 2.468497 | 0.599200 |
| C | 3.257575 | 0.284086 | 0.285299 |
| H | 4.297527 | 0.147993 | -0.082878 |
| H | 3.258796 | 1.229659 | 0.839567 |
| C | 2.984149 | -0.855332 | 1.282695 |
| H | 3.799919 | -0.861258 | 2.025998 |
| H | 3.010449 | -1.820158 | 0.766114 |
| O | 1.721470 | -0.809835 | 1.920260 |
| C | -2.675588 | -0.155755 | 1.727545 |
| H | -2.446506 | -1.200405 | 1.959251 |
| H | -3.773017 | -0.030816 | 1.861350 |
| C | -2.013489 | 0.745871 | 2.786765 |
| H | -2.324438 | 0.393412 | 3.782380 |
| H | -2.386527 | 1.772020 | 2.685533 |
| O | -0.600687 | 0.830337 | 2.691179 |
| C | 1.603903 | -0.011427 | 3.078106 |
| H | 2.239773 | -0.407202 | 3.889887 |
| H | 1.900447 | 1.033183 | 2.896598 |
| C | 0.147427 | -0.041629 | 3.521936 |
| H | -0.217006 | -1.076253 | 3.455290 |
| H | 0.078367 | 0.282124 | 4.574732 |
| H | -1.619943 | 3.446830 | -0.226479 |
| N | 0.343131 | -1.786349 | -0.295453 |
| N | -0.317547 | -2.369938 | 0.552350 |
| N | -0.754083 | -2.977891 | 1.419594 |

B3LYP / 6-31G(d) : -1201.441654
B3LYP / 6-31G(d) + ZPE: -1200.986711

Calculated geometry (B3LYP / 6-31G(d)) of cryptand 1xNa⁺ (azido group pointing towards the larger bridge)

| | | | |
|----|-----------|-----------|-----------|
| H | 0.659704 | 0.481040 | 5.006733 |
| C | 0.435970 | 0.060807 | 4.031210 |
| C | -0.174678 | -1.155214 | 1.625256 |
| C | -0.845202 | 0.188486 | 3.492296 |
| C | 1.452735 | -0.512417 | 3.264987 |
| C | 1.172768 | -1.097654 | 2.027105 |
| C | -1.164033 | -0.364754 | 2.245780 |
| H | -1.601077 | 0.760346 | 4.025314 |
| H | 2.477790 | -0.498748 | 3.626703 |
| C | -2.378366 | 0.126570 | 1.460950 |
| H | -3.082318 | 0.624127 | 2.145062 |
| H | -2.936478 | -0.683146 | 0.984374 |
| C | 2.263328 | -1.487660 | 1.040957 |
| H | 3.231751 | -1.560917 | 1.556941 |
| H | 2.049920 | -2.465949 | 0.604253 |
| N | -1.917186 | 1.057433 | 0.383793 |
| N | 2.315036 | -0.498593 | -0.081382 |
| C | 2.956501 | 0.780256 | 0.299959 |
| H | 3.948984 | 0.882388 | -0.165520 |
| H | 3.115106 | 0.777242 | 1.381610 |
| C | 2.129370 | 2.034648 | -0.033234 |
| H | 2.013349 | 2.173635 | -1.118662 |
| O | 0.847284 | 1.875265 | 0.572609 |
| C | -1.457434 | 2.364771 | 0.914272 |
| H | -2.227899 | 3.140805 | 0.792514 |
| H | -1.273374 | 2.261793 | 1.985305 |
| C | -0.149492 | 2.851736 | 0.279589 |
| H | 0.122894 | 3.828994 | 0.702730 |
| H | -0.249084 | 2.977733 | -0.812546 |
| C | -2.848731 | 1.217613 | -0.751474 |
| H | -3.884323 | 1.412778 | -0.420496 |
| H | -2.526816 | 2.108078 | -1.303355 |
| C | -2.879034 | 0.031359 | -1.730105 |
| H | -3.521140 | 0.288833 | -2.581703 |
| H | -3.306888 | -0.859455 | -1.260088 |
| O | -1.572196 | -0.354688 | -2.182650 |
| C | 2.786784 | -1.080547 | -1.350411 |
| H | 2.284857 | -2.047045 | -1.468818 |
| H | 3.874921 | -1.277833 | -1.347076 |
| C | 2.493842 | -0.219566 | -2.592883 |
| H | 2.770042 | -0.791196 | -3.486661 |
| H | 3.100891 | 0.691569 | -2.590189 |
| O | 1.121405 | 0.204910 | -2.674996 |
| C | -1.136383 | 0.088245 | -3.469866 |
| H | -1.776384 | -0.330657 | -4.258260 |
| H | -1.167314 | 1.185299 | -3.540991 |
| C | 0.291603 | -0.406031 | -3.670643 |
| H | 0.321253 | -1.500389 | -3.577538 |
| H | 0.632849 | -0.127541 | -4.676714 |
| H | 2.641969 | 2.920807 | 0.367538 |
| N | -0.431530 | -1.903515 | 0.424199 |
| N | -1.475617 | -2.571064 | 0.354360 |
| N | -2.382807 | -3.228821 | 0.158429 |
| Na | 0.062028 | 0.119232 | -0.678947 |

