# —Electronic Supplementary Information—

# Effect of aromatic ring fluorination on CH…π interactions: Microwave spectrum and structure of the 1,2-difluorobenzene…acetylene dimer

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**Table S1** Rotational constants, dipole moment components and relative energies of the planar form of 1,2-DFBZ…HCCH (relative to the non-planar form at each level). $\mu_c$ is zero by symmetry. Values in parentheses give the results for BSSE corrected optimizations. [a)]

| | MP2/ 6-311++G(2d,2p) | MP2/ aug-cc-pvdz | M06-2X/ 6-311++G(2d,2p) | M06-2X/ aug-cc-pvdz | ωB97X-D/ 6-311++G(2d,2p) | ωB97X-D/ aug-cc-pvdz |
|---|---|---|---|---|---|---|
| *A* / MHz | 2150.3(2157.3) | 2114.0(2119.2) | 2172.7(2174.1) | 2158.2(2157.1) | 2168.6(2169.0) | 2147.7(2146.5) |
| *B* / MHz | 711.0(688.6) | 715.5(683.8) | 723.8(720.1) | 722.1(715.1) | 710.0(707.4) | 711.8(702.3) |
| *C* / MHz | 534.3(522.0) | 534.6(517.0) | 542.9(540.9) | 541.1(537.1) | 534.9(533.4) | 534.6(529.1) |
| $\mu_a$ / D | 0.29(0.36) | 0.25(0.37) | 0.32(0.32) | 0.33(0.33) | 0.21(0.21) | 0.19 |
| $\mu_b$ / D | 2.65(2.65) | 2.71(2.69) | 2.68(2.69) | 2.67(2.67) | 2.65(2.65) | 2.66 |
| $\Delta E$ / $cm^{-1}$ [a)] | 489(234) | 663(243) | 298(219) | 331(236) | 253(206) | 293(218) |

[a)] $\Delta E$ is the relative energy of the planar form with respect to the non-planar form calculated with the same level and basis set.

