molecules

MDPI

# Exploring Orthogonality between Halogen and Hydrogen Bonding Involving Benzene

**Alessandra Forni [1,*], Rosario Russo [2], Giacomo Rapeti [2], Stefano Pieraccini [1,2,*] and Maurizio Sironi [1,2,*]**

[1] Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" – CNR and INSTM RU, via Golgi 19, 20133 Milan, Italy
[2] Department of Chemistry, Università degli Studi di Milano and INSTM RU, via Golgi 19, 20133 Milano, Italy
* Correspondence: alessandra.forni@scitec.cnr.it (A.F.); stefano.pieraccini@unimi.it (S.P.); maurizio.sironi@unimi.it (M.S.)

# Supplementary Material

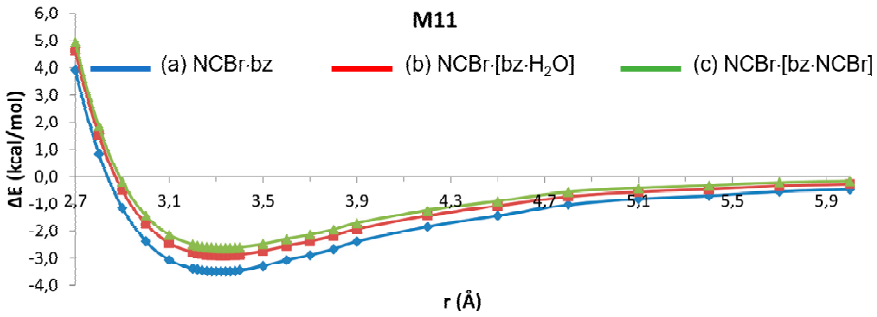


**Figure S1.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·H2O] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the T-shaped approach at the M11/aug-cc-PVTZ level of theory.

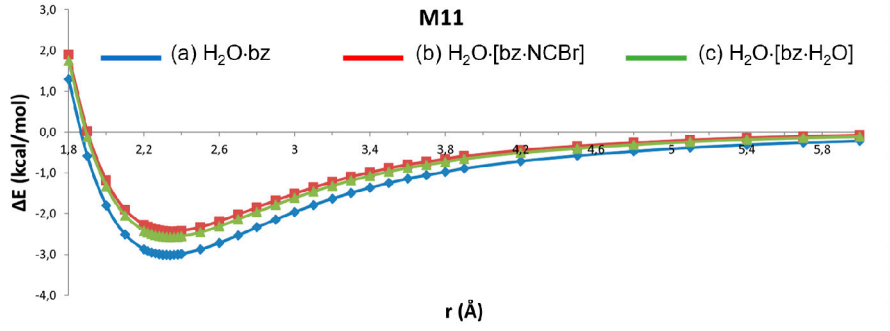


**Figure S2.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) H2O·bz (blue line), (b) H2O·[bz·NCBr] (red line) and (c) H2O·[bz·H2O] (green line) systems in the T-shaped approach at the M11/aug-cc-PVTZ level of theory.

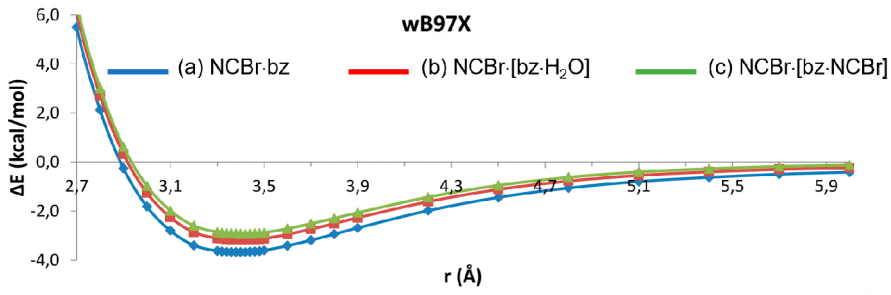


**Figure S3.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·H2O] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the T-shaped approach at the *ω*B97X/aug-cc-PVTZ level of theory.

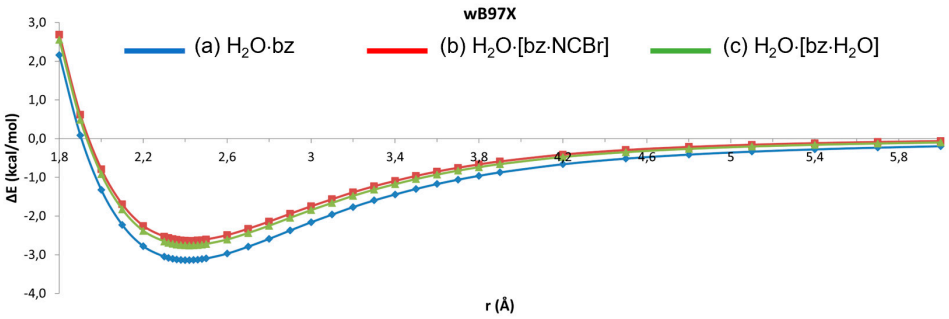


**Figure S4.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) H2O·bz (blue line), (b) H2O·[bz·NCBr] (red line) and (c) H2O·[bz·H2O] (green line) systems in the T-shaped approach at the *ω*B97X/aug-cc-PVTZ level of theory.

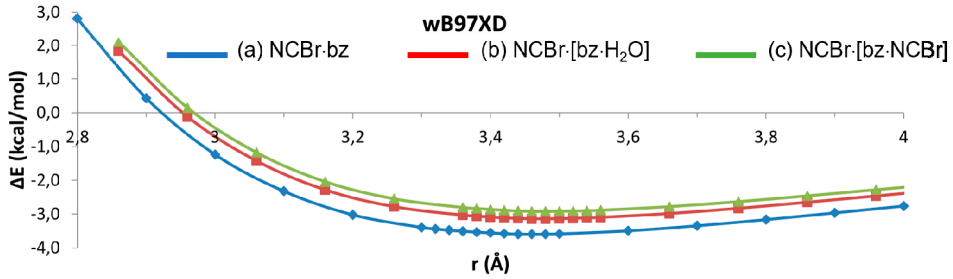


**Figure S5.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·H2O] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the T-shaped approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

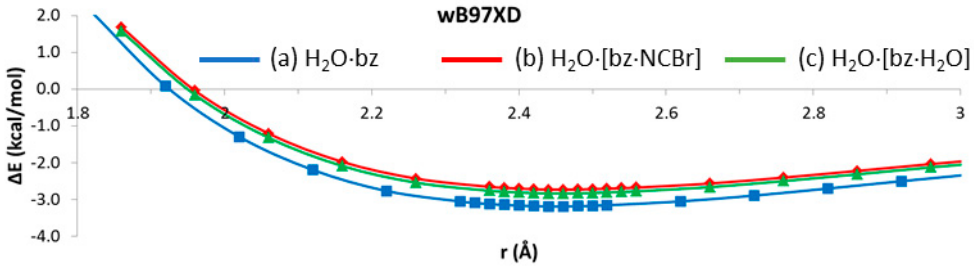


**Figure S6.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) H2O·bz (blue line), (b) H2O·[bz·NCBr] (red line) and (c) H2O·[bz·H2O] (green line) systems in the T-shaped approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

