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# Synthesis, Characterization and X-Ray Crystal Structures of Cyclam Derivatives. Part VI. Proton Binding Studies of a Pyridine-Strapped 5,12-Dioxocyclam-Based Macrobicycle

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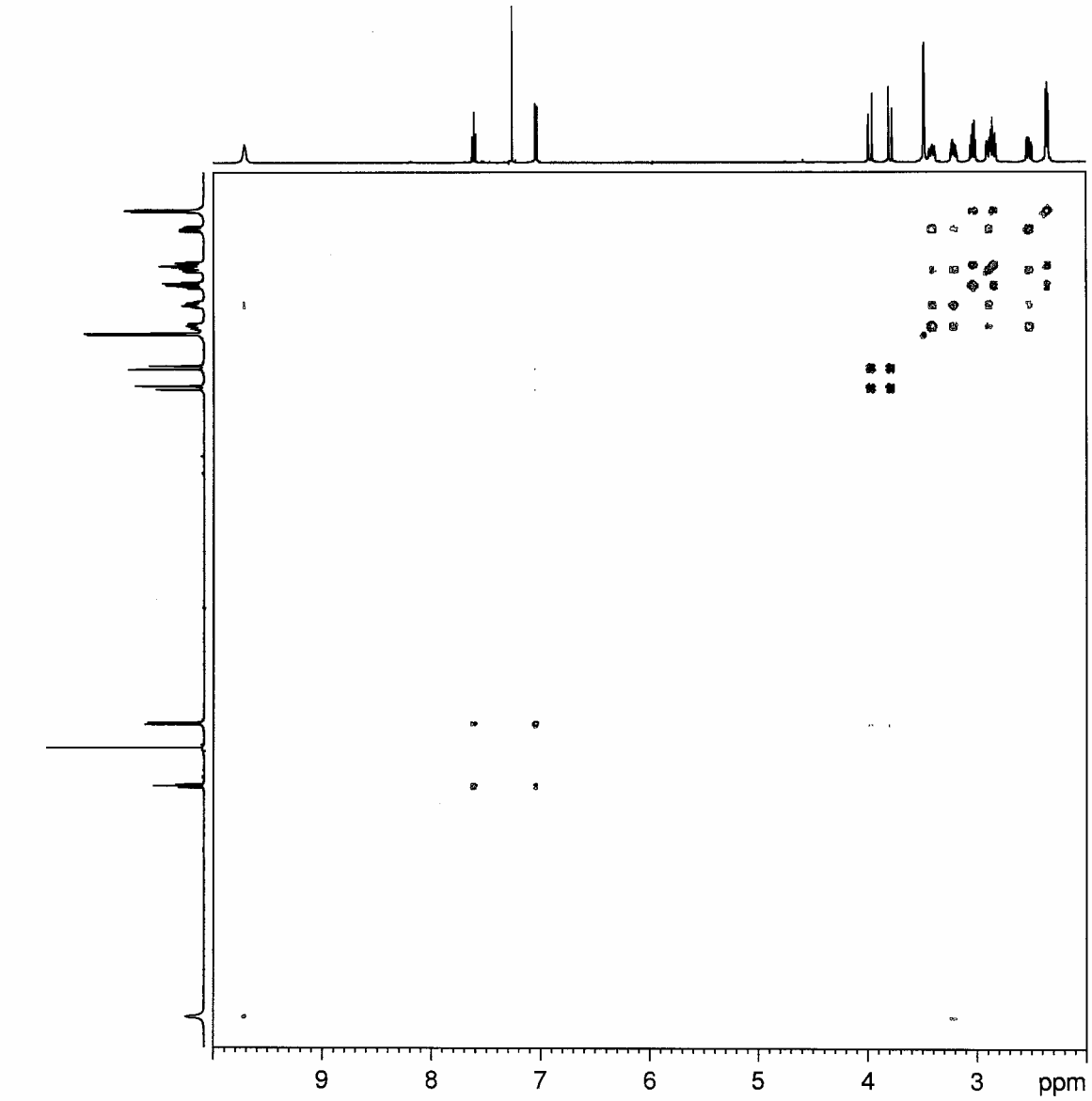



