Electronic Supplementary Material for PCCP


# Accurate structures from combined gas electron diffraction and liquid crystal NMR data; the importance of anisotropy of indirect couplings for 1,4-difluorobenzene

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## Electronic supplementary information

**Table S1** Nozzle-to-plate distances, weighting functions, scale factors, correlation parameters and electron wavelengths used in the joint electron-diffraction and LCNMR study of 1,4-difluorobenzene.

| | | |
|---|---|---|
| Nozzle-to-camera distance / mm | 285.96 | 128.22 |
| $\Delta s$ / nm$^{-1}$ | 2 | 4 |
| $s_{min}$ / nm$^{-1}$ | 20 | 60 |
| $s_{w1}$ / nm$^{-1}$ | 40 | 80 |
| $s_{w2}$ / nm$^{-1}$ | 124 | 308 |
| $s_{max}$ / nm$^{-1}$ | 144 | 320 |
| Correlation parameter, $q$ | 0.476 | 0.140 |
| Scale factor | 0.725(3) | 0.724(8) |
| Wavelength / pm | 5.749 | 5.749 |

**Table S2** Dipolar coupling constants / Hz. See text for a more detailed description of the values.

| Constant | Observed | Corrected | Calculated | Uncertainty | Difference |
|---|---|---|---|---|---|
| ZLI 1167 | | | | | |
| $D_{1,8}$ | 87.48 | 89.61 | 89.46 | 0.22 | 0.15 |
| $D_{2,8}$ | 766.30 | 827.17 | 826.10 | 6.20 | 1.07 |
| $D_{7,8}$ | 228.58 | 231.26 | 231.48 | 0.27 | –0.22 |
| $D_{1,9}$ | 31.81 | 32.10 | 31.96 | 0.10 | 0.14 |
| $D_{2,9}$ | 132.81 | 135.82 | 135.76 | 0.30 | 0.06 |
| $D_{8,9}$ | 363.61 | 369.14 | 369.46 | 0.55 | –0.32 |
| $D_{8,10}$ | 54.73 | 54.99 | 54.98 | 0.10 | 0.01 |
| $D_{2,11}$ | 17.75 | 17.84 | 17.61 | 0.20 | 0.23 |
| $D_{8,11}$ | 33.47 | 33.65 | 33.60 | 0.10 | 0.05 |
| $D_{2,12}$ | 22.40 | 22.57 | 22.70 | 0.20 | –0.13 |
| $D_{8,12}$ | 44.21 | 44.56 | 44.55 | 0.10 | 0.01 |
| $D_{7,10}$ | 33.87 | 33.85 | 33.78 | 0.10 | 0.07 |
| $D_{1,10}$ | 21.31 | 21.26 | 20.99 | 0.10 | 0.27 |
| $D_{1,7}$ | 554.68 | 566.01 | 566.28 | 1.30 | –0.27 |
| $D_{2,10}$ | 27.45 | 27.45 | 27.28 | 0.10 | 0.17 |
| $D_{2,7}$ | 95.35 | 95.90 | 96.03 | 0.10 | –0.13 |
| ZLI 1132 ($^1$H) | | | | | |
| $D_{1,8}$ | –185.73 | –190.38 | –190.01 | 0.60 | –0.37 |
| $D_{2,8}$ | –1689.53 | –1826.80 | –1822.72 | 13.80 | –4.08 |
| $D_{7,8}$ | –506.69 | –512.75 | –513.37 | 0.60 | 0.62 |
| $D_{1,9}$ | –72.38 | –73.05 | –72.81 | 0.30 | –0.24 |
| $D_{2,9}$ | –307.00 | –313.96 | –314.14 | 0.80 | 0.18 |
| $D_{8,9}$ | –850.37 | –863.06 | –864.16 | 1.30 | 1.10 |
| $D_{8,10}$ | –126.26 | –126.86 | –126.85 | 0.10 | –0.01 |
| $D_{2,11}$ | –38.47 | –38.67 | –38.77 | 0.30 | 0.10 |
| $D_{8,11}$ | –73.71 | –74.11 | –74.01 | 0.10 | –0.10 |
| $D_{2,12}$ | –47.98 | –48.36 | –48.42 | 0.36 | 0.06 |
| $D_{8,12}$ | –93.80 | –94.57 | –94.59 | 0.10 | 0.02 |
| $D_{7,10}$ | –79.14 | –79.09 | –79.02 | 0.10 | –0.07 |
| ZLI 1695 ($^1$H) | | | | | |
| $D_{1,8}$ | 115.33 | 118.09 | 118.10 | 0.37 | –0.01 |
| $D_{2,8}$ | 987.32 | 1066.68 | 1063.07 | 7.90 | 3.61 |
| $D_{7,8}$ | 293.16 | 296.54 | 296.82 | 0.34 | –0.28 |
| $D_{1,9}$ | 40.15 | 40.52 | 40.20 | 0.20 | 0.32 |
| $D_{2,9}$ | 165.06 | 168.80 | 168.80 | 0.40 | 0.00 |
| $D_{8,9}$ | 448.28 | 455.19 | 455.64 | 0.68 | –0.45 |
| $D_{8,10}$ | 68.22 | 68.55 | 68.50 | 0.10 | 0.05 |
| $D_{2,11}$ | 22.65 | 22.76 | 22.69 | 0.28 | 0.07 |
| $D_{8,11}$ | 43.12 | 43.35 | 43.28 | 0.10 | 0.07 |
| $D_{2,12}$ | 29.84 | 30.07 | 29.89 | 0.28 | 0.18 |
| $D_{8,12}$ | 58.37 | 58.83 | 58.84 | 0.10 | –0.01 |
| $D_{7,10}$ | 41.72 | 41.69 | 41.67 | 0.10 | 0.03 |
| Mixture | | | | | |
| $D_{1,8}$ | –114.31 | –118.32 | –118.16 | 0.50 | –0.16 |
| $D_{2,8}$ | –1573.47 | –1708.79 | –1705.37 | 13.60 | –3.42 |
| $D_{7,8}$ | –493.35 | –500.35 | –501.61 | 0.70 | 1.26 |
| $D_{1,9}$ | –86.20 | –87.02 | –86.68 | 0.40 | –0.34 |
| $D_{2,9}$ | –403.21 | –412.35 | –411.88 | 1.00 | –0.47 |
| $D_{8,9}$ | –1190.30 | –1206.21 | –1204.36 | 1.60 | –1.85 |
| $D_{8,10}$ | –162.94 | –163.72 | –163.57 | 0.10 | –0.15 |
| $D_{2,11}$ | –35.36 | –35.55 | –35.64 | 0.60 | 0.09 |