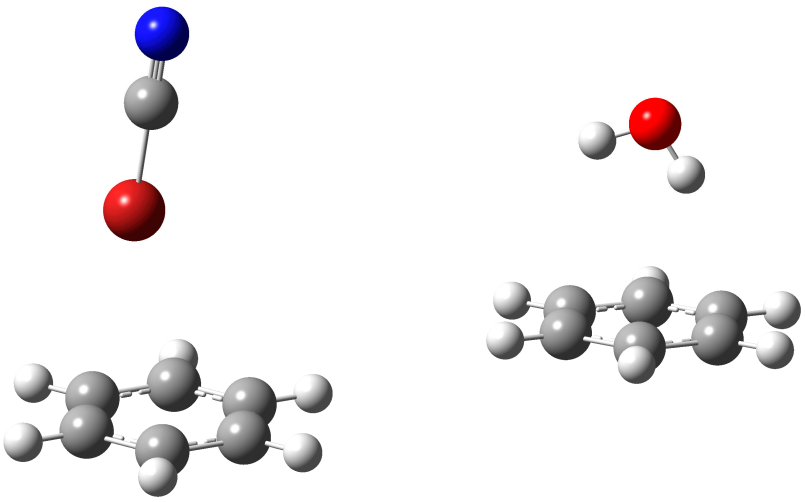

**Figure S7.** *ω*B97XD/aug-cc-PVTZ fully optimized geometries of the NCBr·bz (left) and $H_2O$·bz (right) dimers.

**Table S1.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the T-shaped approach at the M06-2X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) NCBr·bz | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 1.8 | 171.7322 | 172.5443 | 173.0282 |
| 1.9 | 129.8621 | 130.6326 | 131.1122 |
| 2 | 96.7615 | 97.5063 | 97.9688 |
| 2.1 | 70.8899 | 71.6055 | 72.0583 |
| 2.2 | 50.7751 | 51.4770 | 51.9042 |
| 2.3 | 35.3370 | 36.0170 | 36.4322 |
| 2.4 | 23.6149 | 24.2869 | 24.6784 |
| 2.5 | 14.8787 | 15.5343 | 15.9134 |
| 2.6 | 8.4525 | 9.1019 | 9.4616 |
| 2.7 | 3.8912 | 4.5249 | 4.8744 |
| 2.8 | 0.7301 | 1.3577 | 1.6900 |
| 2.9 | -1.4017 | -0.7917 | -0.4685 |
| 3 | -2.6810 | -2.0836 | -1.7749 |
| 3.1 | -3.4185 | -2.8356 | -2.5360 |
| 3.16 | -3.6841 | -3.1151 | -2.8195 |
| 3.18 | -3.7436 | -3.1775 | -2.8853 |
| 3.2 | -3.7881 | -3.2249 | -2.9361 |
| 3.22 | -3.8169 | -3.2572 | -2.9714 |
| 3.24 | -3.8294 | -3.2734 | -2.9901 |
| 3.26 | -3.8280 | -3.2752 | -2.9943 |
| 3.28 | -3.8176 | -3.2675 | -2.9887 |
| 3.3 | -3.8019 | -3.2546 | -2.9777 |
| 3.32 | -3.7831 | -3.2389 | -2.9634 |
| 3.34 | -3.7617 | -3.2209 | -2.9467 |

| | | | |
|---|---|---|---|
| 3.4 | -3.6868 | -3.1580 | -2.8864 |
| 3.5 | -3.4970 | -2.9892 | -2.7289 |
| 3.6 | -3.2055 | -2.7165 | -2.4665 |
| 3.7 | -2.9331 | -2.4626 | -2.2194 |
| 3.8 | -2.6811 | -2.2311 | -1.9959 |
| 3.9 | -2.4485 | -2.0163 | -1.7920 |
| 4.2 | -1.8928 | -1.5154 | -1.3115 |
| 4.5 | -1.4852 | -1.1519 | -0.9708 |
| 4.8 | -1.1878 | -0.8888 | -0.7261 |
| 5.1 | -0.9275 | -0.6670 | -0.5163 |
| 5.4 | -0.7230 | -0.4929 | -0.3537 |
| 5.7 | -0.5669 | -0.3598 | -0.2323 |
| 6 | -0.4580 | -0.2714 | -0.1537 |

**Table S2.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the T-shaped approach at the M06-2X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) $H_2O$·bz | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 1.8 | 1.0186 | 1.5986 | 1.4464 |
| 1.9 | -0.9010 | -0.3169 | -0.4681 |
| 2 | -2.1457 | -1.5615 | -1.7110 |
| 2.1 | -2.9025 | -2.3240 | -2.4702 |
| 2.2 | -3.2926 | -2.7217 | -2.8643 |
| 2.22 | -3.3359 | -2.7671 | -2.9089 |
| 2.24 | -3.3706 | -2.8040 | -2.9449 |
| 2.26 | -3.3974 | -2.8330 | -2.9730 |
| 2.28 | -3.4167 | -2.8546 | -2.9938 |
| 2.3 | -3.4289 | -2.8694 | -3.0076 |
| 2.32 | -3.4345 | -2.8775 | -3.0148 |
| 2.34 | -3.4337 | -2.8792 | -3.0157 |
| 2.36 | -3.4266 | -2.8746 | -3.0102 |
| 2.38 | -3.4134 | -2.8640 | -2.9987 |
| 2.4 | -3.3947 | -2.8480 | -2.9819 |
| 2.5 | -3.2475 | -2.7166 | -2.8460 |
| 2.6 | -3.0479 | -2.5337 | -2.6587 |
| 2.7 | -2.8163 | -2.3195 | -2.4403 |
| 2.8 | -2.5871 | -2.1090 | -2.2255 |
| 2.9 | -2.3671 | -1.9060 | -2.0190 |
| 3 | -2.1612 | -1.7196 | -1.8277 |
| 3.1 | -1.9874 | -1.5642 | -1.6682 |
| 3.2 | -1.8187 | -1.4121 | -1.5126 |
| 3.3 | -1.6692 | -1.2814 | -1.3770 |
| 3.4 | -1.5410 | -1.1689 | -1.2609 |

| | | | |
|---|---|---|---|
| 3.5 | -1.4183 | -1.0619 | -1.1503 |
| 3.6 | -1.3071 | -0.9653 | -1.0505 |
| 3.7 | -1.1974 | -0.8690 | -0.9509 |
| 3.8 | -1.1029 | -0.7897 | -0.8675 |
| 3.9 | -1.0211 | -0.7199 | -0.7951 |
| 4.2 | -0.7895 | -0.5242 | -0.5907 |
| 4.5 | -0.6094 | -0.3734 | -0.4333 |
| 4.8 | -0.4796 | -0.2662 | -0.3212 |
| 5.1 | -0.3819 | -0.1917 | -0.2412 |
| 5.4 | -0.3070 | -0.1357 | -0.1810 |
| 5.7 | -0.2510 | -0.0964 | -0.1378 |
| 6 | -0.2080 | -0.0678 | -0.1058 |