**Fig. S1** $^{1}H–^{1}H$ COSY (500 MHz) spectrum of ligand $\mathbf{L^1}$ recorded in $CDCl_3$ at room temperature.

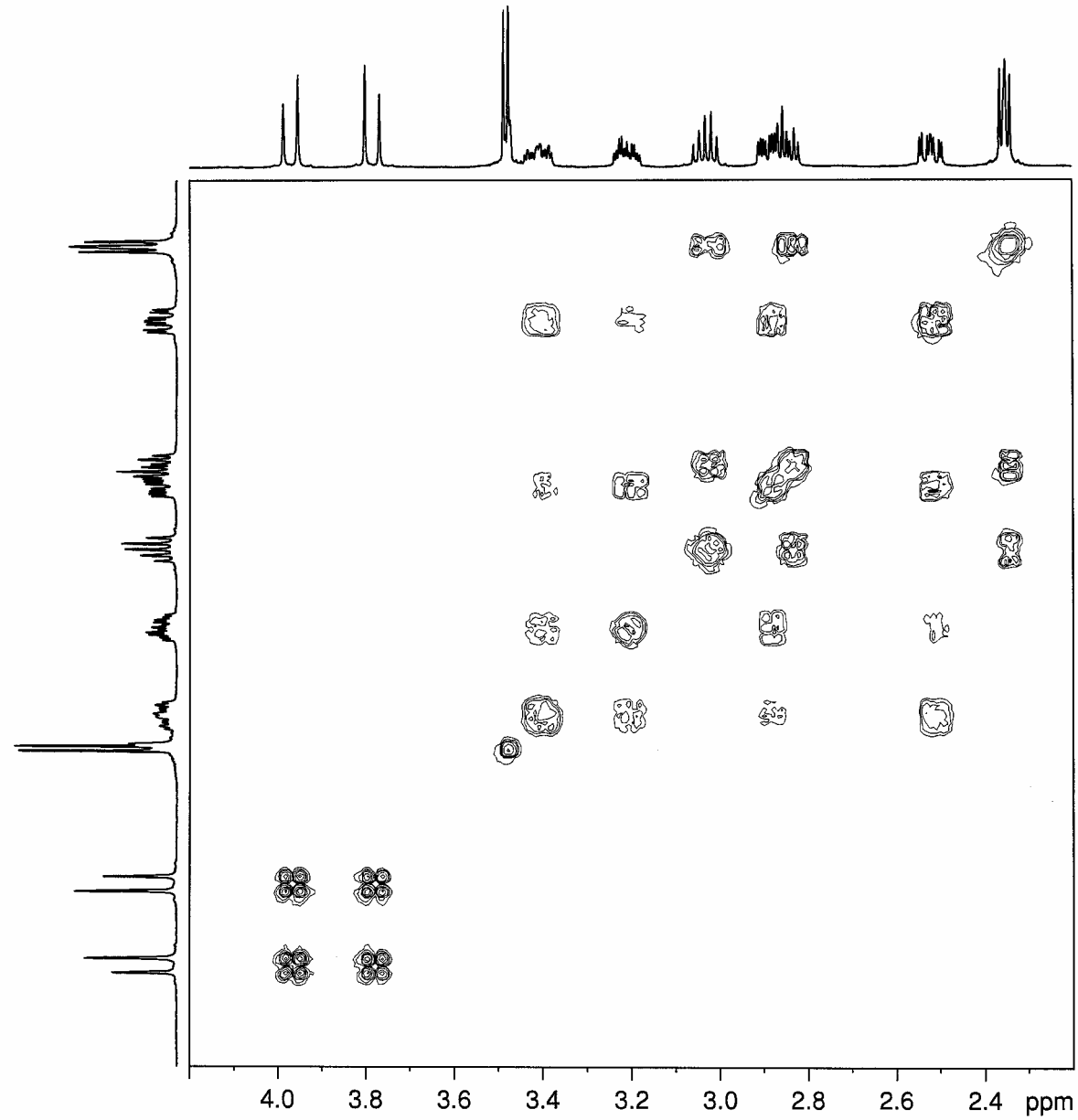



**Fig. S2** Enlargement showing the aliphatic region of the $^{1}H$–$^{1}H$ COSY spectrum of ligand **L**[1] recorded in $CDCl_3$ at room temperature.