**Table S2** Observed transition frequencies for all isotopologues of 1,2-DFBZ…HCCH.

**Table S2a** Rotational transition frequencies for parent isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$ - $\nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 2 | 2 | 2 | 1 | 6113.7585 | -0.0014 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6302.3277 | 0.0007 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6310.4284 | -0.0018 |
| 3 | 2 | 2 | 2 | 1 | 1 | 6769.8473 | 0.0005 |
| 4 | 2 | 2 | 3 | 3 | 1 | 7205.2467 | -0.0035 |
| 3 | 2 | 1 | 2 | 1 | 2 | 7496.6987 | -0.0020 |
| 3 | 3 | 1 | 2 | 2 | 0 | 7572.8438 | -0.0005 |
| 3 | 3 | 0 | 2 | 2 | 1 | 7647.2727 | -0.0004 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7734.5482 | 0.0002 |
| 4 | 1 | 4 | 3 | 1 | 3 | 7751.4884 | 0.0025 |
| 4 | 0 | 4 | 3 | 0 | 3 | 7784.4398 | 0.0009 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7801.3768 | 0.0000 |
| 4 | 1 | 3 | 3 | 2 | 2 | 7830.6180 | -0.0004 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8236.5499 | -0.0008 |
| 5 | 3 | 3 | 4 | 4 | 0 | 8268.5027 | 0.0031 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8298.1368 | -0.0014 |
| 5 | 2 | 4 | 4 | 3 | 1 | 8310.5701 | -0.0024 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8317.7960 | 0.0049 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8467.6647 | 0.0005 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8571.0655 | 0.0010 |
| 4 | 3 | 2 | 3 | 2 | 1 | 9498.9648 | 0.0000 |
| 5 | 2 | 3 | 4 | 3 | 2 | 9538.3610 | -0.0003 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9636.7337 | -0.0016 |
| 5 | 1 | 5 | 4 | 1 | 4 | 9641.8660 | -0.0004 |
| 5 | 0 | 5 | 4 | 0 | 4 | 9653.6730 | -0.0002 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9658.8055 | 0.0012 |
| 6 | 2 | 5 | 5 | 3 | 2 | 9786.7401 | 0.0038 |
| 4 | 3 | 1 | 3 | 2 | 2 | 9851.3033 | -0.0011 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9931.0595 | -0.0013 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10058.3298 | -0.0023 |
| 4 | 2 | 2 | 3 | 1 | 3 | 10117.7738 | -0.0027 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10203.9853 | -0.0019 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10232.3297 | -0.0006 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10250.7285 | 0.0016 |
| 5 | 3 | 3 | 4 | 3 | 2 | 10282.6758 | 0.0000 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10331.2581 | -0.0003 |
| 5 | 4 | 1 | 4 | 4 | 0 | 10339.3433 | 0.0025 |
| 5 | 3 | 2 | 4 | 3 | 1 | 10504.7793 | 0.0029 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10569.6616 | -0.0002 |
| 6 | 3 | 3 | 5 | 4 | 2 | 10973.8178 | -0.0004 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4 | 3 | 2 | 3 | 0 | 3 | 11198.9695 | 0.0016 |
| 5 | 3 | 3 | 4 | 2 | 2 | 11313.9774 | 0.0011 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11523.5298 | -0.0029 |
| 6 | 1 | 6 | 5 | 1 | 5 | 11524.9788 | -0.0014 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11528.6635 | -0.0003 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11530.1102 | -0.0010 |
| 6 | 2 | 4 | 5 | 3 | 3 | 11840.4148 | 0.0009 |
| 6 | 1 | 5 | 5 | 2 | 4 | 11931.6647 | 0.0001 |
| 6 | 2 | 5 | 5 | 1 | 4 | 12108.2115 | 0.0000 |
| 5 | 4 | 2 | 4 | 3 | 1 | 12230.0496 | -0.0018 |
| 5 | 3 | 2 | 4 | 2 | 3 | 12252.5377 | 0.0017 |
| 5 | 4 | 1 | 4 | 3 | 2 | 12353.5159 | -0.0011 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12584.7276 | -0.0008 |
| 6 | 3 | 3 | 5 | 3 | 2 | 12699.0922 | -0.0009 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12871.6414 | 0.0023 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12875.4429 | 0.0027 |
| 6 | 3 | 4 | 5 | 2 | 3 | 13041.3767 | 0.0017 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13404.4738 | 0.0015 |
| 7 | 0 | 7 | 6 | 0 | 6 | 13405.9182 | -0.0017 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13406.3105 | 0.0021 |
| 7 | 3 | 4 | 6 | 4 | 3 | 13411.9367 | 0.0025 |
| 7 | 1 | 6 | 6 | 2 | 5 | 13863.4311 | -0.0001 |
| 7 | 2 | 6 | 6 | 2 | 5 | 13880.2639 | 0.0002 |
| 7 | 2 | 6 | 6 | 1 | 5 | 13929.5370 | -0.0023 |
| 7 | 2 | 5 | 6 | 3 | 4 | 14041.1465 | -0.0001 |
| 6 | 4 | 3 | 5 | 3 | 2 | 14121.3640 | -0.0013 |
| 7 | 3 | 5 | 6 | 3 | 4 | 14272.2913 | -0.0017 |
| 7 | 4 | 4 | 6 | 4 | 3 | 14460.7914 | -0.0022 |
| 6 | 4 | 2 | 5 | 3 | 3 | 14559.7040 | 0.0016 |
| 7 | 3 | 5 | 6 | 2 | 4 | 14728.9412 | 0.0016 |
| 6 | 3 | 3 | 5 | 2 | 4 | 14893.3002 | 0.0031 |
| 6 | 5 | 2 | 5 | 4 | 1 | 14907.3602 | -0.0009 |
| 6 | 6 | 1 | 5 | 5 | 0 | 15504.6142 | -0.0018 |
| 8 | 2 | 7 | 7 | 1 | 6 | 15782.9885 | 0.0024 |
| 8 | 3 | 5 | 7 | 4 | 4 | 15822.9895 | -0.0017 |
| 8 | 2 | 6 | 7 | 3 | 5 | 16111.4099 | -0.0004 |
| 8 | 3 | 5 | 7 | 3 | 4 | 16871.8517 | 0.0011 |
| 7 | 5 | 3 | 6 | 4 | 2 | 16887.0140 | -0.0011 |
| 7 | 4 | 3 | 6 | 3 | 4 | 16959.8855 | -0.0002 |
| 7 | 5 | 2 | 6 | 4 | 3 | 17041.9824 | -0.0051 |
| 8 | 4 | 5 | 7 | 3 | 4 | 17542.9382 | -0.0002 |
| 7 | 6 | 2 | 6 | 5 | 1 | 17551.1741 | -0.0005 |
| 7 | 6 | 1 | 6 | 5 | 2 | 17558.8644 | 0.0040 |