**Table S3.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the T-shaped approach at the M11/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) NCBr·bz | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 1.8 | 178.1634 | 179.0501 | 179.4914 |
| 1.9 | 134.7102 | 135.5517 | 135.9873 |
| 2 | 100.1798 | 100.9890 | 101.4122 |
| 2.1 | 73.0510 | 73.8365 | 74.2441 |
| 2.2 | 52.0081 | 52.7750 | 53.1664 |
| 2.3 | 35.9179 | 36.6701 | 37.0451 |
| 2.4 | 23.8164 | 24.5556 | 24.9154 |
| 2.5 | 14.8875 | 15.6132 | 15.9604 |
| 2.6 | 8.4450 | 9.1548 | 9.4926 |
| 2.7 | 3.9216 | 4.6144 | 4.9443 |
| 2.8 | 0.8492 | 1.5245 | 1.8469 |
| 2.9 | -1.1490 | -0.4924 | -0.1774 |
| 3 | -2.3735 | -1.7355 | -1.4283 |
| 3.1 | -3.0632 | -2.4445 | -2.1450 |
| 3.2 | -3.3862 | -2.7855 | -2.4973 |
| 3.22 | -3.4182 | -2.8211 | -2.5351 |
| 3.24 | -3.4421 | -2.8485 | -2.5646 |
| 3.26 | -3.4588 | -2.8689 | -2.5868 |
| 3.28 | -3.4695 | -2.8832 | -2.6028 |
| 3.3 | -3.4750 | -2.8922 | -2.6136 |
| 3.32 | -3.4760 | -2.8968 | -2.6198 |
| 3.34 | -3.4726 | -2.8970 | -2.6218 |
| 3.36 | -3.4650 | -2.8930 | -2.6197 |
| 3.38 | -3.4528 | -2.8846 | -2.6134 |
| 3.4 | -3.4359 | -2.8715 | -2.6025 |
| 3.5 | -3.2789 | -2.7352 | -2.4779 |

| | | | |
|---|---|---|---|
| 3.6 | -3.0688 | -2.5438 | -2.2943 |
| 3.7 | -2.8875 | -2.3812 | -2.1372 |
| 3.8 | -2.6622 | -2.1790 | -1.9444 |
| 3.9 | -2.3904 | -1.9265 | -1.7010 |
| 4.2 | -1.8423 | -1.4317 | -1.2363 |
| 4.5 | -1.4366 | -1.0707 | -0.8937 |
| 4.8 | -1.0369 | -0.7292 | -0.5558 |
| 5.1 | -0.8176 | -0.5565 | -0.4096 |
| 5.4 | -0.6992 | -0.4540 | -0.3200 |
| 5.7 | -0.5445 | -0.3333 | -0.2056 |
| 6 | -0.4649 | -0.2736 | -0.1571 |

**Table S4.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the T-shaped approach at the M11/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) $H_2O$·bz | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 1.8 | 1.2958 | 1.8958 | 1.7560 |
| 1.9 | -0.5876 | 0.0210 | -0.1209 |
| 2 | -1.7946 | -1.1847 | -1.3272 |
| 2.1 | -2.5082 | -1.9031 | -2.0448 |
| 2.2 | -2.8745 | -2.2788 | -2.4183 |
| 2.22 | -2.9166 | -2.3232 | -2.4622 |
| 2.24 | -2.9501 | -2.3593 | -2.4976 |
| 2.26 | -2.9758 | -2.3877 | -2.5253 |
| 2.28 | -2.9944 | -2.4090 | -2.5460 |
| 2.3 | -3.0064 | -2.4240 | -2.5602 |
| 2.32 | -3.0124 | -2.4330 | -2.5685 |
| 2.34 | -3.0129 | -2.4368 | -2.5714 |
| 2.36 | -3.0086 | -2.4357 | -2.5696 |
| 2.38 | -2.9998 | -2.4303 | -2.5633 |
| 2.4 | -2.9870 | -2.4210 | -2.5531 |
| 2.5 | -2.8763 | -2.3284 | -2.4562 |
| 2.6 | -2.7152 | -2.1867 | -2.3100 |
| 2.7 | -2.5293 | -2.0206 | -2.1393 |
| 2.8 | -2.3342 | -1.8454 | -1.9595 |
| 2.9 | -2.1432 | -1.6742 | -1.7836 |
| 3 | -1.9598 | -1.5100 | -1.6148 |
| 3.1 | -1.7880 | -1.3578 | -1.4580 |
| 3.2 | -1.6320 | -1.2196 | -1.3158 |
| 3.3 | -1.4888 | -1.0946 | -1.1865 |
| 3.4 | -1.3637 | -0.9877 | -1.0754 |
| 3.5 | -1.2478 | -0.8859 | -0.9711 |
| 3.6 | -1.1411 | -0.7958 | -0.8770 |

| | | | |
|---|---|---|---|
| 3.7 | -1.0572 | -0.7291 | -0.8062 |
| 3.8 | -0.9750 | -0.6575 | -0.7334 |
| 3.9 | -0.8903 | -0.5859 | -0.6589 |
| 4.2 | -0.7128 | -0.4426 | -0.5086 |
| 4.5 | -0.5801 | -0.3409 | -0.3996 |
| 4.8 | -0.4702 | -0.2600 | -0.3119 |
| 5.1 | -0.3796 | -0.1913 | -0.2383 |
| 5.4 | -0.3112 | -0.1401 | -0.1835 |
| 5.7 | -0.2581 | -0.1037 | -0.1433 |
| 6 | -0.2167 | -0.0765 | -0.1128 |

**Table S5.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the T-shaped approach at the *ω*B97X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) NCBr·bz | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 1.8 | 175.3732 | 176.1069 | 176.5309 |
| 1.9 | 133.0952 | 133.7828 | 134.2224 |
| 2.0 | 99.5822 | 100.2626 | 100.6763 |
| 2.1 | 73.4014 | 74.0654 | 74.4714 |
| 2.2 | 53.1105 | 53.7611 | 54.1529 |
| 2.3 | 37.5376 | 38.1807 | 38.5546 |
| 2.4 | 25.7282 | 26.3573 | 26.7185 |
| 2.5 | 16.8673 | 17.4921 | 17.8354 |
| 2.6 | 10.2907 | 10.9065 | 11.2322 |
| 2.7 | 5.5230 | 6.1250 | 6.4418 |
| 2.8 | 2.1188 | 2.7104 | 3.0154 |
| 2.9 | -0.2519 | 0.3234 | 0.6182 |
| 3 | -1.8109 | -1.2474 | -0.9638 |
| 3.1 | -2.7924 | -2.2453 | -1.9682 |
| 3.2 | -3.3884 | -2.8577 | -2.5900 |
| 3.3 | -3.6221 | -3.1052 | -2.8494 |
| 3.32 | -3.6395 | -3.1265 | -2.8713 |
| 3.34 | -3.6518 | -3.1423 | -2.8872 |
| 3.36 | -3.6614 | -3.1551 | -2.9007 |
| 3.38 | -3.6675 | -3.1643 | -2.9114 |
| 3.4 | -3.6701 | -3.1696 | -2.9188 |
| 3.42 | -3.6681 | -3.1720 | -2.9221 |
| 3.44 | -3.6603 | -3.1689 | -2.9196 |
| 3.46 | -3.6477 | -3.1587 | -2.9125 |
| 3.48 | -3.6266 | -3.1414 | -2.8981 |
| 3.5 | -3.5993 | -3.1174 | -2.8758 |
| 3.6 | -3.4077 | -2.9421 | -2.7098 |
| 3.7 | -3.1807 | -2.7312 | -2.5059 |
| 3.8 | -2.9344 | -2.5030 | -2.2855 |
| 3.9 | -2.6796 | -2.2642 | -2.0561 |
| 4.2 | -1.9774 | -1.6113 | -1.4233 |

| | | | |
|---|---|---|---|
| 4.5 | -1.4363 | -1.1118 | -0.9434 |
| 4.8 | -1.0542 | -0.7699 | -0.6156 |
| 5.1 | -0.7901 | -0.5406 | -0.3993 |
| 5.4 | -0.6198 | -0.3978 | -0.2682 |
| 5.7 | -0.4925 | -0.2955 | -0.1751 |
| 6 | -0.4110 | -0.2338 | -0.1226 |