| | | | | | |
|---|---|---|---|---|---|
| $D_{8,11}$ | –67.91 | –68.29 | –68.31 | 0.10 | 0.02 |
| $D_{2,12}$ | –31.67 | –31.96 | –31.80 | 0.60 | –0.16 |
| $D_{8,12}$ | –57.89 | –58.51 | –58.47 | 0.10 | –0.04 |
| $D_{7,10}$ | –110.13 | –110.06 | –110.13 | 0.10 | 0.07 |
| $D_{1,10}$ | –65.36 | –66.55 | –68.41 | 0.35 | 1.86 |
| $D_{1,7}$ | –1777.12 | –1848.74 | –1845.94 | 5.00 | –2.81 |
| $D_{2,10}$ | –84.59 | –84.59 | –85.21 | 0.20 | –0.62 |
| $D_{2,7}$ | –272.98 | –280.02 | –279.95 | 0.30 | –0.07 |
| ZLI 1132 ($^{19}$F) | | | | | |
| $D_{7,8}$ | –450.81 | –456.20 | –456.13 | 0.60 | –0.07 |
| $D_{8,9}$ | –762.53 | –773.91 | –774.86 | 1.20 | 0.94 |
| $D_{8,10}$ | –112.90 | –113.44 | –113.48 | 0.10 | 0.04 |
| $D_{8,11}$ | –65.31 | –65.67 | –65.68 | 0.13 | 0.01 |
| $D_{8,12}$ | –82.64 | –83.32 | –83.38 | 0.22 | 0.06 |
| $D_{7,10}$ | –70.87 | –70.83 | –70.85 | 0.10 | 0.02 |
| $D_{1,10}$ | –44.06 | –44.10 | –44.01 | 0.27 | –0.09 |
| $D_{1,7}$ | –1160.49 | –1187.89 | –1187.63 | 2.80 | –0.26 |
| $D_{2,10}$ | –57.17 | –57.35 | –56.78 | 0.30 | –0.57 |
| $D_{2,7}$ | –195.97 | –197.72 | –197.56 | 0.20 | –0.16 |
| ZLI 1695 ($^{19}$F) | | | | | |
| $D_{7,8}$ | 264.87 | 267.92 | 268.11 | 0.31 | –0.19 |
| $D_{8,9}$ | 408.31 | 414.60 | 415.29 | 0.64 | –0.69 |
| $D_{8,10}$ | 61.98 | 62.28 | 62.29 | 0.11 | –0.01 |
| $D_{8,11}$ | 38.87 | 39.08 | 39.06 | 0.11 | 0.02 |
| $D_{8,12}$ | 52.43 | 52.84 | 52.80 | 0.11 | 0.04 |
| $D_{7,10}$ | 38.01 | 37.99 | 37.97 | 0.10 | 0.02 |
| $D_{1,10}$ | 23.73 | 23.76 | 23.59 | 0.10 | 0.17 |
| $D_{1,7}$ | 621.10 | 635.97 | 636.52 | 1.50 | –0.55 |
| $D_{2,10}$ | 30.83 | 30.93 | 30.78 | 0.10 | 0.15 |
| $D_{2,7}$ | 108.02 | 109.00 | 108.98 | 0.11 | 0.02 |

