Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Unraveling the Molecular Recognition of "three methylene spacer" Bis(benzimidazolium) Moiety by Dibenzo-24-crown-8: Pseudorotaxanes Under Study

Chhanda Mukhopadhyay*, Sabari Ghosh and

Ann Marie Schmiedekamp

Supplementary Information
Part 1

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(1) General procedure for preparation of solutions for pseudorotaxane formation: The solutions of the pseudorotaxanes were made by dilutions using volumetric glassware and pipettes. A typical experiment is as follows. **1f** (50.8 mg, 0.0001 mol) and dibenzo-24-crown-8 (44.8 mg, 0.0001 mol) were dissolved in CD_3CN (5 ml) giving a thread and crown concentration of 20 mM each respectively. The ^1H NMR spectrum of this clear solution was recorded immediately. The ratio for bound to unbound threads was obtained from the integration of the thread and crown peaks in the ^1H NMR spectra and averaged over two experiments. The resonances for the aromatic protons were chosen for this purpose, since the resolution was better in this region (δ 6.5 - 8.0) minimizing errors. The association constant (K_a) was then measured.

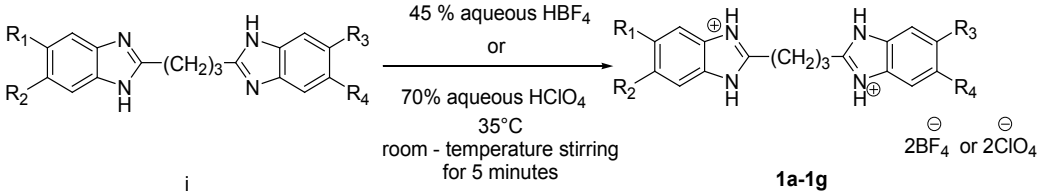
(2) The association constants reported in the paper should be considered as approximate as they do not take into account the extent of ion pair dissociation[1-4] of the dicationic thread and its counter ions as an intrinsic part of the thread / crown binding event. K_a was calculated from the formula below.

K_a = [pseudorotaxane] / {[thread] $_{unbound}$ x [crown] $_{unbound}$}

$[thread]_{unbound}$ and $[crown]_{unbound}$ are the original concentrations of thread and crown set up in the experiment minus the concentration of thread or crown bound in the pseudorotaxane. These values are calculated from the ratio of bound and unbound thread and crown obtained from the integrals of the ^1H NMR experiment. The units of K_a are expressed in M^{-1}.

(3) Materials and methods: All the reagents used were purchased from Aldrich and used as received without further purification. NMR spectra were recorded in CD_3CN unless otherwise mentioned. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker 300 MHz spectrometer. Only the low temperature ^1H NMR spectra at 240 K and 253 K were recorded on a Bruker 400 MHz spectrometer. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multilpet and br = broad. Letters in diagrams below are used to specify hydrogen positions in ^1H NMR of pseudorotaxanes, their corresponding salts and also carbon positions in ^{13}C NMR spectra of the salts.

(4) Scheme S1. Schematic representation for formation of the salts prior to complexation with the crown to form the pseudorotaxane complex.

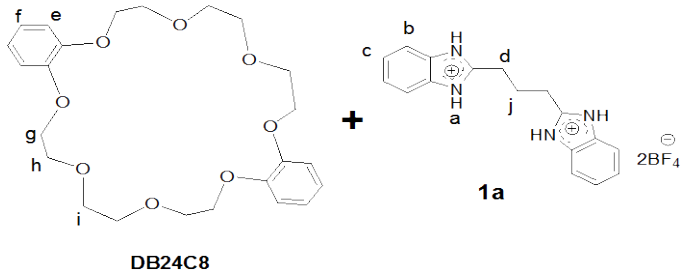


i 1a-1g

General procedure for the formation of the salts **1a-1g**: Initially, the bis-1*H*-benzimidazoles (i) were prepared by the methodology developed in our laboratory.[5] Next, for the preparation of the salts, to 1.0 mmol of a bis-benzimidazole, 1.0 mmol of 45 % aqueous fluoroboric acid / 1.0 mmol of 70 % perchloric acid was added and stirred at room temperature for 5 minutes. The solid was filtered, washed with a small amount of water and air-dried to get the corresponding salt. The salt was finally recrystallised by dissolving in acetonitrile and filtering, then adding diethyl ether till saturation. On standing colourless flakes separated.

(5) Spectral data of the pseudorotaxane followed by that of its corresponding salt:

1a ⊂ dibenzo-24-crown-8 (BF_4)$_2$



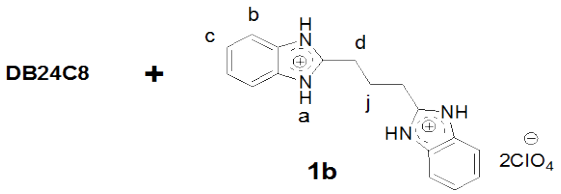
DB24C8 + **1a**

^{1}H NMR: separate sets of peaks for bound and unbound signals not possible at room temperature (308 K).

Spectral data for the corresponding salt **1a**.

^{1}H NMR: δ 7.79-7.73 (m, 4H, *b*), 7.58-7.53 (m, 4H, *c*), 3.30 (t, *J* = 7.5 Hz, 4H, *d*) and 2.51-2.43 (m, 2H, *j*). **^{13}C NMR**: δ 153.0 (N_a-C-C_d), 131.0 (N_a-C-C_b), 126.2 (C_b), 113.9 (C_c), 25.4 (C_d) and 23.9 (C_j). **FT-IR** (cm^{-1}): 3343.9, 1630.9, 1570.0, 1464.5, 1070.0, 763.2, 622.8 and 519.6. Anal. calcd. for $C_{17}H_{18}B_2F_8N_4$: C: 44.98; H: 4.44; N: 12.34 and found C: 44.90; H: 4.42; N: 12.36. Melting point (CH_3CN-Et_2O): 230 °C. Yield: 95 % (grey solid).

1b ⊂ dibenzo-24-crown-8 (ClO_4)$_2$



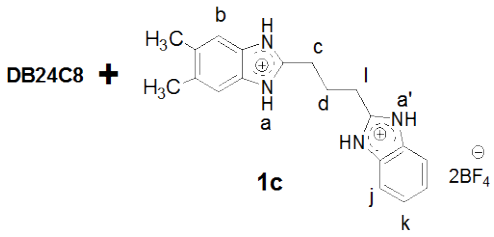
In ^{1}H NMR spectra, separate sets of peaks for bound and unbound signals were not observed at room temperature (308 K). Spectra were obtained at 240 K and 253 K. The splitting patterns of these two spectra were similar at both 240 K and 253 K; the extent of threading was different.

^{1}H NMR (at 240 K): δ 12.48-12.42 (br s, 8H, *a* and threaded *a*), 7.76 (br s, 4H, *b*), 7.63-7.52 (m, 8H, *c* and threaded *b*), 7.33 (br s, 4H, threaded *c*), 6.84 (s, 8H, *e* and *f*), 6.62 (br s, threaded *e* and threaded *f*), 4.04-3.98 (m, 16H, *g* and threaded *g*), 3.78 (br s, 16H, *h* and threaded *h*), 3.69 (br s, 8H, *i*), 3.58-3.55 (m, 8H, threaded *i*), 3.36- 3.27 (m, 8H, *d* and threaded *d*), 2.67 (m, 2H, *j*) and 2.42 (m, 2H, threaded *j*).

Spectral data for the corresponding salt **1b**.

^{1}H NMR: δ 12.23 (br s, 4H, *a*), 7.88-7.71 (m, 4H, *b*), 7.61-7.54 (m, 4H, *c*), 3.36 (t, *J* = 7.5 Hz, 4H, *d*) and 2.56-2.48 (m, 2H, *j*). **^{13}C NMR**: δ 152.8 (N_a-C-C_d), 130.4 (N_a-C-C_b), 126.6 (C_b), 113.9 (C_c), 25.4 (C_d) and 23.8 (C_j). **FT-IR** (cm^{-1}): 3305.9, 1628.0, 1566.7, 1462.2, 1106.4, 759.8 and 618.6. Anal. calcd. for $C_{17}H_{18}Cl_2N_4O_8$: C: 42.60; H: 4.21; N: 11.69 and found C: 42.66; H: 4.18; N: 11.73. Melting point (CH_3CN-Et_2O): 232 °C. Yield: 93 % (light brown solid).

1c ⊂ dibenzo-24-crown-8 (BF_4)$_2$



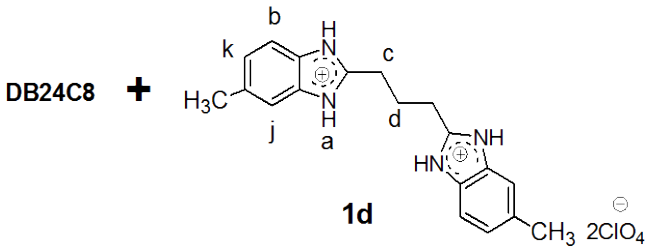
^{1}H NMR: δ 7.75 (br s, 2H, *j*), 7.57-7.48 (m, 6H, *b*, threaded *b*, threaded *j* and threaded *k*), 7.27 (s, 2H, *k*), 6.90 (s, 8H, *e* and *f*), 6.69-6.66 (m, 8H, threaded *e* and threaded *f*), 4.26-4.25 (m, 16H, *g* and threaded *g*), 4.09-3.80 (m, 16H, *h* and threaded *h*),3.70 (s, 8H, *i*), 3.60 (s, 8H, threaded *i*), 3.32-3.24 (m, 8H, *c*, *l*, threaded *c* and threaded *l*), 2.40-2.29 (m, 8H, *d* and C$\underline{H}_3$) and 2.13-2.09 (m, 8H, threaded *d* and threaded C$\underline{H}_3$). ESI-MS: m/z $C_{43}H_{53}N_4O_8$[{**1c ⊂** dibenzo-24-crown-8} – H^+]$^+$ calc.: 753.39, found: 753.41.

Spectral data for the corresponding salt **1c**

^{1}H NMR: δ 7.77 (br s, 2H, *j*), 7.58 (br s, 2H, *b*), 7.49 (d, *J* = 6.6 Hz, 2H, *k*), 3.32-3.28 (m, 4H, *c* and *l*) and 2.40 (br s, 8H, *d* and C$\underline{H}_3$). **^{13}C NMR**: δ 151.4 (N_a-C-C_c), 143.2 ($N_{a'}$-C-C_l), 136.7 (N_a-C-C_b), 130.4 ($N_{a'}$-C-C_j), 128.9 (C-CH_3), 126.5 (C_k), 113.8 (C_j), 113.3 (C_b), 25.3 (C_c and C_l), 23.9 (C_d) and 19.4 (C$\underline{H}_3$). Anal. calcd. for $C_{19}H_{22}B_2F_8N_4$: C: 47.54; H:

4.62; N: 11.67 and found C: 47.55; H: 4.60; N: 11.66. GC-MS (EI+): 480. **FT-IR** (cm^{-1}): 3347.8, 2928.0, 1629.0, 1465.5, 1060.3 and 756.2. Melting point (CH_3CN-Et_2O): 200 °C. Yield: 95 % (off-white solid).

1d ⊂ dibenzo-24-crown-8 $(ClO_4)_2$

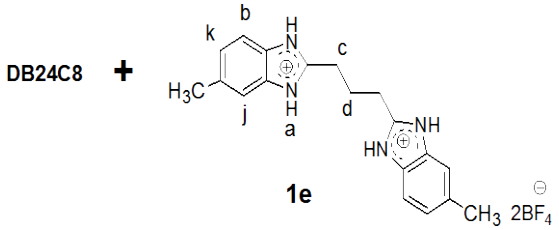


^{1}H NMR: δ 7.62-7.54 (m, 4H, *b* and *j*), 7.42-7.21 (m, 8H, *k*, threaded *b*, threaded *j* and threaded *k*), 6.91 (s, 8H, *e* and *f*), 6.70-6.65 (m, 8H, threaded *e* and threaded *f*), 4.09 (br s, 16H, *g* and threaded *g*), 3.82-3.59 (m, 32H, *h* , *i*, threaded *h* and threaded *i*), 3.30 (br s, *c* and threaded *c*) and 2.51-2.42 (m, 16H, *d*, C<u>H</u>$_3$, threaded *d* and threaded C<u>H</u>$_3$). ESI-MS: m/z $C_{43}H_{53}N_4O_8$[{**1d ⊂** dibenzo-24-crown-8} – H^+]$^+$ calc.: 753.39, found: 753.40.

<u>Spectral data for the corresponding salt **1d**</u>

^{1}H NMR: δ 12.04 (br s, 4H, *a*), 7.64 (d, *J* = 8.4 Hz, 2H, *b*), 7.55 (s, 2H, *j*), 7.41 (d, *J* = 8.4 Hz, 2H, *k*), 3.30 (t, *J* = 7.5 Hz, 4H, *c*) and 2.51-2.41 (m, 8H, *d* and C<u>H</u>$_3$). **^{13}C NMR**: δ 151.8 (N_a-<u>C</u>-C_c), 137.0 (N_a-<u>C</u>-C_b and N_a-<u>C</u>-C_j), 128.1 (C_k), 127.7 (<u>C</u>- CH_3), 113.0 (C_b), 112.9 (C_j), 24.9 (C_c), 23.5 (C_d) and 20.2 (<u>C</u>H$_3$). **FT-IR** (cm^{-1}): 3184.4, 1629.2, 1568.4, 1459.8, 1419.8, 1090.9, 814.8 and 622.8. Anal. calcd. for $C_{19}H_{22}Cl_2N_4O_8$: C: 45.16; H: 4.39; N: 11.09 and found C: 45.18; H: 4.37; N: 11.09. GC-MS (EI+): 504. Melting point (CH_3CN-Et_2O): 172 °C. Yield: 90 % (greenish-blue solid).

1e ⊂ dibenzo-24-crown-8 $(BF_4)_2$

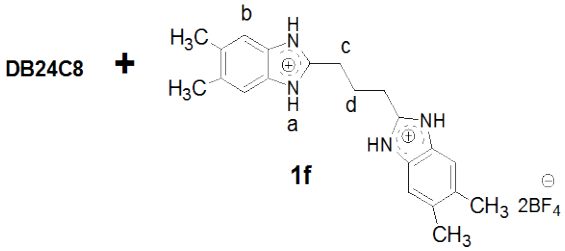


^{1}H NMR: δ 7.64-7.62 (d, *J* = 7.5 Hz, 2H, *b*), 7.54 (s, 2H, *j*), 7.42-7.39 (m, 8H, *k*, threaded *b*, threaded *j* and threaded *k*), 6.95 (s, 8H, *e* and *f*), 6.69-6.65 (m, 8H, threaded *e* and threaded *f*), 4.12 (br s, 16H, *g* and threaded *g*), 3.80-3.79 (m, 16H, *h* and threaded *h*), 3.69-3.66 (m, 16H, *i* and threaded *i*), 3.29-3.26 (m, 8H, *c* and threaded *c*) and 2.51-2.41 (m, 16H, *d*, C<u>H</u>$_3$, threaded *d* and threaded C<u>H</u>$_3$). ESI-MS: m/z $C_{43}H_{53}N_4O_8$[{**1e ⊂** dibenzo-24-crown-8} – H^+]$^+$ calc.: 753.39, found: 753.40.