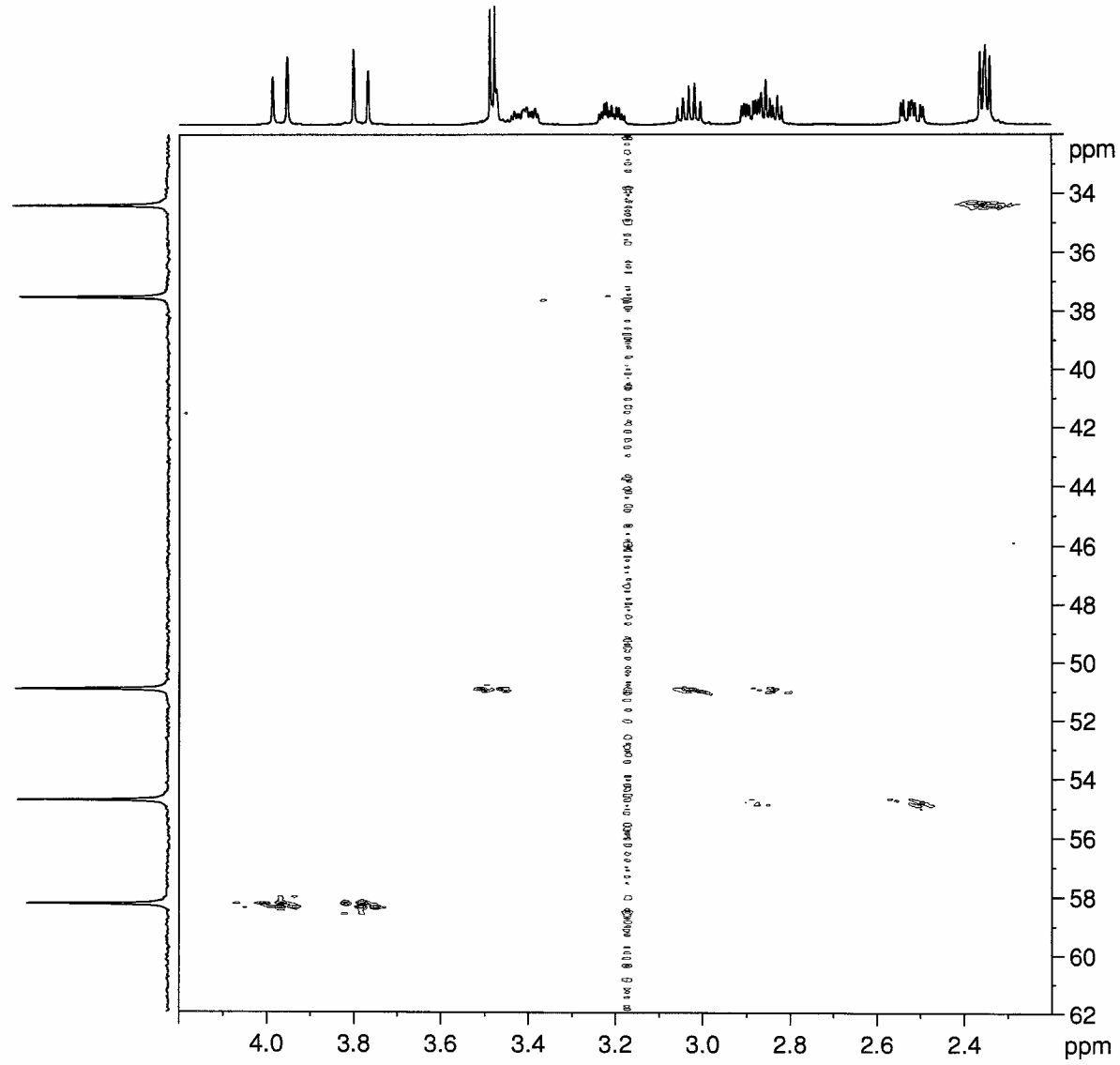



**Fig. S3** $^{1}H–^{13}C$ HETCOR spectrum of ligand $\mathbf{L^1}$ recorded in $CDCl_3$ at room temperature.

**Table S1** DFT-calculated energies (B3LYP/6-31G*) of $\mathbf{L^1}$ in different geometries.

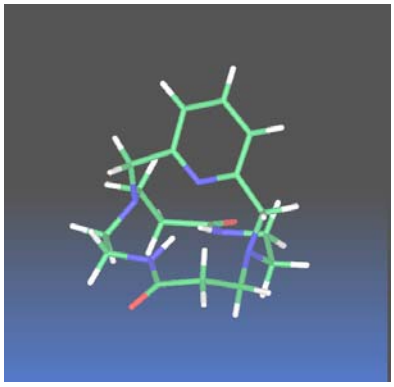
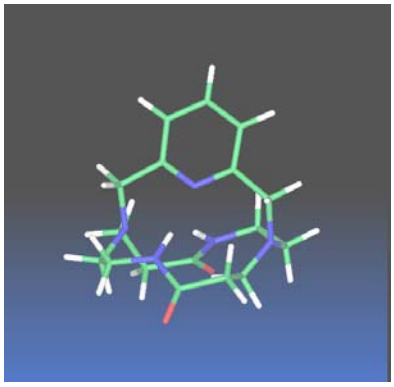
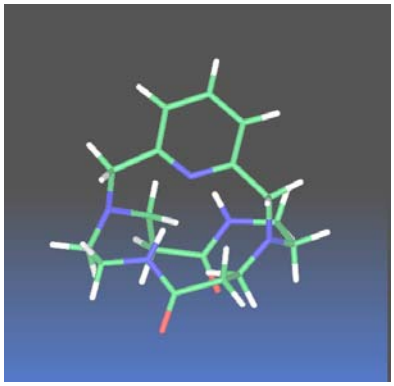
| $\mathbf{L^1}$ | $E$ (ua mol$^{-1}$) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|
|  | *in*-N, $N_{py}$, *in*-N | |
| | -1086.423576 | 0 |
|  | *in*-N, $N_{py}$, *out*-N | |
| | -1086.408717 | -9.32408525 |
|  | *out*-N, $N_{py}$, *out*-N | |
| | -1086.367948 | -34.90675825 |