**Table S2b** Rotational transition frequencies for $^{13}C_1$ isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs} - \nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 2 | 2 | 1 | 1 | 6710.7912 | 0.0053 |
| 3 | 3 | 1 | 2 | 2 | 0 | 7505.6305 | 0.0004 |
| 3 | 3 | 0 | 2 | 2 | 1 | 7585.1313 | 0.0005 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7676.5403 | -0.0049 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7736.6354 | -0.0003 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9561.1367 | -0.0016 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9580.2658 | -0.0014 |
| 4 | 3 | 1 | 3 | 2 | 2 | 9788.4969 | -0.0172 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9876.3172 | 0.0087 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10142.6642 | -0.0022 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10240.6430 | 0.0002 |
| 5 | 3 | 3 | 4 | 2 | 2 | 11209.8807 | 0.0153 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11431.4397 | 0.0010 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11436.9301 | -0.0045 |
| 5 | 4 | 1 | 4 | 3 | 2 | 12260.3839 | 0.0122 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12758.9378 | -0.0023 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12763.3503 | -0.0003 |
| 6 | 3 | 4 | 5 | 2 | 3 | 12918.6340 | -0.0116 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13296.4713 | 0.0024 |

**Table S2c** Rotational transition frequencies for $^{13}C_2$ isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs} - \nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 1 | 2 | 1 | 2 | 7444.1044 | -0.0038 |
| 3 | 3 | 1 | 2 | 2 | 0 | 7531.3027 | 0.0035 |
| 3 | 3 | 0 | 2 | 2 | 1 | 7602.2286 | -0.0002 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7713.3504 | -0.0044 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7781.7659 | -0.0021 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8540.6416 | 0.0106 |
| 4 | 3 | 2 | 3 | 2 | 1 | 9453.4841 | 0.0005 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9612.2107 | -0.0003 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9635.1386 | -0.0076 |
| 4 | 3 | 1 | 3 | 2 | 2 | 9790.0228 | -0.0032 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9891.7107 | 0.0109 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10174.2334 | -0.0041 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10191.4670 | 0.0002 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11495.5234 | -0.0084 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11502.4856 | 0.0132 |
| 6 | 2 | 5 | 5 | 1 | 4 | 12072.5078 | -0.0124 |
| 5 | 4 | 2 | 4 | 3 | 1 | 12166.1403 | 0.0012 |
| 5 | 4 | 1 | 4 | 3 | 2 | 12282.0574 | 0.0002 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12797.6369 | 0.0009 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12801.1332 | -0.0007 |
| 6 | 3 | 4 | 5 | 2 | 3 | 12995.6935 | 0.0055 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13372.8664 | 0.0023 |
| 7 | 2 | 6 | 6 | 1 | 5 | 13888.9920 | -0.0022 |

**Table S2d** Rotational transition frequencies for $^{13}C_3$ isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$ - $\nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 3 | 0 | 2 | 2 | 1 | 7632.4507 | -0.0063 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7725.6685 | 0.0102 |
| 4 | 1 | 3 | 3 | 2 | 2 | 7820.9573 | 0.0057 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8558.6012 | -0.0006 |
| 4 | 3 | 2 | 3 | 2 | 1 | 9482.4004 | 0.0049 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9625.8097 | 0.0009 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9647.8155 | -0.0004 |
| 4 | 3 | 1 | 3 | 2 | 2 | 9832.8700 | 0.0017 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9918.5281 | -0.0034 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10212.4932 | -0.0006 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10230.7830 | 0.0009 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10317.3581 | -0.0099 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11517.1880 | -0.0025 |
| 6 | 1 | 5 | 5 | 2 | 4 | 11916.7310 | -0.0116 |
| 6 | 2 | 5 | 5 | 1 | 4 | 12092.7657 | -0.0032 |
| 5 | 4 | 2 | 4 | 3 | 1 | 12207.7329 | 0.0093 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12846.4659 | -0.0145 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12850.2681 | 0.0110 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13389.6201 | 0.0098 |

**Table S2e** Rotational transition frequencies for $^{13}C_{12}$ isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$ - $\nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 2 | 2 | 1 | 1 | 6722.6840 | -0.0074 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7630.2659 | 0.0001 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7707.1452 | 0.0035 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8499.6272 | -0.0007 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9510.3172 | -0.0049 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9536.8696 | -0.0011 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10213.0955 | 0.0057 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10232.7443 | 0.0012 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11373.4525 | 0.0004 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11381.7367 | 0.0073 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12829.1241 | -0.0014 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12832.3092 | -0.0010 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13229.9210 | -0.0022 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13232.3389 | -0.0010 |