B3LYP / 6-31G(d): -1363.665638

B3LYP / 6-31G(d) + ZPE: -1363.207847

Calculated geometry (B3LYP / 6-31G(d)) of cryptand 1xLi⁺ (azido group pointing towards larger bridge)

| | | | |
|----|-----------|-----------|-----------|
| H | 0.574157 | 0.569657 | 5.087579 |
| C | 0.398174 | 0.154524 | 4.100059 |
| C | -0.075231 | -1.013894 | 1.644530 |
| C | -0.880426 | 0.204101 | 3.540808 |
| C | 1.467069 | -0.342819 | 3.350541 |
| C | 1.249697 | -0.909347 | 2.091743 |
| C | -1.133227 | -0.338115 | 2.274939 |
| H | -1.685374 | 0.704098 | 4.073982 |
| H | 2.479875 | -0.281330 | 3.740610 |
| C | -2.381038 | 0.024907 | 1.481852 |
| H | -3.110476 | 0.516947 | 2.143789 |
| H | -2.887749 | -0.852974 | 1.069934 |
| C | 2.368758 | -1.259006 | 1.129101 |
| H | 3.342299 | -1.201255 | 1.637801 |
| H | 2.252480 | -2.283574 | 0.766451 |
| N | -1.993428 | 0.904683 | 0.342819 |
| N | 2.313096 | -0.356936 | -0.058930 |
| C | 2.831354 | 0.995775 | 0.236823 |
| H | 3.857435 | 1.130933 | -0.140212 |
| H | 2.871417 | 1.108988 | 1.322944 |
| C | 1.937648 | 2.125408 | -0.299305 |
| H | 2.006041 | 2.245713 | -1.387921 |
| O | 0.603095 | 1.782987 | 0.066638 |
| C | -1.596092 | 2.257779 | 0.780555 |
| H | -2.430925 | 2.973989 | 0.725450 |
| H | -1.283766 | 2.203936 | 1.825535 |
| C | -0.405745 | 2.786553 | -0.021549 |
| H | -0.051765 | 3.729803 | 0.415594 |
| H | -0.660612 | 2.977135 | -1.075776 |
| C | -2.963896 | 0.939475 | -0.762143 |
| H | -4.007942 | 1.006976 | -0.409789 |
| H | -2.771631 | 1.850473 | -1.339187 |
| C | -2.834084 | -0.265181 | -1.697577 |
| H | -3.494308 | -0.139167 | -2.564325 |
| H | -3.127447 | -1.192417 | -1.197605 |
| O | -1.477098 | -0.459133 | -2.127461 |
| C | 2.873366 | -0.976202 | -1.267692 |
| H | 2.477746 | -1.995662 | -1.320968 |
| H | 3.975841 | -1.050052 | -1.239811 |
| C | 2.483280 | -0.239700 | -2.553451 |
| H | 2.723962 | -0.873879 | -3.414017 |
| H | 3.038149 | 0.697943 | -2.669911 |
| O | 1.080047 | 0.071796 | -2.539709 |
| C | -1.124711 | 0.061509 | -3.409273 |
| H | -1.776376 | -0.350873 | -4.190869 |
| H | -1.213125 | 1.157638 | -3.422082 |
| C | 0.312511 | -0.357566 | -3.667245 |
| H | 0.377953 | -1.449166 | -3.768084 |
| H | 0.677524 | 0.108960 | -4.591566 |
| H | 2.232662 | 3.074126 | 0.169102 |
| N | -0.256559 | -1.682983 | 0.381366 |
| N | -1.169701 | -2.519455 | 0.288210 |
| N | -1.956201 | -3.311346 | 0.070644 |
| Li | 0.080236 | 0.040292 | -0.775820 |