**Table S2** DFT-calculated energies (B3LYP/6-31G*) of $[H(\mathbf{L^1})]^+$ in different geometries.

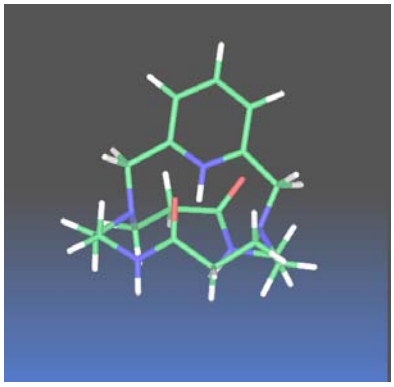
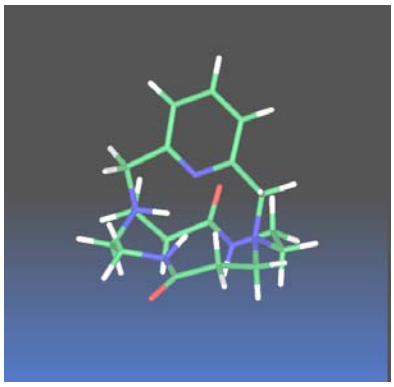
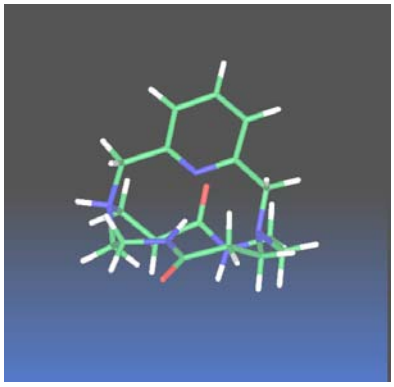
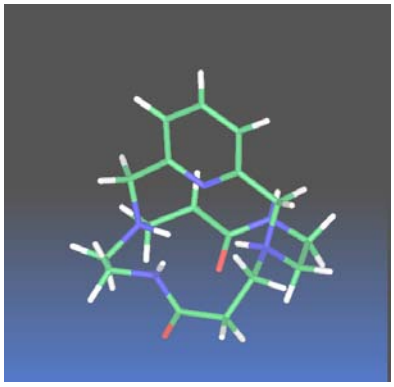
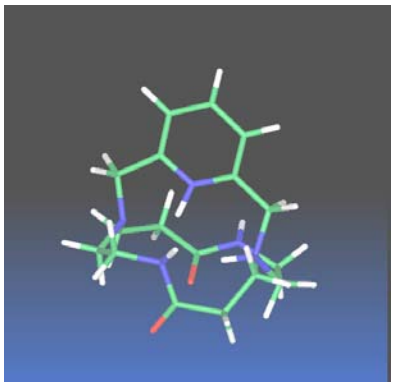
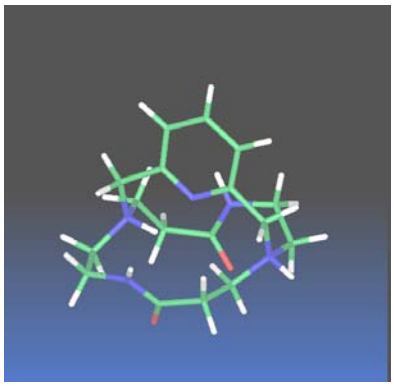
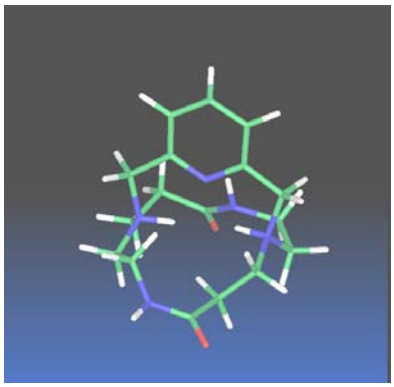
| $[H(\mathbf{L^1})]^+$ | $E$ (ua mol$^{-1}$) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|
|  | *in*-N, $(N_{py}H)^+$, *in*-N | |
| | -1086.834101 | 0 |
|  | *in*-$(NH)^+$, $N_{py}$, *in*-N | |
| | -1086.814206 | 12.48404975 |
|  | *out*-$(NH)^+$, $N_{py}$, *in*-N | |
| | -1086.786038 | 30.15959525 |

**Table S3** DFT-calculated energies (B3LYP/6-31G*) of $[H_2(\mathbf{L^1})]^{2+}$ in different geometries.

| $[H(\mathbf{L^1})]^+$ | $E$ (ua mol$^{-1}$) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|
|  | *in*-$(NH)^+$, $N_{py}$, *in*-$(NH)^+$ | |
| | -1087.11241 | 0 |
|  | *in*-N, $(N_{py}H)^+$, *in*-$(NH)^+$ | |
| | -1087.082982 | 18.4656935 |
|  | *in*-$(NH)^+$, $N_{py}$, *out*-$(NH)^+$ | |
| | -1087.07336 | 24.50368675 |
|  | *in*-$(NH)^+$, $N_{py}$, *in*-$(NH)^+$ | |
| | -1087.053624 | 36.88827775 |