**Table S2f** Rotational transition frequencies for $^{13}C_{13}$ isotopic species of 1,2-difluorobenzene…HCCH complex

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$ - $\nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 2 | 2 | 1 | 1 | 6710.0940 | -0.0003 |
| 3 | 3 | 1 | 2 | 2 | 0 | 7553.7996 | -0.0133 |
| 4 | 0 | 4 | 3 | 1 | 3 | 7562.8776 | 0.0025 |
| 3 | 3 | 0 | 2 | 2 | 1 | 7615.7975 | 0.0114 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7654.9981 | 0.0012 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8474.0082 | -0.0019 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9432.3381 | 0.0012 |
| 4 | 3 | 2 | 3 | 2 | 1 | 9446.0230 | 0.0005 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9466.1273 | 0.0024 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9660.8808 | -0.0059 |
| 4 | 3 | 1 | 3 | 2 | 2 | 9743.8784 | 0.0047 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10191.0521 | -0.0034 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10209.9835 | -0.0019 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10223.5009 | -0.0001 |
| 5 | 3 | 3 | 4 | 2 | 2 | 11231.9212 | 0.0016 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11282.7041 | 0.0008 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11293.8923 | 0.0003 |

**Table S2g** Rotational transition frequencies for the 1,2-difluorobenzene…DCCD isotopic species

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$ - $\nu_{calc}$ / MHz |
|---|---|---|---|---|---|---|---|
| 3 | 2 | 2 | 2 | 1 | 1 | 6618.4920 | -0.0010 |
| 3 | 2 | 1 | 2 | 1 | 2 | 7278.5833 | -0.0002 |
| 3 | 3 | 1 | 2 | 2 | 0 | 7484.9149 | 0.0035 |
| 4 | 1 | 4 | 3 | 0 | 3 | 7496.5404 | -0.0009 |
| 4 | 2 | 3 | 3 | 1 | 2 | 8341.3644 | 0.0001 |
| 5 | 1 | 5 | 4 | 0 | 4 | 9263.4047 | 0.0021 |
| 4 | 3 | 2 | 3 | 2 | 1 | 9338.2528 | 0.0057 |
| 5 | 1 | 4 | 4 | 2 | 3 | 9426.4593 | 0.0003 |
| 5 | 2 | 4 | 4 | 1 | 3 | 10015.3968 | -0.0037 |
| 4 | 4 | 1 | 3 | 3 | 0 | 10120.7320 | 0.0030 |
| 4 | 4 | 0 | 3 | 3 | 1 | 10132.8746 | -0.0109 |
| 5 | 5 | 1 | 4 | 4 | 0 | 12738.4876 | 0.0031 |
| 5 | 5 | 0 | 4 | 4 | 1 | 12740.5974 | -0.0008 |

**Table S3** Principal axis coordinates of 1,2-DFBZ…HCCH and estimated uncertainties resulting from least-squares fit of moments of inertia. The numbering used in Figure 3 of the manuscript is also given

| ATOM [a] | Fig. 3 numbering | *a* | *da*[b] | *b* | *db* | *c* | *dc* |
|---|---|---|---|---|---|---|---|
| X1 | | –0.26271 | 0.01605 | –1.54354 | 0.00096 | 0 | 0 |
| X2 | | –0.54958 | 0.00581 | –0.58557 | 0.00402 | 0 | 0 |
| C3 | C4 | –0.54958 | 0.00581 | –0.58557 | 0.00402 | 0.68775 | 0 |
| F4 | F16 | –0.21154 | 0.01788 | –1.71442 | 0.00041 | 1.34525 | 0 |
| C5 | C3 | –0.54958 | 0.00581 | –0.58557 | 0.00402 | –0.68775 | 0 |
| F6 | F15 | –0.21154 | 0.01788 | –1.71442 | 0.00041 | –1.34525 | 0 |
| C7 | C5 | –0.88797 | 0.00628 | 0.54443 | 0.00764 | 1.40128 | 0 |
| H8 | H9 | –0.87935 | 0.00597 | 0.51564 | 0.00755 | 2.48377 | 0 |
| C9 | C2 | –0.88797 | 0.00628 | 0.54443 | 0.00764 | –1.40128 | 0 |
| H10 | H8 | –0.87935 | 0.00597 | 0.51564 | 0.00755 | –2.48377 | 0 |
| C11 | C6 | –1.23504 | 0.01867 | 1.70342 | 0.01135 | 0.69601 | 0 |
| H12 | H10 | –1.50310 | 0.02824 | 2.59859 | 0.01422 | 1.24009 | 0 |
| C13 | C1 | –1.23504 | 0.01867 | 1.70342 | 0.01135 | –0.69601 | 0 |
| H14 | H7 | –1.50310 | 0.02824 | 2.59859 | 0.01422 | –1.24009 | 0 |
| X15 | X18 | –0.88797 | 0.00628 | 0.54443 | 0.00764 | 0 | 0 |
| X16 | X17 | 2.95907 | 0.00581 | 0.72921 | 0.02352 | 0 | 0 |
| C17 | C13 | 3.44715 | 0.01111 | 0.37767 | 0.01637 | 0 | 0 |
| X18 | | 4.03159 | 0.00207 | 1.18911 | 0.00860 | 0 | 0 |
| X19 | | 4.89252 | 0.00821 | 0.56903 | 0.00896 | 0 | 0 |
| H20 | H14 | 4.30809 | 0.02057 | –0.24241 | 0.00616 | 0 | 0 |
| H21 | H11 | 1.61005 | 0.00939 | 1.70083 | 0.04386 | 0 | 0 |
| X22 | | 2.19448 | 0.02176 | 2.51227 | 0.03500 | 0 | 0 |
| X23 | | 3.05542 | 0.01230 | 1.89219 | 0.02209 | 0 | 0 |
| C24 | C12 | 2.47099 | 0.00151 | 1.08075 | 0.03082 | 0 | 0 |
| X25 | X19 | –0.67512 | 0.00133 | –0.16637 | 0.00537 | 0 | 0 |