**Table S6.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the T-shaped approach at the *ω*B97X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) $H_2O$·bz | (b) $H_2O$·[bz·NCBr] | (c)$H_2O$·[bz·$H_2O$] |
| 1.8 | 2.1563 | 2.6831 | 2.5516 |
| 1.9 | 0.0884 | 0.6210 | 0.4892 |
| 2 | -1.3217 | -0.7879 | -0.9188 |
| 2.1 | -2.2273 | -1.6972 | -1.8262 |
| 2.2 | -2.7773 | -2.2541 | -2.3804 |
| 2.3 | -3.0479 | -2.5336 | -2.6569 |
| 2.32 | -3.0790 | -2.5673 | -2.6898 |
| 2.34 | -3.1039 | -2.5947 | -2.7163 |
| 2.36 | -3.1214 | -2.6140 | -2.7351 |
| 2.38 | -3.1320 | -2.6269 | -2.7473 |
| 2.4 | -3.1376 | -2.6354 | -2.7549 |
| 2.42 | -3.1388 | -2.6395 | -2.7582 |
| 2.44 | -3.1351 | -2.6381 | -2.7562 |
| 2.46 | -3.1261 | -2.6315 | -2.7489 |
| 2.48 | -3.1124 | -2.6204 | -2.7372 |
| 2.5 | -3.0949 | -2.6055 | -2.7216 |
| 2.6 | -2.9678 | -2.4930 | -2.6054 |
| 2.7 | -2.7884 | -2.3294 | -2.4381 |
| 2.8 | -2.5871 | -2.1437 | -2.2488 |
| 2.9 | -2.3702 | -1.9425 | -2.0443 |
| 3 | -2.1581 | -1.7479 | -1.8455 |
| 3.1 | -1.9605 | -1.5657 | -1.6600 |
| 3.2 | -1.7670 | -1.3877 | -1.4786 |
| 3.3 | -1.5938 | -1.2314 | -1.3179 |
| 3.4 | -1.4408 | -1.0930 | -1.1761 |
| 3.5 | -1.2976 | -0.9641 | -1.0441 |
| 3.6 | -1.1708 | -0.8518 | -0.9283 |
| 3.7 | -1.0588 | -0.7533 | -0.8266 |
| 3.8 | -0.9595 | -0.6664 | -0.7370 |
| 3.9 | -0.8708 | -0.5901 | -0.6578 |
| 4.2 | -0.6606 | -0.4126 | -0.4731 |
| 4.5 | -0.5147 | -0.2943 | -0.3489 |
| 4.8 | -0.4111 | -0.2145 | -0.2639 |

| | | | |
|---|---|---|---|
| 5.1 | -0.3345 | -0.1583 | -0.2033 |
| 5.4 | -0.2766 | -0.1177 | -0.1589 |
| 5.7 | -0.2317 | -0.0880 | -0.1256 |
| 6 | -0.1952 | -0.0648 | -0.0994 |

**Table S7.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the T-shaped approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) NCBr·bz | | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 2.80 | 2.8148 | 2.86 | 1.8384 | 2.1076 |
| 2.90 | 0.4349 | 2.96 | -0.1196 | 0.1463 |
| 3.00 | -1.2346 | 3.06 | -1.4250 | -1.1731 |
| 3.10 | -2.3213 | 3.16 | -2.2844 | -2.0394 |
| 3.20 | -3.0199 | 3.26 | -2.7824 | -2.5454 |
| 3.30 | -3.3925 | 3.36 | -3.0331 | -2.8025 |
| 3.32 | -3.4386 | 3.38 | -3.0628 | -2.8329 |
| 3.34 | -3.4759 | 3.4 | -3.0881 | -2.8596 |
| 3.36 | -3.5066 | 3.42 | -3.1119 | -2.8837 |
| 3.38 | -3.5327 | 3.44 | -3.1301 | -2.9048 |
| 3.40 | -3.5551 | 3.46 | -3.1398 | -2.9179 |
| 3.42 | -3.5752 | 3.48 | -3.1412 | -2.9194 |
| 3.44 | -3.5912 | 3.5 | -3.1354 | -2.9154 |
| 3.46 | -3.5973 | 3.52 | -3.1267 | -2.9085 |
| 3.48 | -3.5926 | 3.54 | -3.1122 | -2.8963 |
| 3.50 | -3.5843 | 3.56 | -3.0985 | -2.8835 |
| 3.60 | -3.4932 | 3.66 | -2.9844 | -2.7757 |
| 3.70 | -3.3441 | 3.76 | -2.8310 | -2.6298 |
| 3.80 | -3.1623 | 3.86 | -2.6511 | -2.4579 |
| 3.90 | -2.9626 | 3.96 | -2.4642 | -2.2764 |
| 4.00 | -2.7599 | 4.06 | -2.2766 | -2.0955 |

**Table S8.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the T-shaped approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) $H_2O$·bz | | (b) $H_2O$·[bz·NCBr] | (c)$H_2O$·[bz·$H_2O$] |
| 1.82 | 2.0859 | 1.86 | 1.6834 | 1.5698 |
| 1.92 | 0.0788 | 1.96 | -0.0457 | -0.1601 |
| 2.02 | -1.2951 | 2.06 | -1.2095 | -1.3235 |
| 2.12 | -2.1980 | 2.16 | -1.9777 | -2.0898 |
| 2.22 | -2.7704 | 2.26 | -2.4324 | -2.5426 |
| 2.32 | -3.0555 | 2.36 | -2.6575 | -2.7645 |
| 2.34 | -3.0943 | 2.38 | -2.6830 | -2.7894 |
| 2.36 | -3.1254 | 2.40 | -2.7048 | -2.8104 |
| 2.38 | -3.1490 | 2.42 | -2.7218 | -2.8267 |

| | | | | |
|---|---|---|---|---|
| 2.4 | -3.1677 | 2.44 | -2.7315 | -2.8361 |
| 2.42 | -3.1822 | 2.46 | -2.7337 | -2.8379 |
| 2.44 | -3.1902 | 2.48 | -2.7295 | -2.8332 |
| 2.46 | -3.1907 | 2.50 | -2.7201 | -2.8234 |
| 2.48 | -3.1846 | 2.52 | -2.7073 | -2.8100 |
| 2.5 | -3.1730 | 2.54 | -2.6929 | -2.7948 |
| 2.52 | -3.1572 | 2.56 | -2.6774 | -2.7784 |
| 2.62 | -3.0516 | 2.66 | -2.5658 | -2.6639 |
| 2.72 | -2.8943 | 2.76 | -2.4044 | -2.4998 |
| 2.82 | -2.7019 | 2.86 | -2.2225 | -2.3150 |
| 2.92 | -2.5033 | 2.96 | -2.0372 | -2.1266 |
| 3.02 | -2.3087 | 3.06 | -1.8634 | -1.9496 |

**Table S9.** Equilibrium distances $r_{eq}$ (Å) and interaction energies $\Delta E_{XB}$ and $\Delta E_{HB}$ (kcal/mol) for NCBr·bz and $H_2O$·bz dimers in the 45° 'C approach' (Figure S13) and 'bond approach' (Figure S14).

| | **NCBr·bz** | |
|---|---|---|
| | $\mathbf{r_{eq}}$ | $\mathbf{\Delta E_{XB}}$ |
| 'C approach' | 4.12 | -2.00 |
| 'bond approach' | 4.02 | -2.34 |
| | **H(1)OH(2)·bz[a]** | |
| | $\mathbf{r_{eq}}$ | $\mathbf{\Delta E_{HB}}$ |
| 'C approach', H(1) up[b] | 3.12 | -2.29 |
| 'C approach', H(1) down[c] | 3.24 | -1.50 |
| 'bond approach', H(1) up[b] | 3.06 | -2.51 |
| 'bond approach', H(1) down[c] | 3.16 | -1.77 |

[a] H(1) and H(2) indicate the non-interacting and the interacting H atoms, respectively; [b]H(1) up indicates the H(1) points far from the benzene ring; [b]H(1) down indicates the H(1) points towards the benzene ring.