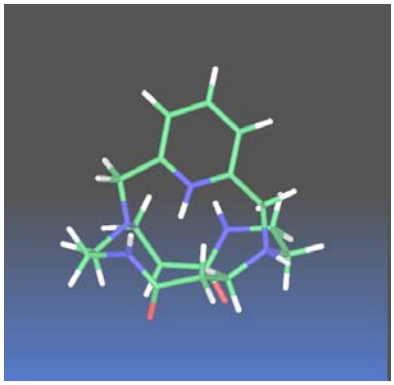
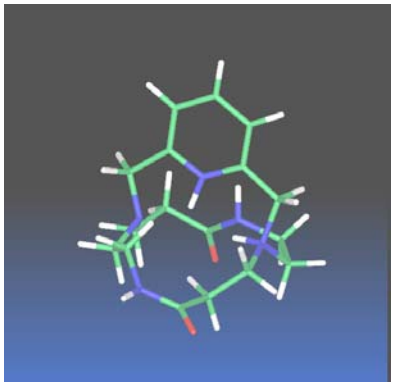
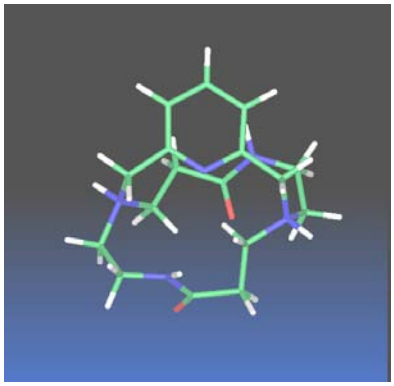
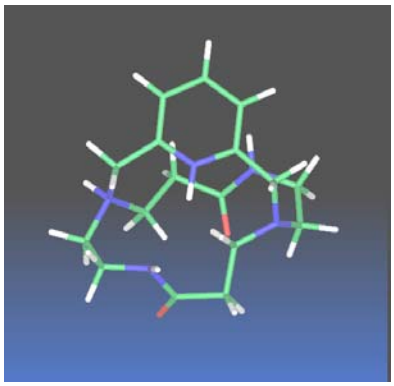
| $[H(\mathbf{L}^1)]^+$ | $E$ (ua mol$^{-1}$) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|
|  | *in*-N, $(N_{py}H)^+$,*out*-$(NH)^+$ | |
| | -1087.051722 | 38.08128075 |
|  | *in*-N, $(N_{py}H)^+$, *in*-$(NH)^+$ | |
| | -1087.029574 | 51.97915075 |
|  | *out*-$(NH)^+$, $N_{py}$, *out*-$(NH)^+$ | |
| | -1087.027026 | 53.57814625 |
|  | *out*-$(NH)^+$, $(N_{py}H)^+$, *out*-N | |
| | -1086.99354 | 74.59061125 |

**Table S4** Cartesian *x*,*y*,*z* coordinates of DFT-minimized (B3LYP/6-31G*) lowest-energy conformers of $\mathbf{L}^1$.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| N | 0.2517 | -1.0308 | -1.9048 |
| C | 0.6645 | -2.4423 | -1.8595 |
| H | 1.6874 | -2.4686 | -1.4668 |
| H | 0.7075 | -2.8699 | -2.8786 |
| C | -0.2089 | -3.3562 | -0.9793 |
| H | 0.0814 | -4.3945 | -1.1667 |
| H | -1.2639 | -3.2749 | -1.2690 |
| C | -0.1058 | -3.1552 | 0.5390 |
| O | -0.0377 | -4.1149 | 1.3033 |
| N | -0.1361 | -1.8576 | 0.9483 |
| H | -0.0951 | -1.1290 | 0.2393 |
| C | -0.0189 | -1.4707 | 2.3416 |
| H | 1.0198 | -1.1883 | 2.5780 |
| H | -0.2514 | -2.3533 | 2.9436 |
| C | -0.9833 | -0.3372 | 2.7102 |
| H | -0.8622 | -0.1236 | 3.7908 |
| H | -2.0071 | -0.6964 | 2.5636 |
| N | -0.8272 | 0.8764 | 1.9003 |
| C | -2.0334 | 1.7151 | 1.8719 |
| H | -2.1336 | 2.3133 | 2.7990 |
| H | -2.8952 | 1.0396 | 1.8460 |
| C | -2.1333 | 2.6739 | 0.6706 |
| H | -1.2111 | 3.2692 | 0.5839 |
| H | -2.9430 | 3.3841 | 0.8599 |
| C | -2.4354 | 2.0683 | -0.7103 |
| O | -3.3134 | 2.5436 | -1.4269 |
| N | -1.6475 | 1.0212 | -1.0853 |
| C | -1.5890 | 0.6007 | -2.4762 |
| C | -0.9932 | -0.8026 | -2.6491 |
| H | -1.7228 | -1.5295 | -2.2819 |
| H | -0.8676 | -0.9921 | -3.7336 |
| H | -1.0204 | 1.3338 | -3.0702 |
| H | -2.6028 | 0.6096 | -2.8859 |
| H | -0.8305 | 0.8123 | -0.5092 |
| C | 0.4209 | 1.5958 | 2.1549 |
| C | 1.5219 | 1.2906 | 1.1353 |
| C | 2.8795 | 1.5370 | 1.3850 |
| C | 3.8027 | 1.2344 | 0.3856 |
| C | 3.3621 | 0.6794 | -0.8205 |
| C | 1.9941 | 0.4621 | -0.9839 |
| N | 1.1160 | 0.7852 | -0.0275 |
| C | 1.3668 | -0.1362 | -2.2404 |
| H | 0.9978 | 0.6899 | -2.8596 |
| H | 2.1345 | -0.6422 | -2.8463 |
| H | 4.0659 | 0.4120 | -1.6043 |
| H | 4.8630 | 1.4098 | 0.5498 |
| H | 3.2014 | 1.9463 | 2.3386 |
| H | 0.8058 | 1.3886 | 3.1682 |
| H | 0.2261 | 2.6756 | 2.1280 |