Spectral data for the corresponding salt **1e**.

^{1}H NMR: δ 7.63 (d, *J* = 8.4 Hz, 2H, *b*), 7.53 (s, 2H, *j*), 7.39 (d, *J* = 7.8 Hz, 2H, *k*), 3.30 (t, *J* = 7.5 Hz, 4H, *c*) and 2.50-2.40 (m, 8H, *d* and C<u>H</u>$_3$). **^{13}C NMR**: δ 151.9 (N$_a$-<u>C</u>-C$_c$), 137.1 (N$_a$-<u>C</u>-C$_b$), 130.4 (N$_a$-<u>C</u>-C$_j$), 128.2 (<u>C</u>- CH$_3$), 127.8 (C$_k$), 113.1 (C$_b$), 112.9 (C$_j$), 25.0 (C$_c$), 23.6 (C$_d$) and 20.3 (<u>C</u>H$_3$). **FT-IR** (cm^{-1}): 3234.1, 1629.4, 1568.5, 1458.2, 1067.9 and 811.9. Anal. calcd. for $C_{19}H_{22}B_2F_8N_4$: C: 47.54; H: 4.62; N: 11.67 and found C: 47.54; H: 4.60; N: 11.66. GC-MS (EI+): 480. Melting point (CH_3CN-Et_2O): 260 °C. Yield: 90 % (grey solid).

1f ⊂ dibenzo-24-crown-8 (<u>B</u>F$_4$)$_2$

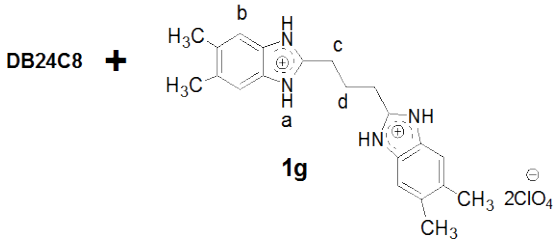


^{1}H NMR: δ 7.47 (s, 4H, *b*), 7.26 (s, 4H, threaded *b*), 6.93-6.86 (m, 8H, *e* and *f*), 6.72-6.69 (m, 4H, threaded *e*), 6.68-6.62 (m, 4H, threaded *f*), 4.10-4.07 (m, 8H, *g*), 4.02- 4.00 (m, 8H, threaded *g*), 3.81-3.76 (m, 16H, *h* and threaded *h*), 3.69 (s, 8H, *i*), 3.60 (s, 8H, threaded *i*), 3.32 (t, *J* = 7.5 Hz, 4H, threaded *c*), 3.22 (t, *J* = 7.5 Hz, 4H, *c*), 2.39 (s, 14 H, C<u>H</u>$_3$ and *d*) and 2.28 (s, 14 H, threaded C<u>H</u>$_3$ and threaded *d*). HR-ESI-MS: m/z $C_{45}H_{57}N_4O_8$[{**1f ⊂** dibenzo-24-crown-8} – H$^+$]$^+$ calc.: 781.4170, found: 781.4172.

Spectral data for the corresponding salt **1f**.

^{1}H NMR: δ 7.49 (s, 4H, *b*), 3.24 (t, *J* = 7.5 Hz, 4H, *c*) and 2.47-2.41 (m, 14 H, C<u>H</u>$_3$ and *d*). **^{13}C NMR**: δ 151.2 (N$_a$-<u>C</u>-C$_c$), 136.1 (N$_a$-<u>C</u>-C$_b$), 129.0 (<u>C</u>- CH$_3$), 113.1 (C$_b$), 25.0 (C$_c$), 23.7 (C$_d$) and 19.1 (<u>C</u>H$_3$). **FT-IR** (cm^{-1}): 3285.9, 2931.3, 1630.0, 1472.5, 1079.4, 861.8 and 776.9. Anal. calcd. for $C_{21}H_{26}B_2F_8N_4$: C: 49.64; H: 5.16; N: 11.03 and found C: 49.62; H: 5.17; N: 11.03. GC-MS (EI+): 508. Melting point (CH_3CN-Et_2O): 260 °C. Yield: 95 % (off-white solid).

1g ⊂ dibenzo-24-crown-8 (<u>Cl</u>O$_4$)$_2$

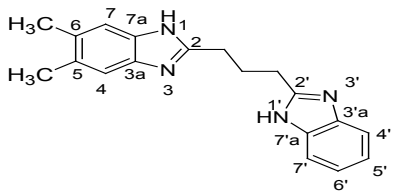


^{1}H NMR: δ 12.11-12.03 (m, 8 H, *a* and threaded *a*), 7.49 (s, 4H, *b*), 7.28 (s, 4H, threaded *b*), 6.94- 6.87 (m, 8H, *e* and *f*), 6.73-6.64 (m, 8H, threaded *e* and threaded *f*), 4.11-4.08 (m, 8H, *g*), 4.03-4.01 (m, 8H, threaded *g*), 3.83- 3.78 (m, 16H, *h* and threaded *h*), 3.71 (s, 8H, *i*), 3.62 (s, 8H, threaded *i*), 3.34 (t, *J* = 7.8 Hz, 4H, threaded *c*), 3.26 (t, *J* = 7.5 Hz, 4H, *c*), 2.50-2.40 (m, 14H, C$\underline{H}_3$ and *d*) and 2.29-2.27 (m, 14H, threaded C$\underline{H}_3$ and threaded *d*). HR-ESI-MS: m/z $C_{45}H_{57}N_4O_8$[{**1g** ⊂ dibenzo-24-crown-8} – H^+]$^+$ calc.: 781.4170, found: 781.4167.

Spectral data for the corresponding salt **1g.**

^{1}H NMR: δ 12.08 (br s, 4H, *a*), 7.49 (s, 4H, *b*), 3.28 (t, *J* = 7.5 Hz, 4H, *c*) and 2.48-2.38 (m, 14H, C$\underline{H}_3$ and *d*). **^{13}C NMR**: δ 151.4 (N_a-$\underline{C}$-C_c), 136.6 (N_a-$\underline{C}$-C_b), 128.9 ($\underline{C}$- CH_3), 113.3 (C_b), 25.3 (C_c), 24.02 (C_d) and 19.4 ($\underline{C}H_3$). **FT-IR** (cm^{-1}): 3223.9, 2948.3, 1626.7, 1470.9, 1111.3, 863.3 and 623.7. Anal. calcd. for $C_{21}H_{26}Cl_2N_4O_8$: C: 47.29; H: 4.91; Cl: 13.29; N: 10.50; O: 24.00 and found C: 47.30; H: 4.90; N: 10.51. GC-MS (EI+): 532. Melting point (CH_3CN-Et_2O): 265 °C. Yield: 93 % (off-white solid).

(6) Spectral data for the compound 5,6-Dimethyl-2, 2'-(1,3-propanediyl)bis-1*H*-benzimidazole:



^{1}H NMR (DMSO-d_6): δ 7.46-7.43 (m, 2H, $C_{4'}$ and $C_{7'}$), 7.20 (s, C_4 and C_7), 7.10-7.07 (m, 2H, $C_{5'}$ and $C_{6'}$), 2.92-2.80 (m, 4H, C_2-C$\underline{H}_2$ and $C_{2'}$-C$\underline{H}_2$) and 2.27-2.23 (m, 8H, C_2-CH_2-C$\underline{H}_2$ and C$\underline{H}_3$). **^{13}C-NMR (DMSO-d_6)**: δ 153.5 (C_2 and $C_{2'}$), 137.0 ($C_{3'a}$ and $C_{7'a}$), 129.3 (C_{7a} and C_{3a}), 117.8 (C_5 and C_6), 114.5 (C_4, C_7, $C_{4'}$, $C_{7'}$, $C_{5'}$ and $C_{6'}$), 27.9 (C_2-$\underline{C}H_2$ and $C_{2'}$-$\underline{C}H_2$), 25.8 (C_2-CH_2-$\underline{C}H_2$) and 19.9 ($\underline{C}H_3$). **FT-IR** (cm^{-1}):2939.2, 1541.8, 1452.7, 1309.6, 999.8 and 847.1.Anal. calcd. for $C_{19}H_{20}N_4$: C: 74.97; H: 6.62; N: 18.41 and found C: 74.92; H: 6.65; N: 18.40. Melting point (DMSO-H_2O): 270 °C. Yield: 75 % (off-white solid).

(7) Solubility chart: Solubilities (mol $\cdot L^{-1}$) at 35°C in solvent acetonitrile.

compound	solubility (mol $\cdot L^{-1}$) in acetonitrile
bis(benzimidazolium)ethane $(BF_4)_2$	0.15
(1,3-propanediyl) bis-1*H*-benzimidazolium $(BF_4)_2$	1.33
(1,3-propanediyl) bis-1*H*-benzimidazolium $(ClO_4)_2$	2.31
5, 6, 5', 6'-Tetramethyl-2,2'-(1,3-propanediyl) bis-1*H*-benzimidazolim $(BF_4)_2$	2.95

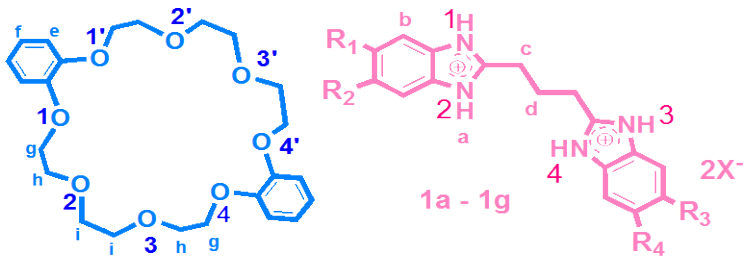
(8) Calculation Methods:

Calculations were used to explore several models of the protonated bis-benzimidazole threaded through the cavity of dibenzo-24-crown-8 ether. Structures were built and then optimized with molecular mechanics with Macromodel[6] using the OPLS 2005 force field. Macromodel geometries were obtained by constraining the crown ether dihedral angles along its backbone to the values in the crystal structure. All hydrogen atoms were allowed to move in the optimization. Then optimizations with the same dihedral angle constraints as in the Macromodel optimizations were performed with the hybrid B3LYP functional as implemented in the program Jaguar.[7] Our choice of basis set was 6-31G**++ and this was based on the work of Pudzianowski[8] who determined that basis sets with diffuse functions when used with the B3LYP functional yield results approaching "chemical accuracy" in the characterization of hydrogen bonding. When a local minimum was reached using this procedure, the entire molecule was optimized, relaxing the dihedral angle constraints. Geometries were optimized to default criteria.

(9) Details of DFT calculations:

Comparison of geometric parameters describing hydrogen bonding of protonated bis-benzimidazole thread to dibenzo-24-crown-8 ether (excluding anion and solvent effects). All bondlengths are in Angstroms and angles are in degrees. Energies are given in Hartrees and ΔE is in kJ/mole. O1, O2, O3, O4 and O1′, O2′, O3′, O4′ are as defined in the Scheme S2 given below.

Scheme S2



$R_1 = R_2 = R_3 = R_4 = H$; $X = BF_4^-$ (1a)
$R_1 = R_2 = R_3 = R_4 = H$; $X = ClO_4^-$ (1b)
$R_1 = R_2 = CH_3$, $R_3 = R_4 = H$; $X = BF_4^-$ (1c)
$R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$, $R_4 = H$; $X = ClO_4^-$ (1d)
$R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$, $R_4 = H$; $X = BF_4^-$ (1e)
$R_1 = R_2 = R_3 = R_4 = CH_3$; $X = BF_4^-$ (1f)
$R_1 = R_2 = R_3 = R_4 = CH_3$; $X = ClO_4^-$ (1g)

A protonated benzimidazole can easily bridge an approximately 7 Å nonbonded distance between O atoms of the crown and there are multiple ways that the bis(benzimidazolium) dication can fit, especially when the crown ether is also allowed to adjust. In each case at least one protonated benzimidazole bridges two available O atoms of the ether, forming two hydrogen bonds, one being approximately 1.8 Å and the other slightly more than 2.0 Å. On the other end of the thread, the second benzimidazole forms a strong hydrogen bond to only one ether O atom. The other NH proton points away from the crown. As protonated bis-benzimidazoles hydrogen bond to O atoms, the dibenzo-24-crown-8 accommodates by increasing most adjacent nonbonded O…O distances. For Cases **F** and cases **B**, **C**, **D**, **E**, one end of the thread bridged O_1 to O_4 and the other end of the thread provided an H bond only to $O_{2'}$. The four cases, **B**, **C**, **D** and **E** were created to compare the binding energy of the thread when CH_3 groups were substituted for H while the locations of the dication H-bonds were preserved. In Table 2, the binding energies are listed relative to case **E**, the lowest energy isomer. Structures **B** and **D** were only slightly more than 1 kJ/mole higher in energy, but in case **C**, where two methyl groups are on the same end of the thread which has the double H-bonds to the crown ether, the energy is 5.69 kJ/mole higher. Therefore hydrogen bond formation is slightly less stable with two methyl substituents. Cases **A** and **H** differ from the other cases because the double H-bond bridge spans between $O_{1'}$ and O_3. These conformations are much higher in energy (15 to 16 kJ /mole). On this end of the thread (R_1 and R_2 end), the hydrogen bonded distances are greater than when the bridge is along one side of the ether and a significant increase in energy occurs.