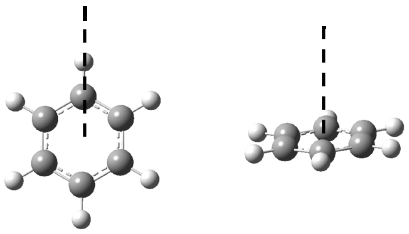

**Figure S8.** Top (left) and side (right) views of the 45° approach of NCBr or $H_2O$ towards the center of benzene ring along the line whose projection on the benzene plane crosses one carbon atom ('C approach').

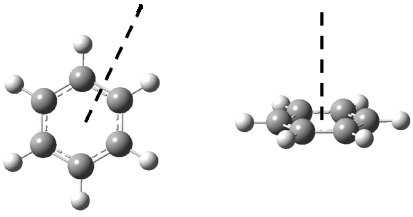

**Figure S9.** Top (left) and side (right) views of the 45° approach of NCBr or $H_2O$ towards the center of benzene ring along the line whose projection on the benzene plane crosses the center of a CC bond ('bond approach').

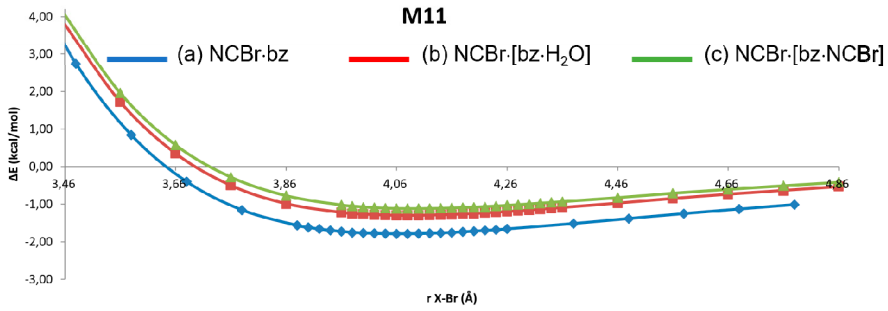


**Figure S10.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·$H_2O$] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the perpendicular approach at the M11/aug-cc-PVTZ level of theory.

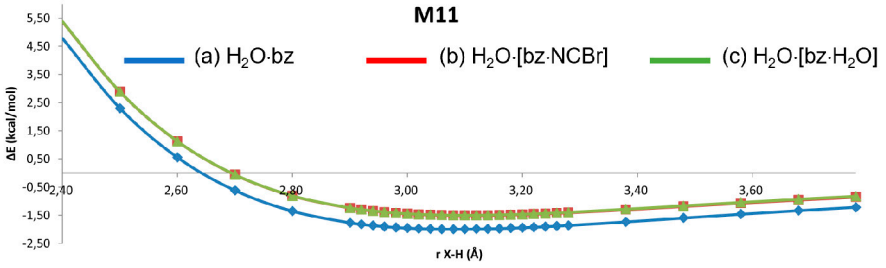


**Figure S11.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz (blue line), (b) $H_2O$·[bz·NCBr] (red line) and (c) $H_2O$·[bz·$H_2O$] (green line) systems in the perpendicular approach at the M11/aug-cc-PVTZ level of theory.

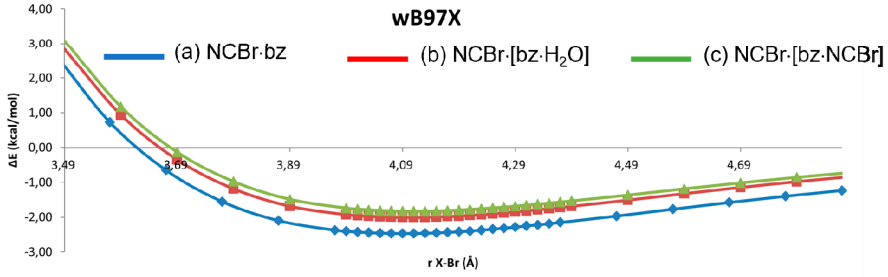


**Figure S12.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·$H_2O$] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the perpendicular approach at the *ω*B97X/aug-cc-PVTZ level of theory.

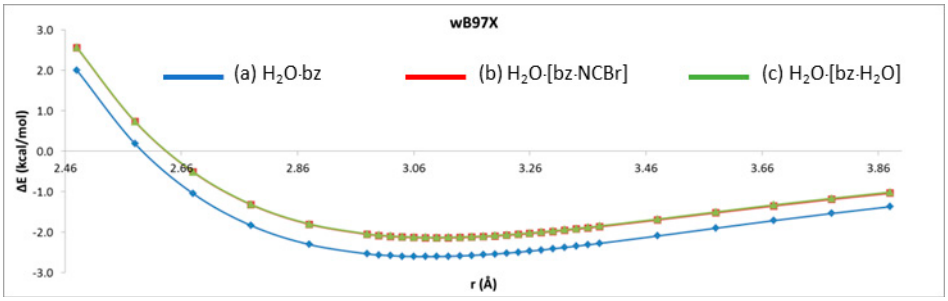


**Figure S13.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz (blue line), (b) $H_2O$·[bz·NCBr] (red line) and (c) $H_2O$·[bz·$H_2O$] (green line) systems in the perpendicular approach at the *ω*B97X/aug-cc-PVTZ level of theory.

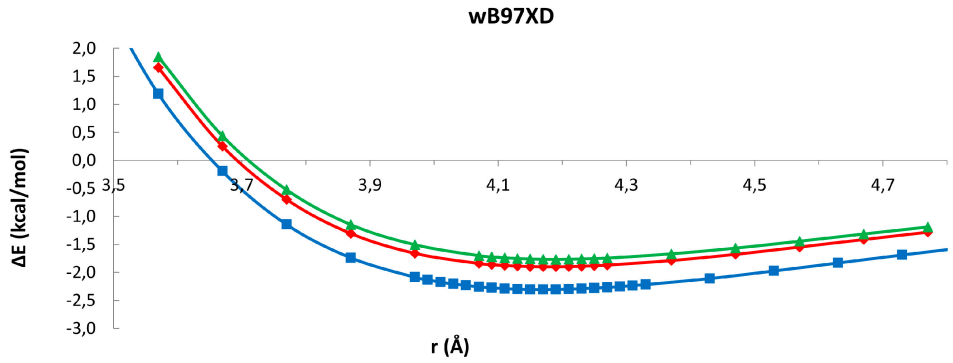


**Figure S14.** Binding energy curves, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz (blue line), (b) NCBr·[bz·$H_2O$] (red line) and (c) NCBr·[bz·NCBr] (green line) systems in the perpendicular approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