[a] X are dummy atoms.

[b] *da*, *db*, and *dc* are uncertainties reported in STRFIT program based on propagated errors from fitted structural parameters only.

**Table S4** ωB97X-D/aug-cc-pVDZ (BSSE corrected) predicted principal axis coordinates (Å) of the non-planar and planar forms of 1,2-DFBZ…HCCH. The numbering scheme in Table S4a follows that of Figure 3 of the manuscript.

**Table S4a** Predicted non-planar form of 1,2-DFBZ…HCCH

| | *a* | *b* | *c* |
|---|---|---|---|
| C1 | –1.1385 | –1.7528 | –0.7005 |
| C2 | –0.8424 | –0.5844 | –1.4041 |
| C3 | –0.5624 | 0.5758 | –0.6997 |
| C4 | –0.5753 | 0.5792 | 0.6923 |
| C5 | –0.8681 | –0.5779 | 1.3971 |
| C6 | –1.1513 | –1.7495 | 0.6939 |
| H7 | –1.3611 | –2.6671 | –1.2488 |
| H8 | –0.8207 | –0.5607 | –2.4924 |
| H9 | –0.8657 | –0.5477 | 2.4854 |
| H10 | –1.3833 | –2.6616 | 1.2422 |
| H11 | 1.6018 | –1.6202 | 0.0209 |
| C12 | 2.4735 | –0.9942 | 0.0176 |
| C13 | 3.4431 | –0.2748 | 0.0136 |
| H14 | 4.3053 | 0.3611 | 0.0095 |
| F15 | –0.2726 | 1.7102 | –1.3532 |
| F16 | –0.2975 | 1.7164 | 1.3459 |

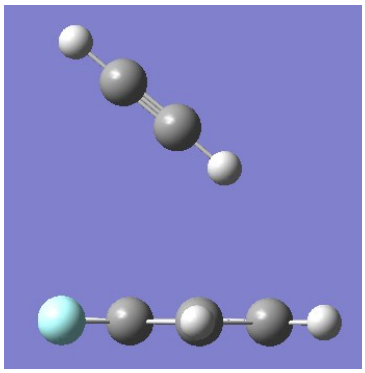

**Table S4b** Predicted planar form of 1,2-DFBZ…HCCH

| | *a* | *b* | *c* |
|---|---|---|---|
| C1 | –1.8433 | –1.8731 | 0.0000 |
| C2 | –0.4565 | –2.0130 | 0.0000 |
| C3 | 0.3667 | –0.8867 | 0.0000 |
| C4 | –0.2173 | 0.3699 | 0.0000 |
| C5 | –1.6014 | 0.5123 | 0.0000 |
| C6 | –2.4227 | –0.6042 | 0.0000 |
| H7 | –2.4825 | –2.7548 | 0.0000 |
| H8 | –0.0067 | –3.0049 | 0.0000 |
| H9 | 1.4533 | –0.9683 | 0.0000 |
| H10 | –3.5028 | –0.4654 | 0.0000 |
| F11 | –2.1336 | 1.7457 | 0.0000 |
| F12 | 0.5510 | 1.4767 | 0.0000 |
| H13 | 5.2237 | –1.3116 | 0.0000 |
| C14 | 4.5526 | –0.4761 | 0.0000 |
| C15 | 3.8070 | 0.4737 | 0.0000 |
| H16 | 3.1321 | 1.3074 | 0.0000 |