**Table S5** Cartesian *x*,*y*,*z* coordinates of DFT-minimized (B3LYP/6-31G*) lowest-energy conformers of $[H(\mathbf{L^1})]^+$.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| N | 0.2519 | -1.0120 | -1.9767 |
| C | 0.5732 | -2.4548 | -1.8681 |
| H | 1.6435 | -2.5480 | -1.6704 |
| H | 0.3606 | -2.9729 | -2.8166 |
| C | -0.1512 | -3.1649 | -0.7186 |
| H | 0.1301 | -4.2263 | -0.7488 |
| H | -1.2418 | -3.1263 | -0.8271 |
| C | 0.2888 | -2.5771 | 0.6200 |
| O | 1.4311 | -2.1500 | 0.7851 |
| N | -0.6590 | -2.5234 | 1.5969 |
| H | -1.5821 | -2.8923 | 1.4087 |
| C | -0.4402 | -1.8265 | 2.8544 |
| H | 0.6386 | -1.6912 | 2.9514 |
| H | -0.7746 | -2.4510 | 3.6909 |
| C | -1.1894 | -0.4857 | 2.9152 |
| H | -1.1130 | -0.0766 | 3.9374 |
| H | -2.2531 | -0.6823 | 2.7453 |
| N | -0.7518 | 0.5044 | 1.9058 |
| C | -1.8370 | 1.4840 | 1.6680 |
| H | -2.1193 | 1.9915 | 2.6086 |
| H | -2.7188 | 0.9047 | 1.3657 |
| C | -1.5517 | 2.5769 | 0.6273 |
| H | -0.7620 | 3.2536 | 0.9664 |
| H | -2.4591 | 3.1922 | 0.5512 |
| C | -1.1369 | 2.1488 | -0.7826 |
| O | -0.2098 | 2.7143 | -1.3562 |
| N | -1.8218 | 1.1093 | -1.3512 |
| C | -1.5305 | 0.6531 | -2.7040 |
| C | -0.9520 | -0.7707 | -2.7889 |
| H | -1.7136 | -1.4832 | -2.4502 |
| H | -0.7753 | -0.9937 | -3.8573 |
| H | -0.8471 | 1.3949 | -3.1231 |
| H | -2.4426 | 0.6800 | -3.3122 |
| H | -2.6312 | 0.7315 | -0.8790 |
| C | 0.5292 | 1.1207 | 2.2670 |
| C | 1.4988 | 1.2479 | 1.1037 |
| C | 2.6644 | 2.0014 | 1.1347 |
| C | 3.5031 | 2.0025 | 0.0186 |
| C | 3.1608 | 1.2777 | -1.1230 |
| C | 1.9773 | 0.5521 | -1.1299 |
| N | 1.2302 | 0.5536 | -0.0142 |
| C | 1.4088 | -0.1879 | -2.3316 |
| H | 1.1295 | 0.5807 | -3.0603 |
| H | 2.2134 | -0.7678 | -2.8048 |
| H | 3.7954 | 1.2886 | -2.0023 |
| H | 4.4238 | 2.5798 | 0.0372 |
| H | 2.9151 | 2.5738 | 2.0211 |
| H | 1.0281 | 0.5034 | 3.0224 |
| H | 0.4058 | 2.1115 | 2.7300 |
| H | 0.3745 | -0.0176 | -0.0451 |