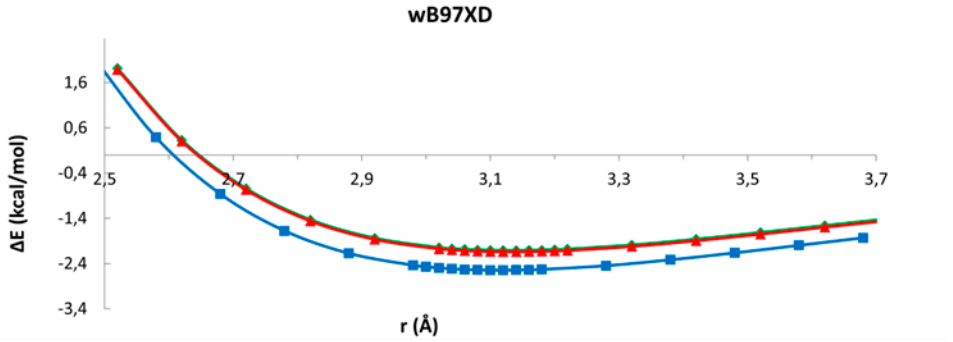


**Figure S15.** Binding energy curves, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz (blue line), (b) $H_2O$·[bz·NCBr] (red line) and (c) $H_2O$·[bz·$H_2O$] (green line) systems in the perpendicular approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

**Table S10.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the perpendicular approach at the M06-2X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) NCBr·bz | | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 3.20 | 12.1989 | 3.34 | 6.5090 | 6.7773 |
| 3.30 | 7.4943 | 3.44 | 3.4488 | 3.6984 |
| 3.40 | 4.0218 | 3.54 | 1.2968 | 1.5331 |
| 3.50 | 1.5405 | 3.64 | -0.1514 | 0.0737 |
| 3.60 | -0.1571 | 3.74 | -1.0591 | -0.8454 |
| 3.70 | -1.2542 | 3.84 | -1.5863 | -1.3840 |
| 3.80 | -1.9043 | 3.86 | -1.6545 | -1.4553 |
| 3.82 | -1.9952 | 3.88 | -1.7123 | -1.5160 |
| 3.84 | -2.0744 | 3.90 | -1.7602 | -1.5668 |
| 3.86 | -2.1419 | 3.92 | -1.7984 | -1.6077 |
| 3.88 | -2.1981 | 3.94 | -1.8276 | -1.6386 |
| 3.90 | -2.2438 | 3.96 | -1.8492 | -1.6613 |
| 3.92 | -2.2797 | 3.98 | -1.8644 | -1.6777 |
| 3.94 | -2.3065 | 4.00 | -1.8739 | -1.6889 |
| 3.96 | -2.3251 | 4.02 | -1.8777 | -1.6951 |

| | | | | |
|---|---|---|---|---|
| 3.98 | -2.3370 | 4.04 | -1.8765 | -1.6968 |
| 4.00 | -2.3433 | 4.06 | -1.8712 | -1.6946 |
| 4.02 | -2.3448 | 4.08 | -1.8626 | -1.6884 |
| 4.04 | -2.3420 | 4.10 | -1.8506 | -1.6778 |
| 4.06 | -2.3353 | 4.12 | -1.8352 | -1.6631 |
| 4.08 | -2.3252 | 4.14 | -1.8164 | -1.6449 |
| 4.10 | -2.3117 | 4.16 | -1.7943 | -1.6236 |
| 4.12 | -2.2947 | 4.18 | -1.7692 | -1.5993 |
| 4.14 | -2.2740 | 4.20 | -1.7409 | -1.5726 |
| 4.16 | -2.2498 | 4.22 | -1.7100 | -1.5439 |
| 4.18 | -2.2222 | 4.32 | -1.5371 | -1.3814 |
| 4.20 | -2.1913 | 4.42 | -1.3647 | -1.2169 |
| 4.30 | -2.0085 | 4.52 | -1.1965 | -1.0611 |
| 4.40 | -1.8268 | 4.62 | -1.0409 | -0.9078 |
| 4.50 | -1.6446 | 4.72 | -0.9088 | -0.7878 |
| 4.60 | -1.4752 | | | |
| 4.70 | -1.3273 | | | |
| 4.80 | -1.2007 | | | |
| 4.90 | -1.0920 | | | |
| 5.00 | -0.9980 | | | |
| 5.10 | -0.9099 | | | |

**Table S11.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the perpendicular approach at the M06-2X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) $H_2O$·bz | | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 1.80 | 48.6053 | 2.38 | 5.0622 | 5.0788 |
| 2.00 | 25.4302 | 2.48 | 2.5218 | 2.5362 |
| 2.20 | 11.6484 | 2.58 | 0.7180 | 0.7313 |
| 2.40 | 3.9324 | 2.68 | -0.5104 | -0.4973 |
| 2.50 | 1.5608 | 2.78 | -1.2977 | -1.2839 |
| 2.60 | -0.1063 | 2.88 | -1.7553 | -1.8773 |
| 2.70 | -1.2241 | 2.90 | -1.8159 | -1.9356 |
| 2.80 | -1.9237 | 2.92 | -1.8680 | -1.9854 |
| 2.90 | -2.3120 | 2.94 | -1.9121 | -2.0272 |
| 2.92 | -2.3610 | 2.96 | -1.9487 | -2.0614 |
| 2.94 | -2.4020 | 2.98 | -1.9783 | -2.0886 |
| 2.96 | -2.4355 | 3.00 | -2.0012 | -2.1092 |
| 2.98 | -2.4619 | 3.02 | -2.0181 | -2.1237 |
| 3.00 | -2.4817 | 3.04 | -2.0295 | -2.1327 |
| 3.02 | -2.4954 | 3.06 | -2.0359 | -2.1367 |
| 3.04 | -2.5035 | 3.08 | -2.0378 | -2.1363 |
| 3.06 | -2.5066 | 3.10 | -2.0356 | -2.1317 |
| 3.08 | -2.5052 | 3.12 | -2.0296 | -2.1234 |

| | | | | |
|---|---|---|---|---|
| 3.10 | -2.4996 | 3.14 | -2.0201 | -2.1116 |
| 3.12 | -2.4902 | 3.16 | -2.0074 | -2.0966 |
| 3.14 | -2.4773 | 3.18 | -1.9917 | -2.0787 |
| 3.16 | -2.4612 | 3.20 | -1.9733 | -2.0581 |
| 3.18 | -2.4421 | 3.22 | -1.9526 | -2.0351 |
| 3.20 | -2.4203 | 3.24 | -1.9298 | -2.0102 |
| 3.22 | -2.3961 | 3.26 | -1.9054 | -1.9836 |
| 3.24 | -2.3699 | 3.36 | -1.7640 | -1.7410 |
| 3.26 | -2.3420 | 3.46 | -1.6052 | -1.5797 |
| 3.28 | -2.3125 | 3.56 | -1.4459 | -1.4186 |
| 3.30 | -2.2816 | 3.66 | -1.2947 | -1.2653 |
| 3.40 | -2.1139 | 3.76 | -1.1591 | -1.1276 |
| 3.50 | -1.9363 | | | |
| 3.60 | -1.7631 | | | |
| 3.70 | -1.6010 | | | |
| 3.80 | -1.4558 | | | |
| 3.90 | -1.3233 | | | |
| 4.00 | -1.2082 | | | |
| 4.20 | -1.0086 | | | |
| 4.40 | -0.8454 | | | |
| 4.60 | -0.7037 | | | |
| 4.80 | -0.5887 | | | |
| 5.00 | -0.4868 | | | |