B3LYP / 6-31G(d): -1208.922024

B3LYP / 6-31G(d) + ZPE: -1208.462330

Calculated geometry (B3LYP / 6-31G(d)) of cryptand **1** (azido group pointing towards smaller bridge)

| | | | |
|---|-----------|-----------|-----------|
| H | 0.808865 | 3.995668 | -0.461784 |
| C | 0.388381 | 3.135459 | 0.051813 |
| C | -0.753262 | 1.084153 | 1.537645 |
| C | -0.899619 | 2.688246 | -0.252204 |
| C | 1.161012 | 2.403279 | 0.949921 |
| C | 0.630158 | 1.323640 | 1.668486 |
| C | -1.464193 | 1.616036 | 0.440699 |
| H | -1.470948 | 3.168890 | -1.043197 |
| H | 2.210071 | 2.655805 | 1.086743 |
| C | -2.655153 | 0.847458 | -0.113567 |
| H | -3.377491 | 1.524919 | -0.592052 |
| H | -3.186491 | 0.330011 | 0.687284 |
| C | 1.592944 | 0.320236 | 2.317159 |
| H | 2.433139 | 0.874055 | 2.759066 |
| H | 1.129252 | -0.236090 | 3.134075 |
| N | -2.132924 | -0.130124 | -1.092717 |
| N | 2.109196 | -0.647639 | 1.355051 |
| C | 3.327503 | -0.346277 | 0.637357 |
| H | 4.184270 | -0.942303 | 1.014724 |
| H | 3.574367 | 0.704677 | 0.811372 |
| C | 3.283243 | -0.573885 | -0.876987 |
| H | 3.183138 | -1.648476 | -1.108056 |
| H | 4.248896 | -0.245011 | -1.301828 |
| O | 2.206040 | 0.143483 | -1.435484 |
| C | 2.159036 | 0.106628 | -2.848487 |
| H | 2.889887 | 0.814724 | -3.275832 |
| H | 2.401339 | -0.898198 | -3.228724 |
| C | 0.758647 | 0.475375 | -3.302734 |
| H | 0.784184 | 0.794247 | -4.359394 |
| H | 0.402534 | 1.317091 | -2.694243 |
| O | -0.074158 | -0.664830 | -3.164537 |
| C | -2.251173 | 0.332491 | -2.465817 |
| H | -3.302033 | 0.328683 | -2.832555 |
| H | -1.928588 | 1.378769 | -2.485588 |
| C | -1.431156 | -0.450968 | -3.503510 |
| H | -1.513636 | 0.083069 | -4.466004 |
| H | -1.852233 | -1.449192 | -3.658674 |
| C | -2.397226 | -1.546621 | -0.892740 |
| H | -3.462835 | -1.824715 | -1.052957 |
| H | -1.822936 | -2.084585 | -1.652071 |
| C | -2.013252 | -2.128208 | 0.480357 |
| H | -2.124319 | -3.224806 | 0.400457 |
| H | -2.715496 | -1.787223 | 1.246974 |
| O | -0.745748 | -1.793625 | 0.999478 |
| C | 1.600619 | -2.003103 | 1.293674 |
| H | 1.281140 | -2.329809 | 2.294613 |
| H | 2.428085 | -2.665150 | 0.997937 |
| C | 0.416531 | -2.267979 | 0.340971 |
| H | 0.333906 | -3.356435 | 0.164389 |
| H | 0.561368 | -1.758289 | -0.618942 |
| N | -1.538698 | 0.303820 | 2.424735 |
| N | -1.163551 | 0.030093 | 3.561542 |
| N | -0.974701 | -0.284197 | 4.646587 |