**Table S6** Cartesian *x*,*y*,*z* coordinates of DFT-minimized (B3LYP/6-31G*) lowest-energy conformers of $[H_2(\mathbf{L^1})]^{2+}$.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| C | -0.9158 | 2.6762 | 1.0510 |
| C | -0.4308 | 1.1484 | -3.4280 |
| C | -0.9277 | -2.5985 | 1.4872 |
| C | 2.3412 | -0.2139 | 1.5695 |
| C | -0.2434 | 1.1465 | -2.0437 |
| C | -0.7189 | -1.2468 | -3.3107 |
| C | -0.6733 | -0.0706 | -4.0639 |
| C | 2.1673 | -1.7425 | 1.5966 |
| C | 1.5950 | 2.7040 | 0.7223 |
| C | -1.7526 | 0.3427 | 1.4221 |
| C | -2.1285 | 1.7461 | 0.9419 |
| C | 2.7602 | 1.8255 | 0.2339 |
| C | 0.0552 | 2.4386 | -1.2869 |
| C | -0.6304 | -2.3708 | -1.0245 |
| C | -0.5330 | -1.1491 | -1.9329 |
| C | 1.3928 | -2.4344 | 0.4652 |
| H | -0.4091 | -2.3254 | 2.4033 |
| H | 3.6287 | 2.0927 | 0.8485 |
| H | 1.7525 | -1.9738 | 2.5796 |
| H | 1.8268 | -2.2036 | -0.5114 |
| H | 0.9611 | 2.9061 | -1.6809 |
| H | -2.9232 | 2.1626 | 1.5740 |
| H | -0.7547 | 3.1620 | -1.4112 |
| H | 3.0108 | 2.0408 | -0.8086 |
| H | 3.1711 | -2.1941 | 1.5848 |
| H | -2.5302 | 1.7031 | -0.0764 |
| H | -0.0860 | -3.2279 | -1.4287 |
| H | 2.8018 | -0.1696 | -0.4432 |
| H | -0.9433 | -3.6894 | 1.3984 |
| H | -0.5626 | 2.6857 | 2.0828 |
| H | -1.1590 | 3.6981 | 0.7506 |
| H | -0.3849 | 2.0707 | -4.0007 |
| H | -0.8200 | -0.1042 | -5.1395 |
| H | 1.4268 | -3.5197 | 0.5930 |
| H | -3.5204 | -0.4527 | 0.7869 |
| H | 1.5395 | 2.6479 | 1.8093 |
| H | -2.7263 | -2.2396 | 2.5637 |
| H | -3.0261 | -2.6790 | 0.8865 |
| H | 1.7257 | 3.7449 | 0.4147 |
| H | -0.9003 | -2.2050 | -3.7881 |
| H | -1.6748 | -2.6743 | -0.9153 |
| N | -2.5935 | -0.6761 | 1.1334 |
| N | -0.3055 | 0.0216 | -1.3210 |
| N | 2.4597 | 0.3926 | 0.3261 |
| N | 0.2568 | 2.2073 | 0.1977 |
| N | -0.0863 | -2.0581 | 0.3495 |
| O | -0.6498 | 0.1464 | 1.9522 |
| O | 2.3383 | 0.4362 | 2.5960 |
| C | -2.3830 | -2.0775 | 1.5341 |
| H | -0.1227 | -1.0294 | 0.4417 |
| H | 0.3016 | 1.1810 | 0.3200 |