DFT Case A

1c ⊂ dibenzo-24-crown-8	**DFT Case A**					
Energy	Δ E	H bond bridge				
-2491.57052	16.16					
R_1	**H**	$O_{1'}$ to O_3	**N…$O_{1'}$**	**H_1…$O_{1'}$**	**<N-H_1-$O_{1'}$**	**N-H_1**
			2.858	1.862	162.6	1.026
R_2	**H**	$O_{1'}$ to O_3	**N….O_3**	**H_2…O_3**	**<N-H_2-O_3**	**N-H_2**
			2.854	1.912	151.5	1.024
R_3	**CH_3**	$O_{4'}$	**N…$O_{4'}$**	**H_3…$O_{4'}$**	**<N-H_3-$O_{4'}$**	**N-H_3**
			2.933	1.960	175	1.029
R_4	**CH_3**	none				
	$O_{1'}$…O_3 bridge		**O_1…$O_{1'}$**	**O_2…$O_{2'}$**	**O_3…$O_{3'}$**	**O_4…$O_{4'}$**
	6.953		2.676	6.236	6.512	2.670

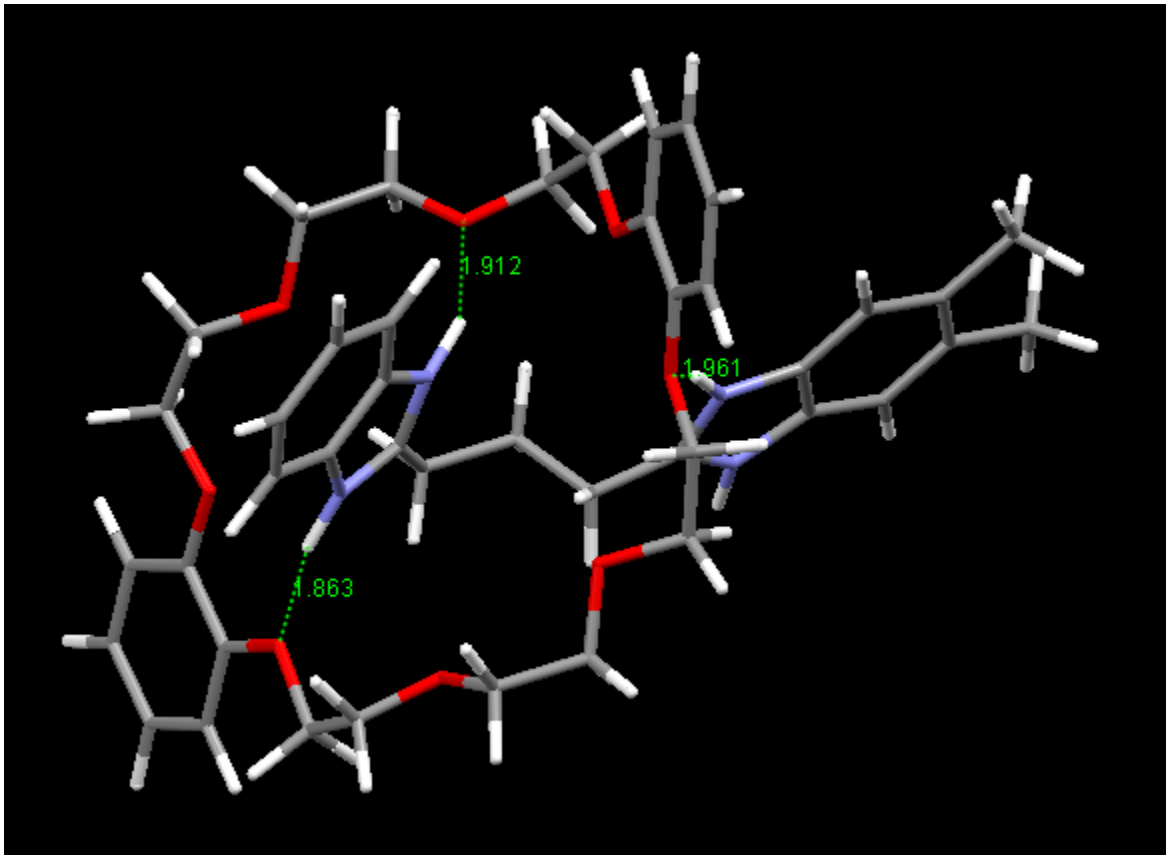


Figure S1. DFT Case **A**.

```
Energy components, in hartrees:
   (A)  Nuclear repulsion.............    8263.27356262336
   (E)  Total one-electron terms.....  -19779.08616419636
   (I)  Total two-electron terms.....    9024.24207803027
   (J)    Coulomb.....................    9373.68000591611
   (K)  Exchange + Correlation.......    -349.43792788584
   (L)  Electronic energy............  -10754.84408616609 (E+I)
   (N)  Total energy.................   -2491.57052354273 (A+L)

 SCFE: SCF energy: DFT (b3lyp)     -2491.57052354273 hartrees


  Final geometry:
                                    Angstroms
  Atom              x                   y                   z
  O1           4.6863030432      0.6791604723     -4.1242082387
  O2           2.0779230764     -0.7695132892     -3.7896721280
  O3           0.3931442609     -1.7721127434     -1.4536841581
  O4           0.5573840363     -3.1202216974      1.1163481502
  C5           5.3952428167      1.8529685769     -4.2842407606
  C6           6.4120365474      2.1210637622     -3.3391135575
  C7           7.1457855105      3.3043437626     -3.4300079545
  C8           6.8955406639      4.2194236664     -4.4590047646
  C9           5.9099318003      3.9505212745     -5.3990511863
  C10          5.1615593214      2.7716581392     -5.3104140648
  C11          3.7405109039      0.3514885020     -5.1514128614
  C12          3.0335212033     -0.9508614316     -4.8403221501
  C13          1.0429496739     -1.7485127137     -3.8075032117
  C14         -0.0290965620     -1.4231457130     -2.7866716114
  C15         -0.6524855144     -1.7751022907     -0.4733210129
  C16         -0.6276374044     -3.0691688563      0.3105139207
  O17          2.6877247651     -3.1837225920      2.7242729235
  O18          5.2766188972     -1.6237712108      2.4220586138
  O19          6.9735122020      0.0754104336      0.4206260867
  O20          6.6316435048      1.1630710854     -2.3517733895
  C21          1.9473548205     -4.3558562462      2.6062288827
  C22          0.8049845712     -4.3128622495      1.7746881527
  C23         -0.0039050510     -5.4463535404      1.6615858864
  C24          0.3220347110     -6.6264161695      2.3393926931
  C25          1.4582039968     -6.6760803559      3.1359477177
  C26          2.2668172070     -5.5417931683      3.2715072860
  C27          3.8821269505     -3.2814751933      3.5260951271
  C28          4.6138655590     -1.9610743366      3.6353586755
  C29          6.4195879852     -0.7851277726      2.6318810912
  C30          7.3679654230     -0.8317903256      1.4510438952
  C31          7.9842866183      0.1949398453     -0.5755586524
  C32          7.7452751051      1.3910057643     -1.4692806406
  H33          7.9225381535      3.5300512428     -2.7112924831
  H34          7.4814285449      5.1304540274     -4.5162528982
  H35          5.7134423478      4.6467582678     -6.2073517613
  H36          4.3998997325      2.5807197121     -6.0549684927
  H37          4.2668123553      0.2453874535     -6.1088479711
  H38          2.9922754674      1.1478914140     -5.2444951066
  H39          2.5157712218     -1.2604640027     -5.7595783916
  H40          3.7528293704     -1.7384560981     -4.5748877962
  H41          1.4490140006     -2.7536616527     -3.6189139886
  H42          0.5635346143     -1.7593861248     -4.7979396165
```

H43	-0.2834752727	-0.3561831318	-2.8339761913
H44	-0.9232062574	-2.0084621071	-3.0371725908
H45	-1.6310688196	-1.6936250010	-0.9606020831
H46	-0.5373578780	-0.9092282290	0.1917711841
H47	-1.5174077023	-3.1316456972	0.9506391415
H48	-0.6381731520	-3.9078870193	-0.3949449954
H49	-0.8965004177	-5.4283993396	1.0499832933
H50	-0.3196522229	-7.4948379127	2.2360402877
H51	1.7250256323	-7.5857541015	3.6631651204
H52	3.1415243861	-5.6037746889	3.9048965601
H53	3.6065286214	-3.5948459148	4.5407138809
H54	4.5496660725	-4.0307807075	3.0868140510
H55	5.3525874580	-2.0935814535	4.4394783584
H56	3.9360647418	-1.1547863268	3.9552178866
H57	6.1131392620	0.2537549332	2.8257934661
H58	6.9687880840	-1.1455933733	3.5130947993
H59	7.4248048115	-1.8597648087	1.0639463476
H60	8.3672384841	-0.5474254353	1.8141504026
H61	8.9630523250	0.3496147207	-0.0965651932
H62	8.0562342131	-0.7288542512	-1.1710407575
H63	8.6488997338	1.5533059483	-2.0682960627
H64	7.5565427242	2.2804770220	-0.8570512176
C65	-1.4001678604	1.1045451892	5.5472721643
C66	-1.3486373548	-0.3286302381	5.5102062633
C67	-0.4479228866	-0.9868169167	4.6718820417
C68	0.3941487381	-0.2084658694	3.8748879522
C69	0.3425496919	1.1895253306	3.9142269494
C70	-0.5490141354	1.8667067391	4.7462453858
N71	1.3889364068	-0.5398527205	2.9508417337
C72	1.9308877418	0.5754261580	2.4426226531
N73	1.3128762057	1.6306496718	3.0086384375
C74	3.8772439858	-0.8505470417	-1.3101019315
N75	3.2082491983	-1.9824954140	-1.0332238184
C76	3.9967007826	-3.0804970525	-1.3813632705
C77	5.2026968923	-2.5557150402	-1.8771685784
N78	5.0769105494	-1.1710903633	-1.8007762984
C79	3.7678050992	-4.4561016645	-1.3069229914
C80	4.7944256758	-5.2826404663	-1.7581375315
C81	6.0035602918	-4.7570068159	-2.2610267262
C82	6.2331109364	-3.3848785535	-2.3290181602
C83	-2.3791144264	1.8031728020	6.4586992471
C84	2.3632670120	0.7649983975	-0.0336389224
C85	-2.2740500236	-1.1382372756	6.3853883275
C86	3.3815270369	0.5517080126	-1.1611895327
C87	2.9776244047	0.6277238188	1.3821182342
H88	-0.4055976632	-2.0705846927	4.6434043070
H89	-0.5851046567	2.9508585393	4.7752724878
H90	1.6993507633	-1.4912039932	2.7142694630
H91	1.5379526909	2.5962084981	2.8078109379
H92	2.1978843441	-2.0132159267	-0.8698522977
H93	5.7330308153	-0.4525642825	-2.1271881153
H94	2.8415766444	-4.8612617301	-0.9141210224
H95	4.6621791048	-6.3589279873	-1.7227001816
H96	6.7732685206	-5.4401354887	-2.6048467734
H97	7.1612942828	-2.9848079808	-2.7227399718
H98	-2.2085672474	1.5363147946	7.5075015410
H99	-3.4125618288	1.5251728556	6.2238433603

H100	-2.2963780937	2.8885651476	6.3719186400
H101	1.9372127573	1.7667925591	-0.1524142617
H102	1.5339374285	0.0622278582	-0.1519977596
H103	-2.1189380026	-0.9127122225	7.4462515413
H104	-3.3250760154	-0.9200690301	6.1656642527
H105	-2.1166264539	-2.2096866516	6.2443683280
H106	2.9183100129	0.8203293009	-2.1164552265
H107	4.2525245208	1.2015669054	-1.0369511715
H108	3.6485285324	1.4715931604	1.5784520182
H109	3.5869266821	-0.2798717083	1.4561487334

DFT Case B

1c ⊂ dibenzo-24-crown-8	**DFT Case B**					
Energy	Δ E	H bond bridge				
-2491.57627	1.08					
R_1	**H**	O_1 to O_4	**N…O_1**	**H_1…O_1**	**<N-H_1-O_1**	**N-H_1**
			2.967	2.029	151.2	1.023
R_2	**H**	O_1 to O_4	**N….O_4**	**H_2…O_4**	**<N-H_2-O_4**	**N-H_2**
			2.862	1.834	174.5	1.031
R_3	**CH_3**	$O_{2'}$	**N…$O_{2'}$**	**H_3…$O_{2'}$**	**<N-H_3-$O_{2'}$**	**N-H_3**
			2.969	1.946	174.0	1.027
R_4	**CH_3**	none				
	O_1…O_4 bridge		**O_1…$O_{1'}$**	**O_2…$O_{2'}$**	**O_3…$O_{3'}$**	**O_4…$O_{4'}$**
	7.321		2.669	6.781	6.302	2.649

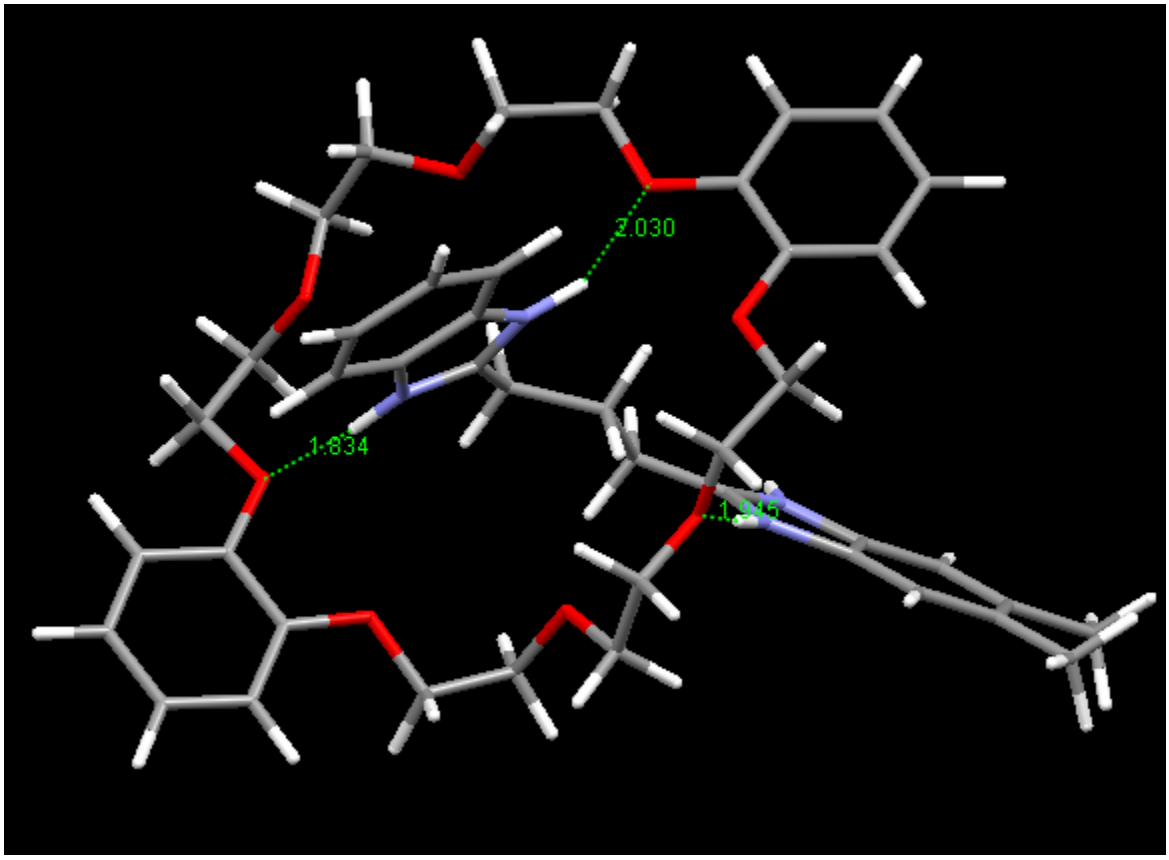


Figure S2. DFT Case **B**.

```
Energy components, in hartrees:
   (A)  Nuclear repulsion.............    8220.03200375063
   (E)  Total one-electron terms.....  -19693.06562764077
```

```
   (I)  Total two-electron terms.....    8981.45735786380
   (J)    Coulomb.....................    9330.89863574739
   (K)    Exchange+Correlation.......    -349.44127788359
   (L)  Electronic energy............  -10711.60826977697  (E+I)
   (N)  Total energy.................   -2491.57626602634  (A+L)
```

final geometry:

		angstroms	
atom	x	y	z
O1	1.3661176982	1.7717772215	-4.6118993499
O2	0.4114298928	-1.0274205293	-4.7993992341
O3	-0.7381010753	-3.0117779938	-3.0375050551
O4	0.8193105018	-4.4020987179	-0.8101427050
C5	1.2902429941	3.1150308518	-4.3183960382
C6	2.2431930895	3.6141529772	-3.4031101251
C7	2.2323984925	4.9626916158	-3.0494370066
C8	1.2836051042	5.8303967770	-3.6030089288
C9	0.3462025591	5.3442547925	-4.5067721103
C10	0.3476434327	3.9907474577	-4.8634457796
C11	0.5304347431	1.2839944436	-5.6606645402
C12	0.8318725053	-0.1885608673	-5.8798027412
C13	-0.9627361374	-1.4040705607	-4.8494268510
C14	-1.4281993447	-1.8301155299	-3.4744906271
C15	-1.1913571905	-3.4296788609	-1.7398789719
C16	-0.4950283630	-4.6966566952	-1.2959852694
O17	3.1207666006	-3.8335140857	0.4150823389
O18	4.8838448955	-1.3601448196	0.3744304354
O19	4.9921276433	1.2642427730	-1.1275971446
O20	3.1572485487	2.6972666162	-2.8939071702
C21	2.8130662636	-5.1747282696	0.2403406464
C22	1.5829366516	-5.4772515174	-0.3888773039
C23	1.2053235271	-6.8115816205	-0.5539888834
C24	2.0397617821	-7.8480198511	-0.1203056055
C25	3.2569066130	-7.5517445975	0.4781868957
C26	3.6413277603	-6.2183094139	0.6589506752
C27	4.2801267814	-3.5534301001	1.2280166756
C28	4.4307208776	-2.0756829210	1.5197585268
C29	5.5824597359	-0.1611187892	0.7263385177
C30	6.0701301101	0.5605757369	-0.5118476330
C31	5.4032344137	2.1162500071	-2.1925841572
C32	4.3964962559	3.2300356904	-2.3846556891
H33	2.9612348188	5.3516725179	-2.3485671895
H34	1.2911935228	6.8788601265	-3.3252880946
H35	-0.3892627955	6.0093058186	-4.9469245741
H36	-0.3854505859	3.6357853389	-5.5769118488
H37	0.7356159890	1.8307792558	-6.5913771618
H38	-0.5275805617	1.4299860013	-5.4053494844
H39	0.3659181767	-0.5121242717	-6.8213095166
H40	1.9139117228	-0.3222162240	-5.9722672726
H41	-1.1067652168	-2.2128817049	-5.5825294092
H42	-1.5958809440	-0.5607471691	-5.1568448259
H43	-1.2498783062	-1.0186579208	-2.7561011674
H44	-2.5083268831	-2.0318068736	-3.5131630180
H45	-2.2706550461	-3.6320160025	-1.7880560778
H46	-1.0257391941	-2.6244760838	-1.0118649476
H47	-1.0843780446	-5.1616714582	-0.4952596447

H48	-0.4448662154	-5.3993495263	-2.1372442233
H49	0.2556259309	-7.0635609739	-1.0078496919
H50	1.7232222670	-8.8774449476	-0.2498700441
H51	3.9126369785	-8.3452653412	0.8200946065
H52	4.5894332646	-6.0114354871	1.1371271390
H53	4.1722124459	-4.0806880490	2.1832084977
H54	5.1808942117	-3.9137143548	0.7181564829
H55	5.1760821767	-2.0000242733	2.3252572684
H56	3.4917381534	-1.6466388418	1.8993738710
H57	4.9323296497	0.5080427739	1.3079901266
H58	6.4543428987	-0.4191870717	1.3453852562
H59	6.5234095506	-0.1565387112	-1.2133558015
H60	6.8490022423	1.2751761134	-0.2073483968
H61	6.3660694704	2.5903653896	-1.9512710552
H62	5.5312845338	1.5428687843	-3.1229939799
H63	4.7932122465	3.9523818402	-3.1071344351
H64	4.2239613935	3.7349299774	-1.4270829320
C65	-0.3167688563	1.7288304265	1.4280972013
C66	-0.4604822341	0.4550221184	2.0171679256
C67	0.1802596763	-0.6685466182	1.4992900718
C68	0.9752003316	-0.4665525363	0.3676836949
C69	1.1209092823	0.8035479987	-0.2171553979
C70	0.4747952224	1.9290500816	0.3000899510
N71	1.7436746867	-1.3369503295	-0.4060481953
C72	2.3371732864	-0.6494492363	-1.3959583272
N73	1.9671172640	0.6312557662	-1.3110138469
C74	2.5405839290	-4.1895306908	-4.8656666298
N75	1.2319322176	-4.4494701121	-4.7302665176
C76	0.8981896688	-5.5971287148	-5.4555962031
C77	2.0804412980	-6.0443288369	-6.0541520630
N78	3.0714043520	-5.1406756820	-5.6561233812
C79	-0.3088663316	-6.2737608433	-5.6419398871
C80	-0.3043930359	-7.4130820547	-6.4475301829
C81	0.9097142450	-7.8696594866	-7.0594590959
C82	2.1076891239	-7.1822341200	-6.8603054013
C83	-1.5934001256	-8.1647565907	-6.6748927995
C84	2.6609682513	-2.5626592648	-2.9598599146
C85	0.8998588516	-9.1016551413	-7.9305881406
C86	3.2729582005	-3.0181565988	-4.2912729163
C87	3.2240051935	-1.2256194592	-2.4498017386
H88	-0.8365499026	2.5739335834	1.8670498269
H89	-1.0857848111	0.3491197532	2.8975042492
H90	0.0709183747	-1.6461807016	1.9564137675
H91	0.5829424533	2.9081369108	-0.1538700457
H92	1.9151108208	-2.3270062950	-0.2137152966
H93	2.3469031258	1.3702634639	-1.9209096256
H94	0.5806645009	-3.8915793039	-4.1653832363
H95	4.0479879022	-5.1810712996	-5.9172129109
H96	-1.2276448367	-5.9237492934	-5.1830666575
H97	3.0265818840	-7.5265604349	-7.3235099235
H98	-1.8514720250	-8.2030380677	-7.7390193721
H99	-1.5182515050	-9.2018791510	-6.3294876136
H100	-2.4253948045	-7.6945506097	-6.1458316728
H101	1.5873282219	-2.4355185851	-3.0971447023
H102	2.8086921891	-3.3412726304	-2.2075753390
H103	0.5569926867	-9.9807975283	-7.3742379704
H104	0.2235022980	-8.9814998120	-8.7842271841

H105	1.8960323647	-9.3199443868	-8.3209410826
H106	3.2212401877	-2.2013877329	-5.0241734615
H107	4.3310952380	-3.2825245133	-4.1831925344
H108	3.2876583999	-0.4914310854	-3.2581003093
H109	4.2238917641	-1.3485477755	-2.0207162039

DFT Case C

1c ⊂ dibenzo-24-crown-8	**DFT Case C**					
Energy	Δ E	H bond bridge				
-2491.57451	5.69					
R_1	**CH_3**	O_1 to O_4	**N…O_1**	**H_1…O_1**	**<N-H_1-O_1**	**N-H_1**
			2.985	2.054	150.3	1.022
R_2	**CH_3**	O_1 to O_4	**N….O_4**	**H_2…O_4**	**<N-H_2-O_4**	**N-H_2**
			2.863	1.837	174.5	1.030
R_3	**H**	$O_{2'}$	**N…$O_{2'}$**	**H_3…$O_{2'}$**	**<N-H_3-$O_{2'}$**	**N-H_3**
			2.955	1.930	173.9	1.028
R_4	**H**	none				
	O_1…O_4 bridge		**O_1…$O_{1'}$**	**O_2…$O_{2'}$**	**O_3…$O_{3'}$**	**O_4…$O_{4'}$**
	7.33		2.667	6.783	6.300	2.644

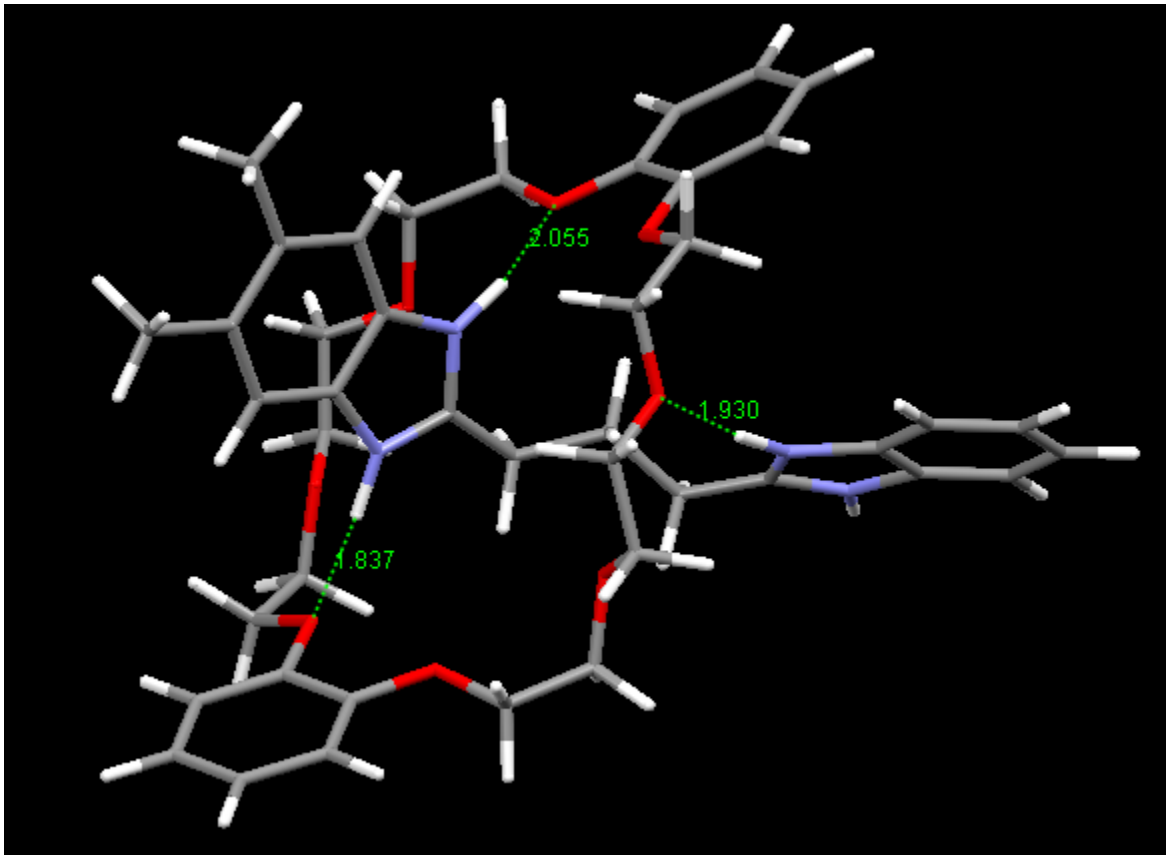


Figure S3. DFT Case **C**.

Energy components, in hartrees:

(A)	Nuclear repulsion.....	8279.52971384305	
(E)	Total one-electron terms.....	-19812.06335643398	
(I)	Total two-electron terms.....	9040.95913116739	
(J)	Coulomb.....	9390.40107371731	
(K)	Exchange+Correlation.....	-349.44194254992	
(L)	Electronic energy.....	-10771.10422526658	(E+I)
(N)	Total energy.....	-2491.57451142353	(A+L)

final geometry:

angstroms

atom	x	y	z
O1	1.3798205539	1.7928269631	-4.5952379305
O2	0.4360790547	-1.0179529837	-4.8080080515
O3	-0.7326446569	-3.0106850473	-3.0546111408
O4	0.8210262816	-4.4033749140	-0.8330117442
C5	1.2920287408	3.1321755298	-4.2872374463
C6	2.2498554495	3.6309711281	-3.3765237438
C7	2.2275105416	4.9749114613	-3.0061881232
C8	1.2627684672	5.8380985905	-3.5393231065
C9	0.3212698507	5.3523658900	-4.4390313522
C10	0.3339811420	4.0031229179	-4.8120252795
C11	0.5429917827	1.3062459010	-5.6431507345
C12	0.8549086719	-0.1624036837	-5.8767672200
C13	-0.9388288007	-1.3921779948	-4.8614950077
C14	-1.4103031948	-1.8202516579	-3.4891932254
C15	-1.1873133982	-3.4237584091	-1.7549511587
C16	-0.4968970647	-4.6936367356	-1.3100004577
O17	3.1251001557	-3.8395664902	0.3856709104
O18	4.8848864252	-1.3614367728	0.3705779044
O19	4.9944597633	1.2777913166	-1.1143498257
O20	3.1771018403	2.7166273621	-2.8900582362
C21	2.8229382305	-5.1791988433	0.1983457910
C22	1.5900481205	-5.4804204378	-0.4264463242
C23	1.2160195556	-6.8141669950	-0.6031254385
C24	2.0579747131	-7.8520090883	-0.1871496661
C25	3.2783390362	-7.5571023001	0.4059199368
C26	3.6583013789	-6.2240667928	0.5995614665
C27	4.2808671938	-3.5614690293	1.2038098661
C28	4.4226174498	-2.0851579955	1.5068674749
C29	5.5671735610	-0.1577988684	0.7374348903
C30	6.0673052184	0.5745070829	-0.4897048235
C31	5.4154645528	2.1449220596	-2.1628931760
C32	4.4032677842	3.2535615189	-2.3558798378
H33	2.9594217800	5.3641277680	-2.3087618841
H34	1.2616179307	6.8833120365	-3.2493517200
H35	-0.4260709076	6.0144241724	-4.8634364010
H36	-0.4027247524	3.6481072988	-5.5218271675
H37	0.7388104391	1.8622750050	-6.5704538471
H38	-0.5150075985	1.4416276374	-5.3817599518
H39	0.3943559045	-0.4782889219	-6.8235305015
H40	1.9381221776	-0.2879429596	-5.9664891246
H41	-1.0834362743	-2.1981132476	-5.5977368060
H42	-1.5696598532	-0.5468698750	-5.1679575345
H43	-1.2250091890	-1.0137387252	-2.7672208906
H44	-2.4920923194	-2.0121936570	-3.5304919285
H45	-2.2677557936	-3.6198037868	-1.8021380403