B3LYP / 6-31G(d): -1201.426756
B3LYP / 6-31G(d) + ZPE: -1200.972370

Calculated geometry (B3LYP / 6 -31G(d)) of cryptand **2**

| | | | |
|---|-----------|-----------|-----------|
| H | 4.736146 | -0.077481 | -1.175599 |
| C | 3.770663 | 0.318164 | -0.873277 |
| C | 1.333063 | 1.400072 | -0.105149 |
| C | 2.846886 | 0.719447 | -1.837101 |
| C | 3.436084 | 0.395903 | 0.478006 |
| C | 2.213837 | 0.934757 | 0.884626 |
| C | 1.590857 | 1.226210 | -1.477196 |
| H | 3.093088 | 0.628668 | -2.892389 |
| H | 4.136733 | 0.048636 | 1.233356 |
| C | 0.510870 | 1.422447 | -2.532718 |
| H | 0.985690 | 1.666878 | -3.499963 |
| H | -0.133005 | 2.272154 | -2.297433 |
| C | 1.826805 | 1.023140 | 2.350628 |
| H | 2.725632 | 0.863826 | 2.968470 |
| H | 1.481317 | 2.038718 | 2.566444 |
| N | -0.333850 | 0.219149 | -2.638232 |
| N | 0.754403 | 0.083185 | 2.702798 |
| C | 1.225007 | -1.224691 | 3.162198 |
| H | 1.090749 | -1.329553 | 4.256399 |
| H | 2.302393 | -1.296676 | 2.975794 |
| C | 0.575276 | -2.428434 | 2.473278 |
| H | -0.515440 | -2.365411 | 2.528761 |
| H | 0.887100 | -3.342934 | 3.006477 |
| O | 0.994458 | -2.501923 | 1.121993 |
| C | -0.075603 | -2.668967 | 0.200130 |
| H | -0.585965 | -3.633496 | 0.356130 |
| H | -0.812276 | -1.864949 | 0.305811 |
| C | 0.508696 | -2.605234 | -1.201278 |
| H | 1.183747 | -3.455440 | -1.395499 |
| H | 1.087758 | -1.680365 | -1.282959 |
| O | -0.593811 | -2.621869 | -2.095972 |
| C | 0.257325 | -0.773010 | -3.531114 |
| H | 0.193330 | -0.477584 | -4.600249 |
| H | 1.324307 | -0.816613 | -3.296159 |
| C | -0.327660 | -2.193155 | -3.409101 |
| H | 0.367214 | -2.877928 | -3.929471 |
| H | -1.289346 | -2.264403 | -3.928665 |
| C | -1.750290 | 0.488449 | -2.876054 |
| H | -1.901703 | 1.263131 | -3.653751 |
| H | -2.216223 | -0.427616 | -3.247130 |
| C | -2.539526 | 0.907482 | -1.634955 |
| H | -3.534126 | 1.253406 | -1.968896 |
| H | -2.059456 | 1.758635 | -1.131674 |
| O | -2.683142 | -0.194462 | -0.757954 |
| C | -0.318103 | 0.670910 | 3.494924 |
| H | -0.528641 | 1.660812 | 3.079722 |
| H | -0.030896 | 0.821880 | 4.558926 |
| C | -1.624019 | -0.138217 | 3.521486 |
| H | -2.355538 | 0.430330 | 4.121925 |
| H | -1.467543 | -1.093118 | 4.033643 |
| O | -2.172082 | -0.469878 | 2.259342 |
| C | -3.535863 | 0.042472 | 0.350087 |
| H | -4.348161 | 0.731226 | 0.064844 |
| H | -3.984984 | -0.922591 | 0.609459 |
| C | -2.840119 | 0.591903 | 1.594650 |
| H | -2.140438 | 1.390610 | 1.318401 |
| H | -3.606462 | 1.022083 | 2.264505 |
| N | 0.131830 | 2.038085 | 0.365120 |
| N | -0.145609 | 3.155738 | -0.079919 |
| N | -0.542987 | 4.178465 | -0.401329 |