**Table S12.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the perpendicular approach at the M11/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) NCBr·bz | | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 3.38 | 5.5218 | 3.46 | 3.7942 | 4.0425 |
| 3.48 | 2.7394 | 3.56 | 1.7195 | 1.9557 |
| 3.58 | 0.8373 | 3.66 | 0.3498 | 0.5755 |
| 3.68 | -0.4006 | 3.76 | -0.5024 | -0.2790 |
| 3.78 | -1.1540 | 3.86 | -0.9880 | -0.7736 |
| 3.88 | -1.5670 | 3.96 | -1.2232 | -1.0224 |
| 3.90 | -1.6188 | 3.98 | -1.2486 | -1.0510 |
| 3.92 | -1.6623 | 4.00 | -1.2682 | -1.0741 |
| 3.94 | -1.6982 | 4.02 | -1.2826 | -1.0920 |
| 3.96 | -1.7271 | 4.04 | -1.2924 | -1.1049 |
| 3.98 | -1.7497 | 4.06 | -1.2980 | -1.1131 |
| 4.00 | -1.7665 | 4.08 | -1.2997 | -1.1169 |
| 4.02 | -1.7782 | 4.10 | -1.2981 | -1.1169 |
| 4.04 | -1.7853 | 4.12 | -1.2934 | -1.1139 |
| 4.06 | -1.7882 | 4.14 | -1.2860 | -1.1084 |

| | | | | |
|---|---|---|---|---|
| 4.08 | -1.7873 | 4.16 | -1.2761 | -1.1007 |
| 4.10 | -1.7829 | 4.18 | -1.2640 | -1.0910 |
| 4.12 | -1.7754 | 4.20 | -1.2499 | -1.0792 |
| 4.14 | -1.7651 | 4.22 | -1.2340 | -1.0654 |
| 4.16 | -1.7522 | 4.24 | -1.2165 | -1.0496 |
| 4.18 | -1.7370 | 4.26 | -1.1976 | -1.0321 |
| 4.20 | -1.7197 | 4.28 | -1.1775 | -1.0133 |
| 4.22 | -1.7007 | 4.30 | -1.1565 | -0.9936 |
| 4.24 | -1.6803 | 4.32 | -1.1348 | -0.9733 |
| 4.26 | -1.6587 | 4.34 | -1.1126 | -0.9527 |
| 4.38 | -1.5154 | 4.36 | -1.0901 | -0.9319 |
| 4.48 | -1.3829 | 4.46 | -0.9739 | -0.8267 |
| 4.58 | -1.2505 | 4.56 | -0.8500 | -0.7094 |
| 4.68 | -1.1297 | 4.66 | -0.7368 | -0.6060 |
| 4.78 | -1.0117 | 4.76 | -0.6358 | -0.5108 |
| | | 4.86 | -0.5343 | -0.4172 |

**Table S13.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the perpendicular approach at the M11/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) $H_2O$·bz | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 2.40 | 4.7774 | 5.3742 | 5.3754 |
| 2.50 | 2.2983 | 2.8843 | 2.8841 |
| 2.60 | 0.5552 | 1.1278 | 1.1277 |
| 2.70 | -0.6147 | -0.0580 | -0.0565 |
| 2.80 | -1.3489 | -0.8093 | -0.8057 |
| 2.90 | -1.7630 | -1.2408 | -1.2356 |
| 2.92 | -1.8161 | -1.2974 | -1.2919 |
| 2.94 | -1.8610 | -1.3458 | -1.3400 |
| 2.96 | -1.8981 | -1.3865 | -1.3805 |
| 2.98 | -1.9283 | -1.4203 | -1.4140 |
| 3.00 | -1.9519 | -1.4476 | -1.4409 |
| 3.02 | -1.9697 | -1.4690 | -1.4620 |
| 3.04 | -1.9820 | -1.4850 | -1.4776 |
| 3.06 | -1.9893 | -1.4961 | -1.4882 |
| 3.08 | -1.9921 | -1.5028 | -1.4944 |
| 3.10 | -1.9909 | -1.5055 | -1.4965 |
| 3.12 | -1.9861 | -1.5045 | -1.4949 |
| 3.14 | -1.9779 | -1.5004 | -1.4900 |
| 3.16 | -1.9669 | -1.4933 | -1.4822 |
| 3.18 | -1.9532 | -1.4836 | -1.4718 |
| 3.20 | -1.9373 | -1.4717 | -1.4592 |
| 3.22 | -1.9193 | -1.4577 | -1.4445 |

| | | | |
|---|---|---|---|
| 3.24 | -1.8996 | -1.4420 | -1.4282 |
| 3.26 | -1.8784 | -1.4248 | -1.4103 |
| 3.28 | -1.8559 | -1.4063 | -1.3910 |
| 3.38 | -1.7295 | -1.2997 | -1.2810 |
| 3.48 | -1.5928 | -1.1818 | -1.1601 |
| 3.58 | -1.4579 | -1.0652 | -1.0409 |
| 3.68 | -1.3300 | -0.9548 | -0.9274 |
| 3.78 | -1.2099 | -0.8519 | -0.8221 |

**Table S14.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the perpendicular approach at the *ωB*97X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) NCBr·bz | | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 3.47 | 2.7645 | 3.49 | 2.8320 | 3.0767 |
| 3.57 | 0.7338 | 3.59 | 0.9359 | 1.1677 |
| 3.67 | -0.6474 | 3.69 | -0.3520 | -0.1344 |
| 3.77 | -1.5518 | 3.79 | -1.1845 | -0.9762 |
| 3.87 | -2.0975 | 3.89 | -1.6838 | -1.4875 |
| 3.97 | -2.3714 | 3.99 | -1.9271 | -1.7389 |
| 3.99 | -2.4019 | 4.01 | -1.9535 | -1.7678 |
| 4.01 | -2.4256 | 4.03 | -1.9730 | -1.7897 |
| 4.03 | -2.4428 | 4.05 | -1.9876 | -1.8070 |
| 4.05 | -2.4551 | 4.07 | -1.9977 | -1.8194 |
| 4.07 | -2.4630 | 4.09 | -2.0028 | -1.8271 |
| 4.09 | -2.4667 | 4.11 | -2.0036 | -1.8296 |
| 4.11 | -2.4658 | 4.13 | -2.0000 | -1.8271 |
| 4.13 | -2.4599 | 4.15 | -1.9924 | -1.8205 |
| 4.15 | -2.4498 | 4.17 | -1.9809 | -1.8099 |
| 4.17 | -2.4353 | 4.19 | -1.9651 | -1.7955 |
| 4.19 | -2.4172 | 4.21 | -1.9462 | -1.7776 |
| 4.21 | -2.3958 | 4.23 | -1.9240 | -1.7567 |
| 4.23 | -2.3705 | 4.25 | -1.8990 | -1.7346 |
| 4.25 | -2.3430 | 4.27 | -1.8722 | -1.7101 |
| 4.27 | -2.3138 | 4.29 | -1.8431 | -1.6837 |
| 4.29 | -2.2831 | 4.31 | -1.8134 | -1.6555 |
| 4.31 | -2.2513 | 4.33 | -1.7830 | -1.6262 |
| 4.33 | -2.2183 | 4.35 | -1.7515 | -1.5959 |
| 4.35 | -2.1843 | 4.37 | -1.7195 | -1.5649 |
| 4.37 | -2.1498 | 4.39 | -1.6863 | -1.5332 |
| -1.97 | -1.9655 | 4.49 | -1.5089 | -1.3654 |
| -1.77 | -1.7686 | 4.59 | -1.3229 | -1.1852 |
| -1.58 | -1.5766 | 4.69 | -1.1445 | -1.0147 |
| -1.40 | -1.3966 | 4.79 | -0.9782 | -0.8552 |