H46	-1.0151076043	-2.6180054170	-1.0294308199
H47	-1.0847950616	-5.1534024215	-0.5051342663
H48	-0.4559022565	-5.3995448373	-2.1491620844
H49	0.2633467528	-7.0651108711	-1.0515357474
H50	1.7446516982	-8.8812772298	-0.3257223220
H51	3.9398167119	-8.3517055200	0.7341142068
H52	4.6085596330	-6.0181347959	1.0740740021
H53	4.1729479957	-4.0975463158	2.1541408086
H54	5.1852384525	-3.9125320030	0.6937441530
H55	5.1597159180	-2.0115286872	2.3202636546
H56	3.4777758780	-1.6623424328	1.8789046495
H57	4.9023691533	0.5030139970	1.3120743005
H58	6.4319636876	-0.4109561839	1.3684724946
H59	6.5331032222	-0.1355721137	-1.1901468338
H60	6.8388264163	1.2904649187	-0.1698483615
H61	6.3711689884	2.6230974791	-1.9018078574
H62	5.5611548186	1.5838632505	-3.0981903066
H63	4.8047417610	3.9891885669	-3.0623225637
H64	4.2120867929	3.7434189363	-1.3939949801
C65	-0.3540618181	1.7768467170	1.3649676791
C66	-0.5148412783	0.4885413637	1.9710373867
C67	0.1404272949	-0.6290739692	1.4493064429
C68	0.9547439131	-0.4501731336	0.3286516347
C69	1.1151537687	0.8103287548	-0.2593787778
C70	0.4639878465	1.9369344019	0.2458382061
N71	1.7275592431	-1.3314853823	-0.4299649897
C72	2.3388212231	-0.6526868666	-1.4165179907
N73	1.9752897803	0.6303662890	-1.3406443815
C74	2.5336240678	-4.2161759558	-4.8576674412
N75	1.2243601860	-4.4683327008	-4.7203666777
C76	0.8857575214	-5.6254372845	-5.4284909974
C77	2.0718497691	-6.0888999323	-6.0181995011
N78	3.0634145118	-5.1809188287	-5.6313598333
C79	-0.3286121991	-6.2937850448	-5.6022320957
C80	-0.2976284934	-7.4413919289	-6.3892594808
C81	0.8970913026	-7.9063738956	-6.9785302063
C82	2.1071705212	-7.2406930662	-6.8057273054
C83	-1.0702206107	2.9773331478	1.9359374630
C84	2.6642205651	-2.5761572685	-2.9646137978
C85	-1.3979259095	0.3304561298	3.1857694344
C86	3.2702421961	-3.0415916440	-4.2955007644
C87	3.2326236666	-1.2394446507	-2.4592813929
H88	-1.2163234501	-7.9933467890	-6.5570349638
H89	0.8707763245	-8.8057533608	-7.5843127364
H90	0.0211879350	-1.6046242769	1.9101531295
H91	0.5866752877	2.9105574441	-0.2175822699
H92	1.8884004577	-2.3213440805	-0.2339649608
H93	2.3650949235	1.3683641058	-1.9433839731
H94	0.5737038257	-3.9001679961	-4.1626415574
H95	4.0410522183	-5.2289505651	-5.8882002758
H96	-1.2492140196	-5.9356040648	-5.1550854051
H97	3.0232390294	-7.6002099580	-7.2616363404
H98	-0.7757598377	3.1623319028	2.9748009549
H99	-2.1569674233	2.8364309927	1.9345623478
H100	-0.8493240412	3.8791871798	1.3606184128
H101	1.5908674297	-2.4454180368	-3.1001508980
H102	2.8102515444	-3.3519902254	-2.2094221059

H103	-1.0476796056	0.9501447597	4.0189603973
H104	-2.4289000567	0.6370957830	2.9759137659
H105	-1.4198767818	-0.7067647237	3.5281305519
H106	3.2137599524	-2.2316796271	-5.0356173955
H107	4.3286427741	-3.3065206591	-4.1920088754
H108	3.3055915383	-0.5106097252	-3.2717458237
H109	4.2292674245	-1.3660951647	-2.0237156401

DFT Case D

1d ⊂ dibenzo-24-crown-8 or **1e ⊂ dibenzo-24-crown-8**	**DFT case D**					
Energy	Δ E	H bond bridge				
-2491.57615	1.39					
R_1	**CH_3**	O_1 to O_4	**$N…O_1$**	**$H_1…O_1$**	**<$N-H_1-O_1$**	**$N-H_1$**
			2.967	2.030	151.2	1.022
R_2	**H**	O_1 to O_4	**$N….O_4$**	**$H_2…O_4$**	**<$N-H_2-O_4$**	**$N-H_2$**
			2.877	1.851	174	1.03
R_3	**CH_3**	$O_{2'}$	**$N…O_{2'}$**	**$H_3…O_{2'}$**	**<$N-H_3-O_{2'}$**	**$N-H_3$**
			2.937	1.914	172.8	1.028
R_4	**H**	none				
	$O_1…O_4$ bridge		**$O_1…O_{1'}$**	**$O_2…O_{2'}$**	**$O_3…O_{3'}$**	**$O_4…O_{4'}$**
	7.329		2.666	6.766	6.277	2.648

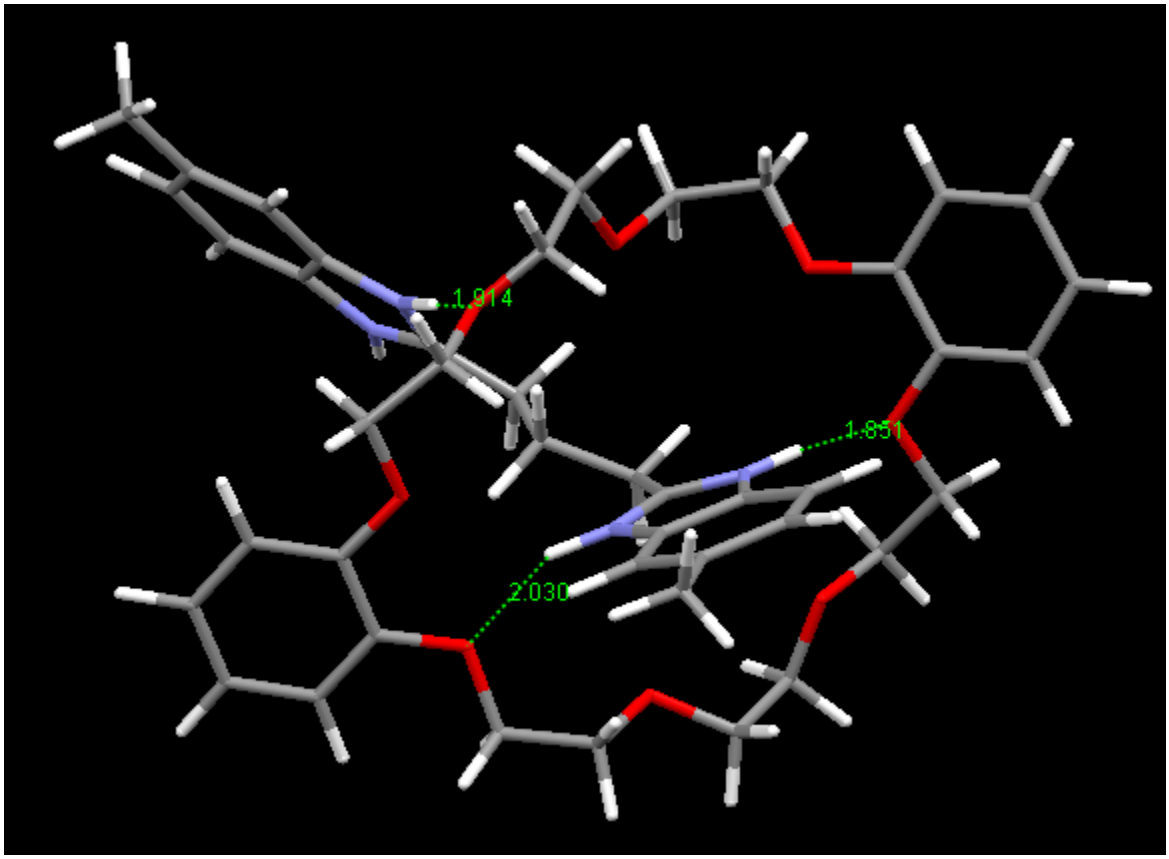


Figure S4. DFT Case **D**.

Energy components, in hartrees:

(A)	Nuclear repulsion.....	8255.37143112118	
(E)	Total one-electron terms.....	-19763.71650436666	
(I)	Total two-electron terms.....	9016.76892577462	
(J)	Coulomb.....	9366.20883765319	
(K)	Exchange+Correlation.....	-349.43991187857	
(L)	Electronic energy.....	-10746.94757859205	(E+I)
(N)	Total energy.....	-2491.57614747087	(A+L)

final geometry:

	angstroms		
atom	x	y	z
O1	1.4085838490	1.7700200375	-4.6391914856
O2	0.4497713824	-1.0272763980	-4.7743302502
O3	-0.7137584424	-3.0046452017	-3.0205873390
O4	0.8489111578	-4.4079296012	-0.8183670507
C5	1.3276426965	3.1184733690	-4.3713598105
C6	2.2511225400	3.6290893334	-3.4328748954
C7	2.2325225586	4.9830123360	-3.1008233539
C8	1.3069620965	5.8447478435	-3.7009198739
C9	0.4000809780	5.3472829119	-4.6293566366
C10	0.4082016373	3.9880388114	-4.9635628010
C11	0.5895993571	1.2635240726	-5.6913797011
C12	0.8840857981	-0.2158632743	-5.8702333571
C13	-0.9297478228	-1.3835362055	-4.8201258469
C14	-1.3929816825	-1.8118765427	-3.4451095728
C15	-1.1695473681	-3.4372697075	-1.7281921441
C16	-0.4671343288	-4.7053834230	-1.2965883674
O17	3.1468850260	-3.8330550664	0.4045670772
O18	4.8813965049	-1.3409586032	0.3998098621
O19	4.9694869161	1.2941170428	-1.0889515334
O20	3.1455075319	2.7186983846	-2.8803423527
C21	2.8538616327	-5.1744092631	0.2133907833
C22	1.6243742213	-5.4813616931	-0.4149269913
C23	1.2596781056	-6.8168604610	-0.5971673057
C24	2.1075567995	-7.8501679654	-0.1817870000
C25	3.3243786373	-7.5490867340	0.4155842088
C26	3.6953585430	-6.2142709561	0.6138066457
C27	4.2982795137	-3.5482546856	1.2270031904
C28	4.4267570743	-2.0716404645	1.5345358062
C29	5.5516189907	-0.1309545033	0.7680507487
C30	6.0477127027	0.6036683639	-0.4590527151
C31	5.3864327124	2.1537088681	-2.1453448263
C32	4.3726681213	3.2586359358	-2.3496646224
H33	2.9368414751	5.3800527677	-2.3796657894
H34	1.3082269218	6.8973865479	-3.4394588768
H35	-0.3166422736	6.0076299393	-5.1059822479
H36	-0.3008234463	3.6242751683	-5.6966703010
H37	0.8168426705	1.7846874009	-6.6317688365
H38	-0.4718338364	1.4250547038	-5.4608118007
H39	0.4253356003	-0.5598695133	-6.8082114031
H40	1.9662657058	-0.3572117079	-5.9486114076
H41	-1.0894445964	-2.1856083168	-5.5575746447
H42	-1.5525472964	-0.5293922071	-5.1186449404
H43	-1.2004232129	-1.0078191388	-2.7222250178
H44	-2.4754591107	-2.0008763602	-3.4791084496
H45	-2.2477378929	-3.6438285372	-1.7818430947

H46	-1.0084967978	-2.6387882530	-0.9920541312
H47	-1.0499408621	-5.1776337270	-0.4952253985
H48	-0.4202332765	-5.4029099349	-2.1424007188
H49	0.3102193421	-7.0722241729	-1.0500054208
H50	1.8017329552	-8.8811355041	-0.3243615197
H51	3.9901400139	-8.3403151008	0.7431502763
H52	4.6432507062	-6.0031142548	1.0907298777
H53	4.1919839817	-4.0880663708	2.1753201690
H54	5.2066007098	-3.8904675135	0.7180754084
H55	5.1634796234	-1.9933754388	2.3477973243
H56	3.4782044429	-1.6587402692	1.9083961453
H57	4.8795091406	0.5242977326	1.3405534075
H58	6.4171968001	-0.3756449474	1.4012790170
H59	6.5226006008	-0.1035249123	-1.1563365876
H60	6.8110718259	1.3283485911	-0.1393468701
H61	6.3408468862	2.6369696549	-1.8888228659
H62	5.5338711181	1.5846698280	-3.0755687797
H63	4.7761564632	3.9857366595	-3.0634835245
H64	4.1801513883	3.7601331167	-1.3940545850
C65	-0.3992313184	1.6407926042	1.4115680200
C66	-0.5367878324	0.3591306580	2.0078868803
C67	0.1496603078	-0.7307749525	1.4678126085
C68	0.9548804984	-0.4995484676	0.3484397047
C69	1.0830862033	0.7733016614	-0.2272114726
C70	0.4003490199	1.8741823091	0.2987202413
N71	1.7471998604	-1.3509488516	-0.4208460126
C72	2.3397713895	-0.6483264324	-1.4018415923
N73	1.9453731740	0.6250857302	-1.3133594787
C74	2.5404683759	-4.1937583410	-4.8479871765
N75	1.2275814982	-4.4261099585	-4.7044899549
C76	0.8634862538	-5.5665367854	-5.4245216630
C77	2.0348808831	-6.0426026379	-6.0275255768
N78	3.0468657485	-5.1584589130	-5.6375546996
C79	-0.3687357491	-6.2028056139	-5.5955367738
C80	-0.3994755275	-7.3448275356	-6.3974236374
C81	0.8002127276	-7.8157314038	-6.9965722983
C82	2.0277831849	-7.1866461148	-6.8293278607
C83	-1.6917529657	-8.0857051938	-6.6405613140
C84	2.6983388381	-2.5666683179	-2.9460643895
C85	-1.4230432414	0.1942967039	3.2195963128
C86	3.2956715951	-3.0317441384	-4.2817969329
C87	3.2390017635	-1.2127428100	-2.4532786289
H88	-0.9431471007	2.4742325684	1.8463848807
H89	0.7532607536	-8.7065421575	-7.6157183851
H90	0.0648956724	-1.7196800123	1.9072334192
H91	0.4865944572	2.8630413986	-0.1386732314
H92	1.9298982035	-2.3394332800	-0.2338092083
H93	2.3187107913	1.3740813074	-1.9138695112
H94	0.5885583438	-3.8574289551	-4.1343140928
H95	4.0210269166	-5.2203443305	-5.9041046224
H96	-1.2708847189	-5.8194830492	-5.1304564450
H97	2.9268531754	-7.5679110094	-7.3012783033
H98	-1.9272164332	-8.1209790957	-7.7096374336
H99	-1.6204220260	-9.1212389048	-6.2914934052
H100	-2.5313877310	-7.6126607087	-6.1258780701
H101	1.6209509342	-2.4594007125	-3.0675349570
H102	2.8701776102	-3.3343225807	-2.1878392863

H103	-1.0743456367	0.8200728893	4.0483198893
H104	-2.4521258405	0.4979571828	2.9984568121
H105	-1.4438555658	-0.8415354455	3.5668968264
H106	3.2478447675	-2.2173649854	-5.0176443031
H107	4.3510517344	-3.3097601142	-4.1829348856
H108	3.2842674103	-0.4849428144	-3.2686771266
H109	4.2427815812	-1.3116517417	-2.0272475120

DFT Case E

1d ⊂ dibenzo-24-crown-8 or 1e ⊂ dibenzo-24-crown-8	**DFT Case E**					
Energy	Δ E	H bond bridge				
-2491.57668	0.00					
R_1	**H**	O_1 to O_4	**N…O_1**	**H_1…O_1**	**<N-H_1-O_1**	**N-H_1**
			3.001	2.083	148.4	1.022
R_2	**CH_3**	O_1 to O_4	**N….O_4**	**H_2…O_4**	**<N-H_2-O_4**	**N-H_2**
			2.854	1.826	175	1.030
R_3	**H**	$O_{2'}$	**N…$O_{2'}$**	**H_3…$O_{2'}$**	**<N-H_3-$O_{2'}$**	**N-H_3**
			2.993	1.968	175.5	1.027
R_4	**CH_3**	none				
	O_1…O_4 bridge		**O_1…$O_{1'}$**	**O_2…$O_{2'}$**	**O_3…$O_{3'}$**	**O_4…$O_{4'}$**
	7.326		2.671	6.804	6.31	2.642