B3LYP / 6-31G(d) : -1355.272752

B3LYP / 6-31G(d) + ZPE: -1354.754804

Calculated geometry (B3LYP / 6 -31G(d)) of cryptand 2xK⁺

| | | | |
|---|-----------|-----------|-----------|
| H | -3.080235 | 2.584289 | 3.292888 |
| C | -2.382479 | 2.384778 | 2.485517 |
| C | -0.597554 | 1.979681 | 0.398600 |
| C | -1.012265 | 2.331901 | 2.740827 |
| C | -2.855738 | 2.148031 | 1.195400 |
| C | -1.979686 | 1.906998 | 0.130652 |
| C | -0.095828 | 2.109399 | 1.707587 |
| H | -0.643292 | 2.484588 | 3.751923 |
| H | -3.926373 | 2.141406 | 1.006785 |
| C | 1.391850 | 1.973919 | 1.971370 |
| H | 1.644612 | 2.434159 | 2.940212 |
| H | 1.946107 | 2.520489 | 1.205430 |
| C | -2.514268 | 1.464642 | -1.223275 |
| H | -3.582533 | 1.720560 | -1.282444 |
| H | -2.035463 | 2.002229 | -2.043308 |
| N | 1.843750 | 0.553167 | 1.933120 |
| N | -2.302811 | 0.006664 | -1.443859 |
| C | -3.332468 | -0.807068 | -0.762798 |
| H | -4.149231 | -1.054357 | -1.460456 |
| H | -3.761763 | -0.204104 | 0.041233 |
| C | -2.850675 | -2.107054 | -0.122703 |
| H | -2.329296 | -2.748062 | -0.849046 |
| H | -3.733059 | -2.653719 | 0.241107 |
| O | -1.989857 | -1.790048 | 0.974248 |
| C | -1.762321 | -2.857920 | 1.890539 |
| H | -2.705123 | -3.155048 | 2.373012 |
| H | -1.352098 | -3.738364 | 1.371693 |
| C | -0.784626 | -2.383604 | 2.952636 |
| H | -0.706210 | -3.146107 | 3.741045 |
| H | -1.159544 | -1.453610 | 3.402407 |
| O | 0.489359 | -2.180249 | 2.340411 |
| C | 1.536946 | -0.107418 | 3.220337 |
| H | 2.247463 | 0.202674 | 4.009030 |
| H | 0.549196 | 0.241125 | 3.537319 |
| C | 1.511502 | -1.640396 | 3.182918 |
| H | 1.390986 | -2.013180 | 4.209369 |
| H | 2.452413 | -2.047150 | 2.799435 |
| C | 3.275773 | 0.456380 | 1.579992 |
| H | 3.865928 | 1.241740 | 2.083647 |
| H | 3.661162 | -0.502666 | 1.937587 |
| C | 3.571233 | 0.527711 | 0.078961 |
| H | 4.659785 | 0.599671 | -0.058095 |
| H | 3.108172 | 1.413413 | -0.374938 |
| O | 3.090550 | -0.668041 | -0.547215 |
| C | -2.059431 | -0.379412 | -2.835066 |
| H | -1.807041 | 0.499245 | -3.439415 |
| H | -2.933648 | -0.867644 | -3.283748 |
| C | 0.277323 | -0.889659 | -3.250419 |
| N | -0.063997 | -1.297127 | -4.384651 |
| N | -0.951082 | -1.377025 | -2.875903 |
| O | 1.219277 | -0.357725 | -2.499187 |
| C | 3.481944 | -0.896672 | -1.895657 |
| H | 4.530002 | -0.609476 | -2.062787 |
| H | 3.399358 | -1.978234 | -2.042347 |
| C | 2.600367 | -0.180978 | -2.927075 |
| H | 2.769979 | 0.897391 | -2.957874 |
| H | 2.747724 | -0.598986 | -3.926714 |
| K | 0.371200 | -1.030935 | -0.034860 |
| N | 0.394203 | 1.816778 | -0.622525 |
| N | 0.290346 | 2.422078 | -1.696484 |
| N | 0.344876 | 2.896101 | -2.732086 |

B3LYP / 6-31G(d) : -2063.3113301

B3LYP / 6-31G(d) + ZPE: -2062.806435