| | | | | |
|---|---|---|---|---|
| -1.23 | -1.2314 | 4.89 | -0.8264 | -0.7096 |

**Table S15.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the perpendicular approach at the *ω*B97X/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | | |
|---|---|---|---|
| | (a) $H_2O$·bz | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 2.48 | 2.0032 | 2.5586 | 2.5679 |
| 2.58 | 0.1876 | 0.7316 | 0.7403 |
| 2.68 | -1.0439 | -0.5138 | -0.5048 |
| 2.78 | -1.8354 | -1.3208 | -1.3107 |
| 2.88 | -2.3032 | -1.8049 | -1.7938 |
| 2.98 | -2.5355 | -2.0540 | -2.0418 |
| 3.00 | -2.5605 | -2.0824 | -2.0700 |
| 3.02 | -2.5795 | -2.1049 | -2.0922 |
| 3.04 | -2.5929 | -2.1217 | -2.1087 |
| 3.06 | -2.6008 | -2.1330 | -2.1196 |
| 3.08 | -2.6034 | -2.1390 | -2.1252 |
| 3.10 | -2.6012 | -2.1403 | -2.1262 |
| 3.12 | -2.5950 | -2.1377 | -2.1233 |
| 3.14 | -2.5855 | -2.1318 | -2.1169 |
| 3.16 | -2.5727 | -2.1225 | -2.1073 |
| 3.18 | -2.5567 | -2.1099 | -2.0945 |
| 3.20 | -2.5379 | -2.0946 | -2.0788 |
| 3.22 | -2.5167 | -2.0768 | -2.0606 |
| 3.24 | -2.4930 | -2.0566 | -2.0400 |
| 3.26 | -2.4670 | -2.0339 | -2.0170 |
| 3.28 | -2.4388 | -2.0092 | -1.9918 |
| 3.30 | -2.4087 | -1.9825 | -1.9648 |
| 3.32 | -2.3770 | -1.9544 | -1.9363 |
| 3.34 | -2.3442 | -1.9251 | -1.9066 |
| 3.36 | -2.3105 | -1.8947 | -1.8759 |
| 3.38 | -2.2757 | -1.8632 | -1.8441 |
| 3.48 | -2.0921 | -1.6964 | -1.6754 |
| 3.58 | -1.9007 | -1.5212 | -1.4987 |
| 3.68 | -1.7120 | -1.3489 | -1.3244 |
| 3.78 | -1.5352 | -1.1877 | -1.1615 |
| 3.88 | -1.3694 | -1.0370 | -1.0089 |

**Table S16.** Binding energy, ΔE, vs. Br distance from the center of benzene ring, r, computed for (a) NCBr·bz, (b) NCBr·[bz·$H_2O$] and (c) NCBr·[bz·NCBr] systems in the perpendicular approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) NCBr·bz | | (b) NCBr·[bz·$H_2O$] | (c) NCBr·[bz·NCBr] |
| 3.47 | 3.1997 | 3.57 | 1.6572 | 1.8516 |
| 3.57 | 1.1912 | 3.67 | 0.2548 | 0.4382 |
| 3.67 | -0.1922 | 3.77 | -0.6947 | -0.5241 |
| 3.77 | -1.1422 | 3.87 | -1.3026 | -1.1454 |

| | | | | |
|---|---|---|---|---|
| 3.87 | -1.7358 | 3.97 | -1.6579 | -1.5044 |
| 3.97 | -2.0838 | 4.07 | -1.8401 | -1.7005 |
| 3.99 | -2.1310 | 4.09 | -1.8602 | -1.7222 |
| 4.01 | -2.1707 | 4.11 | -1.8755 | -1.7396 |
| 4.03 | -2.2032 | 4.13 | -1.8865 | -1.7518 |
| 4.05 | -2.2306 | 4.15 | -1.8941 | -1.7606 |
| 4.07 | -2.2540 | 4.17 | -1.8983 | -1.7664 |
| 4.09 | -2.2734 | 4.19 | -1.8981 | -1.7676 |
| 4.11 | -2.2881 | 4.21 | -1.8952 | -1.7651 |
| 4.13 | -2.2975 | 4.23 | -1.8889 | -1.7596 |
| 4.15 | -2.3029 | 4.25 | -1.8797 | -1.7521 |
| 4.17 | -2.3040 | 4.27 | -1.8681 | -1.7441 |
| 4.19 | -2.3022 | 4.37 | -1.7872 | -1.6682 |
| 4.21 | -2.2974 | 4.47 | -1.6763 | -1.5658 |
| 4.23 | -2.2886 | 4.57 | -1.5453 | -1.4428 |
| 4.25 | -2.2776 | 4.67 | -1.4117 | -1.3136 |
| 4.27 | -2.2648 | 4.77 | -1.2799 | -1.1885 |
| 4.29 | -2.2498 | | | |
| 4.31 | -2.2328 | | | |
| 4.33 | -2.2138 | | | |
| 4.43 | -2.1069 | | | |
| 4.53 | -1.9714 | | | |
| 4.63 | -1.8292 | | | |
| 4.73 | -1.6868 | | | |
| 4.83 | -1.5498 | | | |

**Table S17.** Binding energy, ΔE, vs. (HO)H distance from the center of benzene ring, r, computed for (a) $H_2O$·bz, (b) $H_2O$·[bz·NCBr] and (c) $H_2O$·[bz·$H_2O$] systems in the perpendicular approach at the *ω*B97XD/aug-cc-PVTZ level of theory.

| r (Å) | ΔE (kcal/mol) | r (Å) | ΔE (kcal/mol) | |
|---|---|---|---|---|
| | (a) $H_2O$·bz | | (b) $H_2O$·[bz·NCBr] | (c) $H_2O$·[bz·$H_2O$] |
| 2.48 | 2.2128 | 2.52 | 1.8852 | 1.9131 |
| 2.58 | 0.3886 | 2.62 | 0.2994 | 0.3266 |
| 2.68 | -0.8613 | 2.72 | -0.7700 | -0.7429 |
| 2.78 | -1.6780 | 2.82 | -1.4611 | -1.4332 |
| 2.88 | -2.1750 | 2.92 | -1.8678 | -1.8392 |
| 2.98 | -2.4403 | 3.02 | -2.0768 | -2.0474 |
| 3.00 | -2.4724 | 3.04 | -2.1002 | -2.0705 |
| 3.02 | -2.4984 | 3.06 | -2.1177 | -2.0878 |
| 3.04 | -2.5188 | 3.08 | -2.1298 | -2.0996 |
| 3.06 | -2.5337 | 3.10 | -2.1373 | -2.1068 |
| 3.08 | -2.5431 | 3.12 | -2.1411 | -2.1102 |
| 3.10 | -2.5475 | 3.14 | -2.1418 | -2.1107 |
| 3.12 | -2.5481 | 3.16 | -2.1395 | -2.1081 |
| 3.14 | -2.5457 | 3.18 | -2.1339 | -2.1023 |

| | | | | |
|---|---|---|---|---|
| 3.16 | -2.5404 | 3.20 | -2.1256 | -2.0937 |
| 3.18 | -2.5319 | 3.22 | -2.1147 | -2.0827 |
| 3.28 | -2.4497 | 3.32 | -2.0232 | -1.9897 |
| 3.38 | -2.3191 | 3.42 | -1.8975 | -1.8628 |
| 3.48 | -2.1660 | 3.52 | -1.7518 | -1.7155 |
| 3.58 | -1.9991 | 3.62 | -1.5977 | -1.5602 |
| 3.68 | -1.8323 | 3.72 | -1.4477 | -1.4088 |