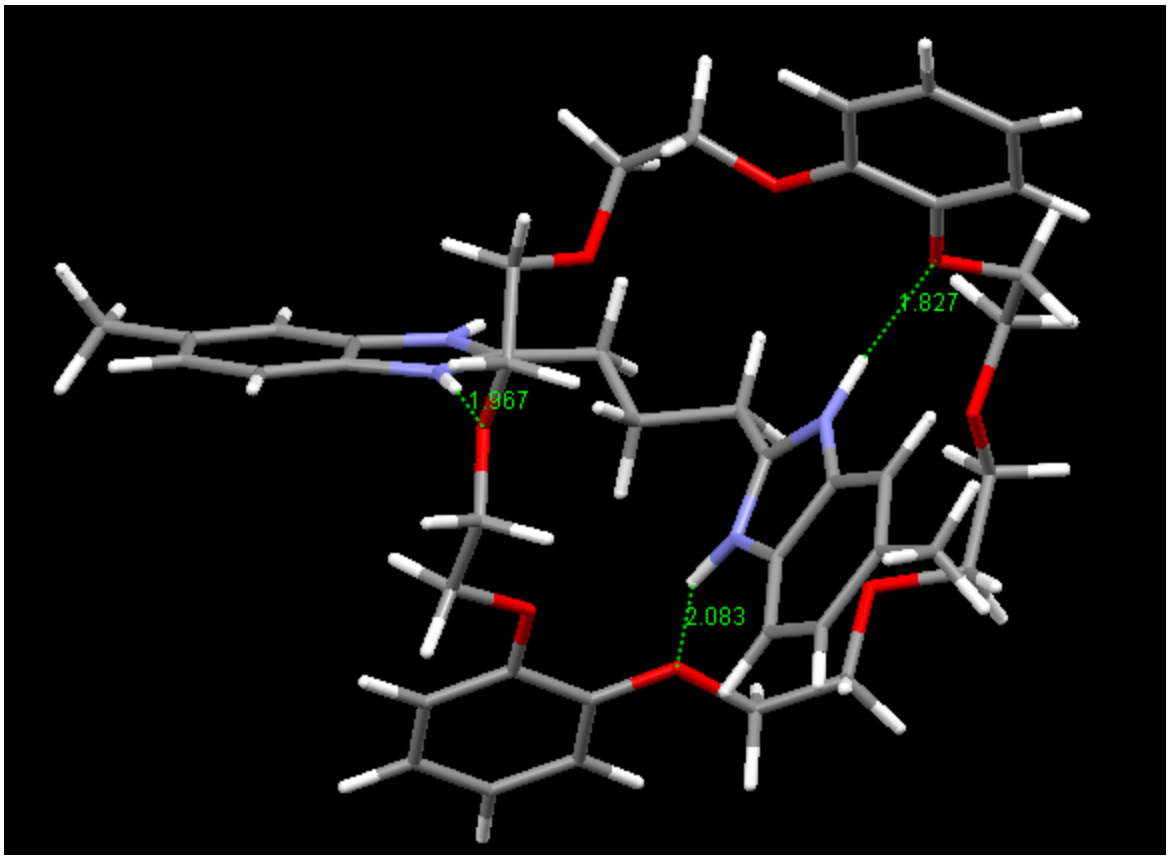


Figure S5. DFT Case **E**.

Energy components, in hartrees:

(A)	Nuclear repulsion.....	8219.10766205818	
(E)	Total one-electron terms.....	-19691.47829383753	
(I)	Total two-electron terms.....	8980.79395585427	
(J)	Coulomb.....	9330.22997757135	
(K)	Exchange+Correlation.....	-349.43602171708	
(L)	Electronic energy.....	-10710.68433798326	(E+I)
(N)	Total energy.....	-2491.57667592508	(A+L)

final geometry:

	angstroms		
atom	x	y	z
O1	1.3318668600	1.8135116058	-4.5472113261
O2	0.3871935596	-1.0044163927	-4.8181129495
O3	-0.7779434299	-3.0450824948	-3.1005542372
O4	0.7679348970	-4.4092657165	-0.8434321731
C5	1.2538112950	3.1483629786	-4.2193157122
C6	2.2441542480	3.6366780768	-3.3381505566
C7	2.2368356412	4.9760662713	-2.9515829836
C8	1.2524486873	5.8450301334	-3.4374805367
C9	0.2770061599	5.3692794922	-4.3059559037
C10	0.2759230950	4.0247366892	-4.6961732263
C11	0.4761680066	1.3423346198	-5.5878925803
C12	0.7987583810	-0.1170735466	-5.8636727806
C13	-0.9755106427	-1.4165301200	-4.9035043943
C14	-1.4675915161	-1.8653819835	-3.5452960506
C15	-1.2350627028	-3.4478072975	-1.7989122001
C16	-0.5421857798	-4.7096296078	-1.3365833443
O17	3.0702822166	-3.8347203278	0.3836959329
O18	4.8643702804	-1.3762924059	0.3170187767
O19	5.0175535274	1.2524658971	-1.1727688170
O20	3.1854204145	2.7145806514	-2.8947834011
C21	2.7595958754	-5.1759188946	0.2184573798
C22	1.5300385345	-5.4815278458	-0.4112286082
C23	1.1500245111	-6.8165585051	-0.5664655394
C24	1.9811164865	-7.8516934137	-0.1235077900
C25	3.1973881347	-7.5531415078	0.4752464259
C26	3.5838893656	-6.2191930100	0.6467894905
C27	4.2320224775	-3.5545434308	1.1921972833
C28	4.3964808647	-2.0751225534	1.4672530307
C29	5.6007539229	-0.1982168015	0.6623137672
C30	6.0870591591	0.5176989009	-0.5799025571
C31	5.4318818148	2.1167566119	-2.2261729458
C32	4.4301222979	3.2390420927	-2.3925530802
H33	2.9955436847	5.3573734027	-2.2788696482
H34	1.2626057223	6.8868752486	-3.1358592428
H35	-0.4865859516	6.0358123521	-4.6928114819
H36	-0.4876023495	3.6772668438	-5.3809920069
H37	0.6458172351	1.9237641269	-6.5045594933
H38	-0.5771807353	1.4582241815	-5.2993335418
H39	0.3382930144	-0.4100982360	-6.8175348759
H40	1.8826796035	-0.2316685567	-5.9603229973
H41	-1.0817773344	-2.2207943416	-5.6479922259
H42	-1.6218895547	-0.5860960631	-5.2187204966
H43	-1.3147513370	-1.0594022626	-2.8149921669
H44	-2.5445099149	-2.0773846149	-3.6112309231

H45	-2.3146178912	-3.6483580852	-1.8473118643
H46	-1.0692699050	-2.6340792653	-1.0805100019
H47	-1.1377565269	-5.1669738720	-0.5360795953
H48	-0.4852647575	-5.4213064009	-2.1700399606
H49	0.2004995995	-7.0703313202	-1.0197419157
H50	1.6623234482	-8.8812387517	-0.2460184936
H51	3.8509036323	-8.3451599124	0.8246072799
H52	4.5312140393	-6.0114362500	1.1258791886
H53	4.1207278575	-4.0697334259	2.1536409251
H54	5.1298114809	-3.9279822093	0.6864015833
H55	5.1383479544	-1.9991198604	2.2757773610
H56	3.4605014214	-1.6312178676	1.8365218740
H57	4.9783282894	0.4853588356	1.2572319311
H58	6.4754090020	-0.4827064391	1.2656968644
H59	6.5104518238	-0.2060922757	-1.2932052310
H60	6.8890207289	1.2098675518	-0.2834525480
H61	6.3997675169	2.5794474189	-1.9826905467
H62	5.5495210235	1.5573803970	-3.1663982102
H63	4.8207753439	3.9713713854	-3.1083473013
H64	4.2695322174	3.7289486237	-1.4251856852
C65	-0.2310770699	1.8997194434	1.4153802039
C66	-0.4212072020	0.6204448682	2.0021241308
C67	0.1548319869	-0.5389314636	1.4928123687
C68	0.9530150963	-0.3944710605	0.3537535335
C69	1.1539933435	0.8637870419	-0.2335814870
C70	0.5681058019	2.0246566319	0.2777015125
N71	1.6734109862	-1.3041965790	-0.4248256452
C72	2.2946062761	-0.6454870103	-1.4181282196
N73	1.9843944316	0.6509574253	-1.3308056840
C74	2.5311982911	-4.2327251776	-4.8693006288
N75	1.2271394810	-4.5229655297	-4.7597160617
C76	0.9391299142	-5.6892782692	-5.4774687433
C77	2.1483483865	-6.1159068895	-6.0427097585
N78	3.1042374471	-5.1810453623	-5.6333033975
C79	-0.2441182534	-6.4044355186	-5.6868829659
C80	-0.1503585722	-7.5441277395	-6.4761449240
C81	1.0696184677	-7.9879817350	-7.0538907905
C82	2.2415857185	-7.2623088474	-6.8335405522
C83	-0.8915207458	3.1093431862	2.0329635569
C84	2.5959258689	-2.5805347004	-2.9760059535
C85	1.0787910363	-9.2369419396	-7.9008469995
C86	3.2266255335	-3.0386885552	-4.2976222869
C87	3.1677257110	-1.2473502825	-2.4690729778
H88	-1.0500227748	-8.1227898349	-6.6637062990
H89	-1.0444105322	0.5459721696	2.8885928675
H90	-0.0067515448	-1.5028046185	1.9638127129
H91	0.7272176260	2.9889182535	-0.1941022658
H92	1.8045221686	-2.2992051395	-0.2325016613
H93	2.3904177010	1.3750206088	-1.9412559245
H94	0.5521884088	-3.9712017513	-4.2162854652
H95	4.0875095290	-5.1990650224	-5.8709419415
H96	-1.1906690572	-6.0866200306	-5.2633526416
H97	3.1857268089	-7.5791550279	-7.2642206216
H98	-0.5210689347	3.2811087697	3.0493527974
H99	-1.9761606532	2.9746495110	2.1028170714
H100	-0.7006670052	4.0129741644	1.4492487287
H101	1.5245901544	-2.4487996797	-3.1278946585

H102	2.7316055979	-3.3569210976	-2.2193944100
H103	0.7261129709	-10.1006914857	-7.3270656402
H104	0.4129417273	-9.1278742738	-8.7637530713
H105	2.0795570826	-9.4651839068	-8.2738595428
H106	3.1619142769	-2.2310282618	-5.0396552388
H107	4.2896356776	-3.2774907337	-4.1778800652
H108	3.2409742038	-0.5187765212	-3.2818525810
H109	4.1668348204	-1.3795204224	-2.0402867022

DFT Case F

1f⊂ dibenzo-24-crown-8 or **1g⊂ dibenzo-24-crown-8**	**DFT case F**					
Energy		H bond bridge				
-2570.22023						
R_1	**CH_3**	O_1 to O_4	**$N…O_1$**	**$H_1…O_1$**	**<$N-H_1-O_1$**	**$N-H_1$**
			2.987	2.059	149.7	1.022
R_2	**CH_3**	O_1 to O_4	**$N….O_4$**	**$H_2…O_4$**	**<$N-H_2-O_4$**	**$N-H_2$**
			2.865	1.839	174.7	1.029
R_3	**CH_3**	$O_{2'}$	**$N…O_{2'}$**	**$H_3…O_{2'}$**	**<$N-H_3-O_{2'}$**	**$N-H_3$**
			2.974	1.951	178.3	1.027
R_4	**CH_3**	none				
	$O_1…O_4$ bridge		**$O_1…O_{1'}$**	**$O_2…O_{2'}$**	**$O_3…O_{3'}$**	**$O_4…O_{4'}$**
	7.326		2.665	6.778	6.298	2.644

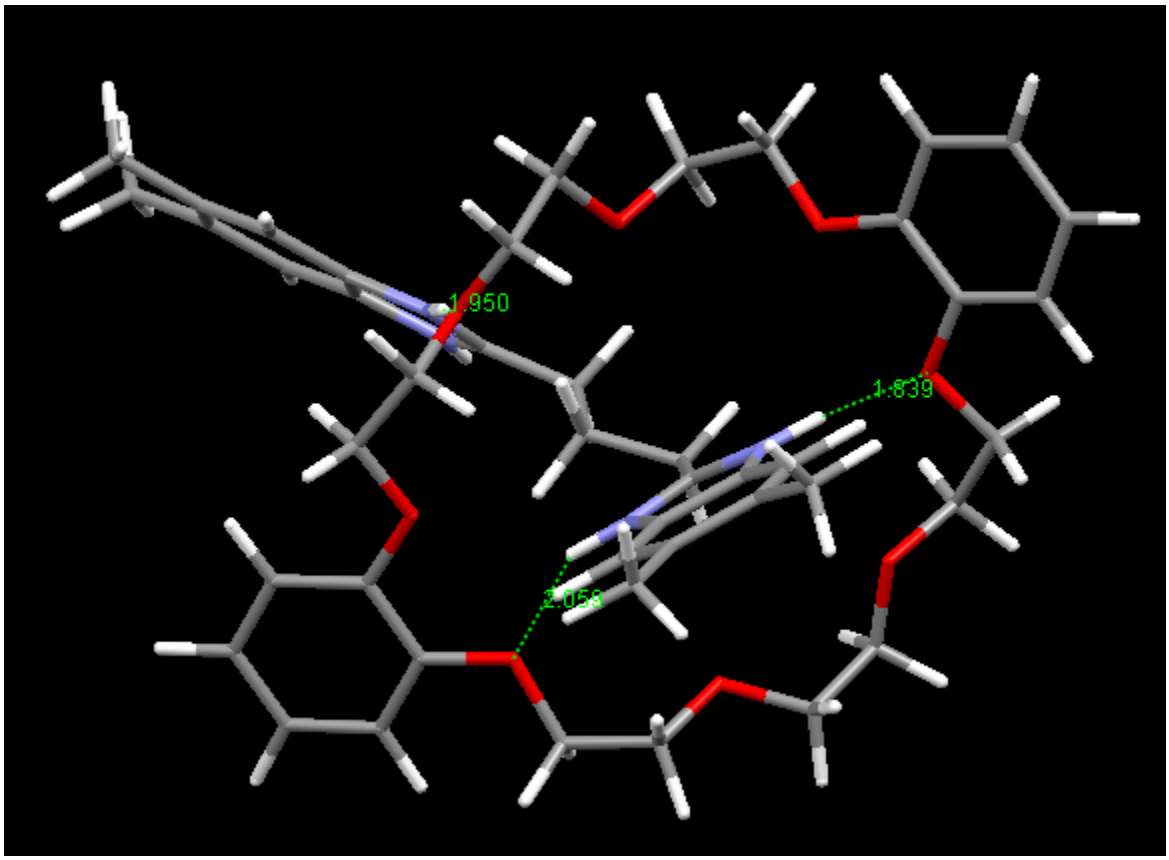


Figure S6. DFT Case **F**.

Energy components, in hartrees:

(A)	Nuclear repulsion.....	8725.14398485008	
(E)	Total one-electron terms.....	-20805.68271188870	
(I)	Total two-electron terms.....	9510.31849790886	
(J)	Coulomb.....	9872.13198386679	
(K)	Exchange+Correlation.....	-361.81348595793	
(L)	Electronic energy.....	-11295.36421397985	(E+I)
(N)	Total energy.....	-2570.22022912977	(A+L)

final geometry:

angstroms

atom	x	y	z
O1	1.3677538913	1.7892045699	-4.5886634664
O2	0.4099139261	-1.0144229152	-4.7857048971
O3	-0.7354557643	-3.0130202238	-3.0288935237
O4	0.8253718549	-4.4099980580	-0.8166011225
C5	1.2924107708	3.1291481325	-4.2821545815
C6	2.2634521786	3.6227798926	-3.3825447440
C7	2.2562295667	4.9679887873	-3.0163949159
C8	1.2924447887	5.8372209986	-3.5414523454
C9	0.3368638661	5.3561906981	-4.4287814467
C10	0.3351192871	4.0060054481	-4.7984231136
C11	0.5168485207	1.3058133817	-5.6268759130
C12	0.8199520170	-0.1644334180	-5.8614842493
C13	-0.9640029201	-1.3922123465	-4.8293647260
C14	-1.4224060955	-1.8256185294	-3.4544899325
C15	-1.1887004372	-3.4394111718	-1.7341276421
C16	-0.4889969951	-4.7072919776	-1.2989466307
O17	3.1262277267	-3.8367721893	0.4004609779
O18	4.8876194186	-1.3623703206	0.3767703411
O19	5.0053261961	1.2619739466	-1.1290727906
O20	3.1871488952	2.7020627344	-2.9016178356
C21	2.8290044294	-5.1777749232	0.2159334583
C22	1.5982339927	-5.4838504539	-0.4104751568
C23	1.2296985357	-6.8190591643	-0.5874910333
C24	2.0742663752	-7.8533838119	-0.1681627265
C25	3.2916779402	-7.5537072542	0.4283760067
C26	3.6667731391	-6.2191660707	0.6211023164
C27	4.2777362031	-3.5544091904	1.2226271751
C28	4.4191492029	-2.0763329373	1.5165200517
C29	5.5729029583	-0.1582383679	0.7350470371
C30	6.0761976672	0.5610859856	-0.4985149319
C31	5.4263238763	2.1107940134	-2.1922963164
C32	4.4257298624	3.2295147773	-2.3874518524
H33	2.9989301406	5.3532228283	-2.3281882477
H34	1.3027099907	6.8832261120	-3.2545586941
H35	-0.4102953563	6.0228150285	-4.8462918416
H36	-0.4121189171	3.6544943167	-5.4988927110
H37	0.7050872206	1.8601863447	-6.5567174943
H38	-0.5374974775	1.4461471563	-5.3535255837
H39	0.3469435184	-0.4806105291	-6.8020047808
H40	1.9014656653	-0.2946694030	-5.9638765902
H41	-1.1119084572	-2.1971521017	-5.5660222552
H42	-1.5996687981	-0.5477346900	-5.1285468574
H43	-1.2363073253	-1.0197134609	-2.7318475517
H44	-2.5036696372	-2.0226771346	-3.4885724465
H45	-2.2676699663	-3.6436565388	-1.7838967317

H46	-1.0240516369	-2.6385963021	-1.0011799334
H47	-1.0742916729	-5.1783073037	-0.4986373962
H48	-0.4397618586	-5.4054301144	-2.1440984958
H49	0.2796591232	-7.0734728759	-1.0394189219
H50	1.7652233423	-8.8839194519	-0.3068904346
H51	3.9548750774	-8.3456407993	0.7594837200
H52	4.6151376980	-6.0094325179	1.0976612581
H53	4.1647936962	-4.0849096620	2.1755931432
H54	5.1846185328	-3.9086372305	0.7192758738
H55	5.1523895391	-1.9973614518	2.3328872563
H56	3.4728294613	-1.6498057906	1.8803988957
H57	4.9094056838	0.5097474110	1.3028831637
H58	6.4361263733	-0.4085389355	1.3694217332
H59	6.5388957009	-0.1575413719	-1.1922725955
H60	6.8504570801	1.2773073387	-0.1859598196
H61	6.3905622561	2.5801372967	-1.9471811727
H62	5.5550565755	1.5365865574	-3.1221194612
H63	4.8278274443	3.9523909280	-3.1065970450
H64	4.2517348412	3.7322161264	-1.4289731268
C65	-0.3725342902	1.7766257976	1.3486864741
C66	-0.5383639168	0.4888861344	1.9541620774
C67	0.1215147595	-0.6290010022	1.4388829990
C68	0.9453835025	-0.4507765120	0.3251056592
C69	1.1106823155	0.8093872334	-0.2625422779
C70	0.4550107454	1.9361184060	0.2364395926
N71	1.7234826372	-1.3329173230	-0.4269036122
C72	2.3416667972	-0.6552078235	-1.4097905519
N73	1.9780522266	0.6280544194	-1.3377349681
C74	2.5423871682	-4.2025664233	-4.8637666997
N75	1.2327615729	-4.4573376014	-4.7269070937
C76	0.8955741537	-5.6082541184	-5.4455341613
C77	2.0768071141	-6.0635308554	-6.0398833607
N78	3.0702764470	-5.1602647064	-5.6480130552
C79	-0.3134106871	-6.2822902720	-5.6284672580
C80	-0.3113658919	-7.4282579397	-6.4246665155
C81	0.9023706304	-7.8946079935	-7.0296533035
C82	2.1019066337	-7.2085692343	-6.8356485249
C83	-1.0935820724	2.9774055432	1.9130110175
C84	-1.6028144649	-8.1766390641	-6.6493218664
C85	2.6673866635	-2.5740689081	-2.9629786723
C86	-1.4317875439	0.3314988890	3.1614596161
C87	0.8911642051	-9.1355241376	-7.8878194166
C88	3.2790450688	-3.0327461497	-4.2929611676
C89	3.2394025235	-1.2431155335	-2.4477821768
H90	-0.0013248696	-1.6043368942	1.8992929509
H91	0.5814505896	2.9093649611	-0.2267199282
H92	1.8795671022	-2.3236045084	-0.2312247552
H93	2.3699195919	1.3628370051	-1.9429302867
H94	0.5837416627	-3.8964596872	-4.1623519193
H95	4.0469704840	-5.2055700057	-5.9077803565
H96	-1.2317292410	-5.9256213607	-5.1738041950
H97	3.0205097147	-7.5597440159	-7.2942531965
H98	-0.8074503713	3.1635323101	2.9540739091
H99	-2.1802353133	2.8362720283	1.9031403598
H100	-0.8683585872	3.8788288454	1.3386960989
H101	-1.8578379043	-8.2229345415	-7.7138762509
H102	-1.5331459594	-9.2110834349	-6.2948506539

H103	-2.4344225955	-7.6983635698	-6.1269078413
H104	1.5952153501	-2.4379782259	-3.1033512327
H105	2.8060175143	-3.3551406184	-2.2115299473
H106	-1.0884802687	0.9514184133	3.9973664565
H107	-2.4609598457	0.6381048543	2.9429503929
H108	-1.4566640771	-0.7055901691	3.5040892189
H109	0.5415583441	-10.0073466347	-7.3242412861
H110	0.2197807821	-9.0208194589	-8.7458021839
H111	1.8882233223	-9.3622258547	-8.2710626771
H112	3.2301626028	-2.2168767478	-5.0271131075
H113	4.3362108568	-3.3007795114	-4.1840888950
H114	3.3225269844	-0.5116712704	-3.2568786364
H115	4.2321057219	-1.3773943901	-2.0058610716

DFT Case G

1a ⊂ dibenzo-24-crown-8 or **1b ⊂ dibenzo-24-crown-8**	**DFT Case G**					
Energy	Δ E	H bond bridge				
-2412.93079	0.00					
R_1	**H**	O_1 to O_4	**N…O_1**	**H_1…O_1**	**<N-H_1-O_1**	**N-H_1**
			2.961	2.023	151.2	1.023
R_2	**H**	O_1 to O_4	**N….O_4**	**H_2…O_4**	**<N-H_2-O_4**	**N-H_2**
			2.856	1.828	174.2	1.031
R_3	**H**	$O_{2'}$	**N…$O_{2'}$**	**H_3…$O_{2'}$**	**<N-H_3-$O_{2'}$**	**N-H_3**
			2.933	1.906	175	1.029
R_4	**H**	none				
	O_1…O_4 bridge		**O_1…$O_{1'}$**	**O_2…$O_{2'}$**	**O_3…$O_{3'}$**	**O_4…$O_{4'}$**
	7.289		2.670	6.781	6.306	2.652

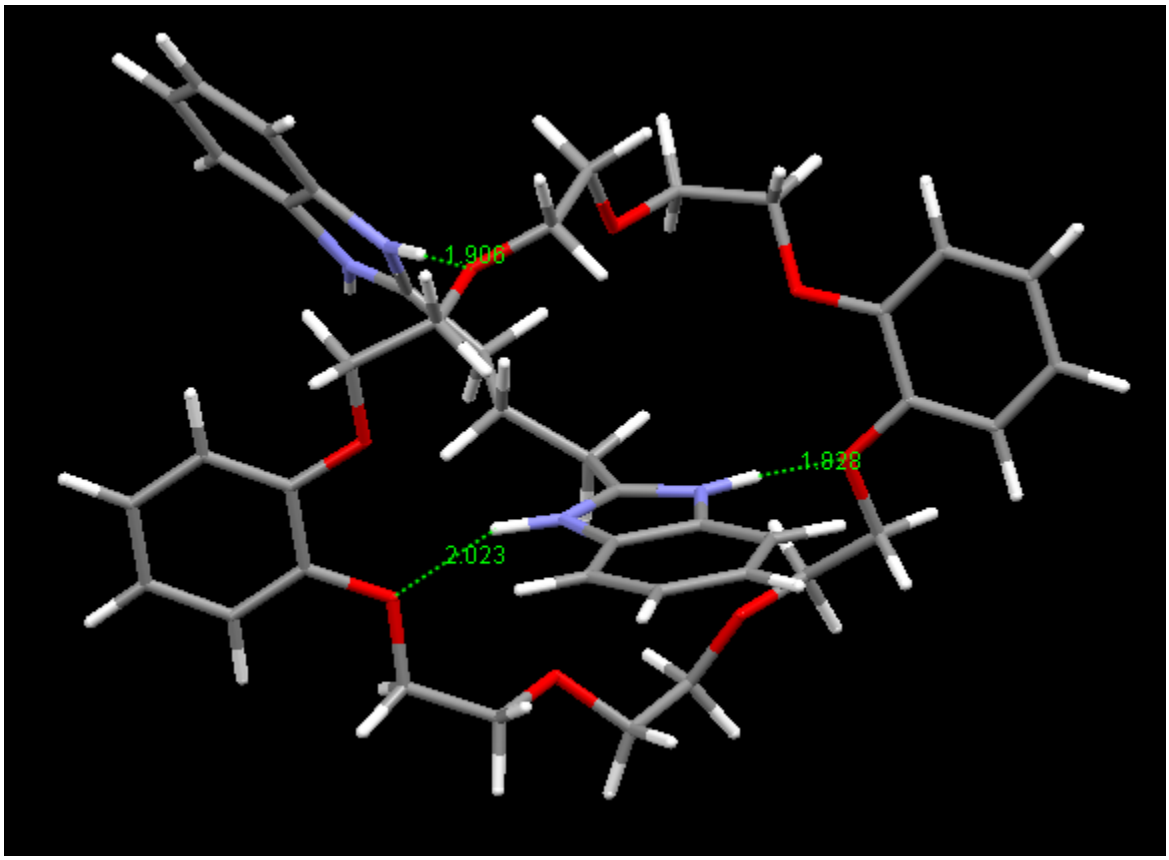


Figure S7. DFT Case **G**.

Energy components, in hartrees:

(A)	Nuclear repulsion.....	7785.99542587105	
(E)	Total one-electron terms.....	-18722.61476565001	
(I)	Total two-electron terms.....	8523.68854803173	
(J)	Coulomb.....	8860.76317153252	
(K)	Exchange+Correlation.....	-337.07462350080	
(L)	Electronic energy.....	-10198.92621761829	(E+I)
(N)	Total energy.....	-2412.93079174723	(A+L)

final geometry:

angstroms

atom	x	y	z
O1	1.3847466503	1.7648515513	-4.6552934317
O2	0.4622479235	-1.0382632661	-4.8871285105
O3	-0.7409483906	-2.9891946489	-3.1067327621
O4	0.7801666197	-4.3689317145	-0.8493643687
C5	1.2844343207	3.1034228339	-4.3469434633
C6	2.2049788086	3.6032168087	-3.4004054163
C7	2.1678141156	4.9465850399	-3.0297879670
C8	1.2247476541	5.8100710613	-3.5983416353
C9	0.3185326139	5.3235189670	-4.5335142815
C10	0.3460681923	3.9749933398	-4.9066431547
C11	0.5800232035	1.2820661348	-5.7299234999
C12	0.8929118705	-0.1871170461	-5.9550913903
C13	-0.9130302063	-1.4110879900	-4.9526356090
C14	-1.4076896945	-1.8064477766	-3.5786164575
C15	-1.2051593779	-3.3644343984	-1.7983683811
C16	-0.5428950444	-4.6391953009	-1.3250359662
O17	3.0979096518	-3.8379732606	0.3653773936
O18	4.8922163139	-1.3824839361	0.3092492927
O19	4.9872532136	1.2665191366	-1.1478485874
O20	3.1157039519	2.6927223354	-2.8726669062
C21	2.7634196278	-5.1740635420	0.1980000108
C22	1.5237643070	-5.4560632573	-0.4219226825
C23	1.1173814757	-6.7834005524	-0.5730994606
C24	1.9339608039	-7.8335756125	-0.1388869065
C25	3.1622406984	-7.5579481463	0.4464336082
C26	3.5744644589	-6.2314348508	0.6155924757
C27	4.2762233025	-3.5771890276	1.1576597612
C28	4.4528883387	-2.1038385229	1.4563626413
C29	5.6132196279	-0.1969047641	0.6630561028
C30	6.0747288241	0.5423335209	-0.5744157760
C31	5.3778331774	2.1251641994	-2.2149071480
C32	4.3617804753	3.2332084291	-2.3859792552
H33	2.8723562396	5.3336040063	-2.3031633860
H34	1.2111494696	6.8549520247	-3.3077224222
H35	-0.4130728138	5.9849959929	-4.9853457330
H36	-0.3635238514	3.6212899535	-5.6440763796
H37	0.8060044874	1.8376025048	-6.6505717865
H38	-0.4843602421	1.4214048151	-5.5011181346
H39	0.4430770407	-0.5059334723	-6.9058923337
H40	1.9769848681	-0.3133706365	-6.0334076175
H41	-1.0479943574	-2.2333051523	-5.6722691926
H42	-1.5369038488	-0.5720494967	-5.2884112134
H43	-1.2314846034	-0.9843666652	-2.8721021593
H44	-2.4890882052	-1.9965223032	-3.6322800881

H45	-2.2892991170	-3.5379051077	-1.8429493544
H46	-1.0167671703	-2.5465355568	-1.0906322903
H47	-1.1429530161	-5.0695614926	-0.5130069729
H48	-0.5148568124	-5.3622751113	-2.1497657570
H49	0.1586342355	-7.0195129938	-1.0163578323
H50	1.5951802930	-8.8570987899	-0.2581259503
H51	3.8052282550	-8.3621300712	0.7875231975
H52	4.5306585325	-6.0408935659	1.0843303605
H53	4.1786817111	-4.1068012677	2.1124620105
H54	5.1616879752	-3.9485527434	0.6292264091
H55	5.2155628418	-2.0460855509	2.2469447104
H56	3.5282439893	-1.6655836930	1.8597423606
H57	4.9861010689	0.4683038534	1.2736273382
H58	6.4984351714	-0.4749990168	1.2537030647
H59	6.5016774841	-0.1662041891	-1.3009550138
H60	6.8687466413	1.2439884051	-0.2791615973
H61	6.3419100953	2.6033719935	-1.9863788812
H62	5.4938164592	1.5566279903	-3.1499436950
H63	4.7396872444	3.9590693702	-3.1146584125
H64	4.2039973441	3.7359786070	-1.4248649121
C65	-0.2198725323	1.6976321034	1.6321741953
C66	-0.3511248212	0.4065821035	2.1858054412
C67	0.2546682526	-0.7043074077	1.6027620365
C68	1.0013810953	-0.4719879082	0.4444853235
C69	1.1353963062	0.8149381681	-0.1048388554
C70	0.5232175192	1.9276259187	0.4772510123
N71	1.7274231000	-1.3243150044	-0.3889726596
C72	2.2884083414	-0.6101323912	-1.3790608662
N73	1.9331663527	0.6706149455	-1.2388399789
C74	2.5340473545	-4.1643852525	-4.8425040170
N75	1.2296261379	-4.4455678526	-4.7185173520
C76	0.9272890535	-5.6174441538	-5.4182367016
C77	2.1316310816	-6.0593800106	-5.9879283480
N78	3.0967265412	-5.1247958114	-5.5983045607
C79	-0.2690905252	-6.3153251004	-5.6005628637
C80	-0.2006992751	-7.4699132730	-6.3748270662
C81	1.0122144207	-7.9131378937	-6.9436643333
C82	2.2044679502	-7.2180438312	-6.7626700026
H83	-1.1040169735	-8.0448508974	-6.5486447362
C84	2.6559139597	-2.5347455197	-2.9323231084
H85	1.0144587328	-8.8190862178	-7.5400833554
C86	3.2330590747	-2.9635949084	-4.2895852500
C87	3.1434995261	-1.1500637720	-2.4776749370
H88	-0.7108327048	2.5328046762	2.1203765395
H89	-0.9380705668	0.2769362432	3.0889190696
H90	0.1546657377	-1.6959414595	2.0309650235
H91	0.6204362757	2.9206650148	0.0521296724
H92	1.9009838232	-2.3198831671	-0.2296628881
H93	2.2990992697	1.4228111696	-1.8419761032
H94	0.5599756390	-3.8852699111	-4.1741408883
H95	4.0781625406	-5.1521331706	-5.8431902872
H96	-1.2037323018	-5.9742319948	-5.1694971345
H97	3.1344399939	-7.5608943351	-7.2029413650
H101	1.5698257524	-2.4936146597	-3.0118296705
H102	2.9035878402	-3.2864526008	-2.1787311955
H106	3.1096431208	-2.1509817827	-5.0175268603
H107	4.3057211673	-3.1777772504	-4.2262613680

H108	3.1032487070	-0.4296644971	-3.3001402089
H109	4.1741101510	-1.1900424497	-2.1098733470

DFT Case H

1a ⊂ dibenzo-24-crown-8 or **1b ⊂ dibenzo-24-crown-8**	**DFT Case H**					
Energy	Δ E	H bond bridge				
-2412.92496	15.31					
R_1	**H**	$O_{1'}$ to O_3	**$N…O_{1'}$**	**$H_1…O_{1'}$**	**$<N-H_1-O_{1'}$**	**$N-H_1$**
			2.855	1.858	162.9	1.027
R_2	**H**	$O_{1'}$ to O_3	**$N….O_3$**	**$H_2…O_3$**	**$<N-H_2-O_3$**	**$N-H_2$**
			2.853	1.911	151.6	1.024
R_3	**H**	$O_{4'}$	**$N…O_{4'}$**	**$H_3…O_{4'}$**	**$<N-H_3-O_{4'}$**	**$N-H_3$**
			2.925	1.929	161.7	1.030
R_4	**H**	none				
	$O_{1'}…O_3$ bridge		**$O_1…O_{1'}$**	**$O_2…O_{2'}$**	**$O_3…O_{3'}$**	**$O_4…O_{4'}$**
	6.95		2.675	6.511	6.232	2.668

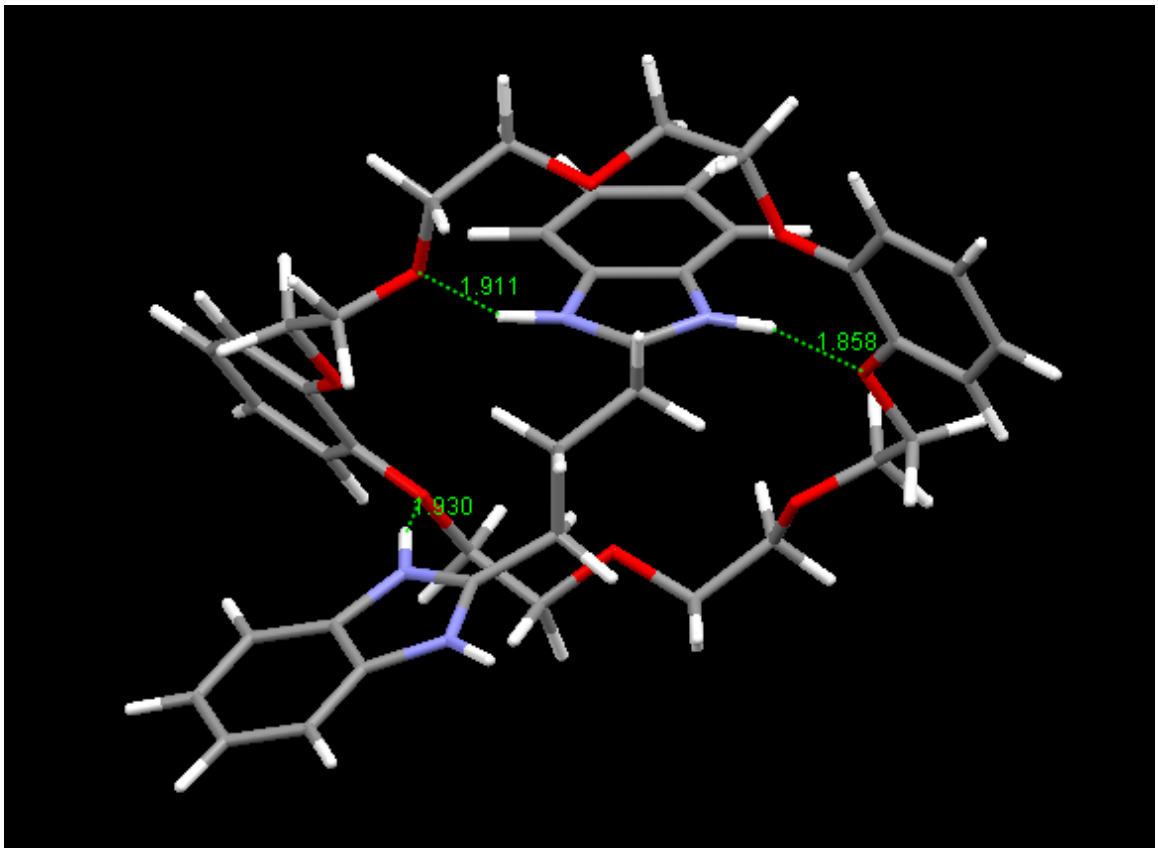


Figure S8. DFT Case **H.**

Energy components, in hartrees:

(A)	Nuclear repulsion.....	7820.43875254055	
(E)	Total one-electron terms.....	-18791.03546582833	
(I)	Total two-electron terms.....	8557.67175154672	
(J)	Coulomb.....	8894.74372777411	
(K)	Exchange+Correlation.....	-337.07197622739	
(L)	Electronic energy.....	-10233.36371428161	(E+I)
(N)	Total energy.....	-2412.92496174106	(A+L)

final geometry:

	angstroms		
atom	x	y	z
O1	4.6939480752	0.6794892252	-4.1320796969
O2	2.0797124578	-0.7591274226	-3.7947889340
O3	0.3986987480	-1.7672050125	-1.4514589599
O4	0.5564003143	-3.1067085093	1.1281564819
C5	5.4039019054	1.8528475691	-4.2903161671
C6	6.4194711660	2.1191904608	-3.3434962055
C7	7.1546022572	3.3015443403	-3.4321558073
C8	6.9066633082	4.2177028936	-4.4605363883
C9	5.9222606586	3.9506360242	-5.4023548558
C10	5.1726653578	2.7725181415	-5.3161454457
C11	3.7450554676	0.3562028131	-5.1578500133
C12	3.0335725871	-0.9435257534	-4.8465684247
C13	1.0464843219	-1.7402943575	-3.8071746433
C14	-0.0235534617	-1.4143513163	-2.7844157165
C15	-0.6481711900	-1.7674608112	-0.4724205247
C16	-0.6259538857	-3.0579187534	0.3174612780
O17	2.6878085302	-3.1677716499	2.7324508699
O18	5.2754237882	-1.6077675914	2.4259633404
O19	6.9752378946	0.0731414761	0.4156492557
O20	6.6365066426	1.1601572352	-2.3562646162
C21	1.9374268234	-4.3362893461	2.6303123921
C22	0.7950445841	-4.2940231864	1.7997524861
C23	-0.0239580774	-5.4215357653	1.7018601881
C24	0.2923522200	-6.5951675960	2.3949643999
C25	1.4292668837	-6.6443174918	3.1904809196
C26	2.2480806001	-5.5157514178	3.3100092806
C27	3.8817957122	-3.2636927508	3.5361237766
C28	4.6159789307	-1.9443422600	3.6408546547
C29	6.4217111030	-0.7722542490	2.6320800283
C30	7.3694377037	-0.8276712536	1.4515017197
C31	7.9872571424	0.1887631199	-0.5801604619
C32	7.7517845069	1.3847124982	-1.4746823482
H33	7.9305666286	3.5258109931	-2.7121054963
H34	7.4934196420	5.1281797145	-4.5159927610
H35	5.7276104602	4.6476864380	-6.2103546991
H36	4.4121572285	2.5829936752	-6.0622962702
H37	4.2690878621	0.2490744397	-6.1163238676
H38	2.9996010910	1.1553741206	-5.2487823951
H39	2.5135783013	-1.2510310380	-5.7651969433
H40	3.7498781043	-1.7339706601	-4.5821820897
H41	1.4548351507	-2.7444596064	-3.6173573684
H42	0.5642799775	-1.7546618166	-4.7962765231

H43	-0.2753217182	-0.3465784050	-2.8292134222
H44	-0.9194519395	-1.9970955254	-3.0344631795
H45	-1.6261580286	-1.6888778524	-0.9615113180
H46	-0.5357208919	-0.8983746591	0.1894199068
H47	-1.5181867078	-3.1157827746	0.9547021803
H48	-0.6351856681	-3.9006390293	-0.3832857007
H49	-0.9167747674	-5.4041396144	1.0905891394
H50	-0.3572111530	-7.4592224341	2.3042725605
H51	1.6885348197	-7.5493711430	3.7291701316
H52	3.1235727665	-5.5777336696	3.9420766359
H53	3.6046804397	-3.5709166357	4.5519878718
H54	4.5474064107	-4.0169571362	3.1011194548
H55	5.3563952207	-2.0770737986	4.4432635341
H56	3.9399859835	-1.1371293207	3.9629309337
H57	6.1186174470	0.2683557451	2.8211614454
H58	6.9693552837	-1.1308206460	3.5147705004
H59	7.4253419649	-1.8582251399	1.0713865475
H60	8.3689552632	-0.5418622992	1.8125552936
H61	8.9660415085	0.3417516542	-0.1005968236
H62	8.0572688126	-0.7360366722	-1.1743581678
H63	8.6555345100	1.5435692652	-2.0743772689
H64	7.5664463045	2.2751021066	-0.8627196615
C65	-1.3950192336	1.0394362176	5.5352991349
C66	-1.3340493731	-0.3698728836	5.4893459972
C67	-0.4417865041	-1.0395141130	4.6573234247
C68	0.3892433294	-0.2402030404	3.8680695533
C69	0.3270793719	1.1621045192	3.9163484159
C70	-0.5656783769	1.8361646866	4.7514947543
N71	1.3863416051	-0.5566441265	2.9417294297
C72	1.9193498812	0.5651027311	2.4412885216
N73	1.2945952790	1.6133375091	3.0122468177
C74	3.8826353440	-0.8538152357	-1.3125669599
N75	3.2143542751	-1.9881710069	-1.0425212009
C76	4.0023469121	-3.0831158140	-1.4009037884
C77	5.2064848630	-2.5540636350	-1.8958399223
N78	5.0809327793	-1.1700980337	-1.8082576040
C79	3.7747397795	-4.4593358795	-1.3351051828
C80	4.8007898155	-5.2819373752	-1.7939880142
C81	6.0081391912	-4.7519034298	-2.2957310152
C82	6.2363643130	-3.3793493201	-2.3551623859
H83	-2.1069823159	1.5144096790	6.2016758886
C84	2.3618877067	0.7570097043	-0.0332697537
H85	-2.0010239227	-0.9451275113	6.1224986262
C86	3.3865217542	0.5476650644	-1.1561358287
C87	2.9710373275	0.6279285091	1.3860187509
H88	-0.3941623971	-2.1224330006	4.6246457989
H89	-0.6139498072	2.9189978822	4.7922200486
H90	1.7083250291	-1.5058376456	2.7047085836
H91	1.5134997748	2.5817405167	2.8172678700
H92	2.2044528177	-2.0205279059	-0.8783310523
H93	5.7353127140	-0.4491676296	-2.1335081103
H94	2.8497459387	-4.8680760244	-0.9433711157
H95	4.6695569180	-6.3585636310	-1.7654466512
H96	6.7775888323	-5.4321322294	-2.6453604015
H97	7.1633614477	-2.9759837546	-2.7477988142
H101	1.9301651184	1.7558122144	-0.1562035963
H102	1.5377596647	0.0486545278	-0.1539222759

H106	2.9273952159	0.8216375751	-2.1120428869
H107	4.2570922828	1.1968293927	-1.0249562162
H108	3.6311585210	1.4793035223	1.5856253711
H109	3.5889117812	-0.2736990687	1.4643243430

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