**Table S3** Interatomic distances ($r_a$/pm), refined and calculated (MM3) amplitudes of vibration ($u$/pm) and perpendicular distance corrections ($k$/pm) from the combined electron diffraction and LCNMR refinement of 1,4-difluorobenzene.[a]

| | Atom pair | $r_a$ | $u$(exp.) | $k$ | $u$(calc.) |
|---|---|---|---|---|---|
| $u_4$ | C(2)–H(8) | 109.2(2) | 7.0(7) | 1.7 | 7.7 |
| $u_3$ | C(1)–F(7) | 134.7(2) | 4.4(tied to $u$1) | 0.6 | 4.4 |
| $u_1$ | C(1)–C(2) | 139.0(1) | 4.5(1) | 0.3 | 4.5 |
| $u_2$ | C(2)–C(3) | 139.6(2) | 4.5(tied to $u$1) | 0.4 | 4.5 |
| $u_7$ | C(1)···H(8) | 214.6(2) | 9.4(tied to $u$12) | 1.0 | 9.8 |
| $u_{13}$ | C(2)···H(9) | 216.8(1) | 9.4(tied to $u$12) | 1.0 | 9.8 |
| $u_{12}$ | C(2)···F(7) | 235.4(1) | 5.9(2) | 0.4 | 6.1 |
| $u_5$ | C(1)···C(3) | 239.6(2) | 5.3(tied to $u$12) | 0.2 | 5.6 |
| $u_{11}$ | C(2)···C(6) | 243.1(2) | 5.4(tied to $u$12) | 0.2 | 5.6 |
| $u_{20}$ | H(8)···H(9) | 252.1(1) | 15.5(fixed) | 1.3 | 15.5 |
| $u_{17}$ | F(7)···H(8) | 258.6(1) | 12.5(tied to $u$12) | 0.9 | 13.0 |
| $u_6$ | C(1)···C(4) | 273.4(4) | 7.2(tied to $u$10) | 0.2 | 6.0 |
| $u_{10}$ | C(2)···C(5) | 280.1(2) | 7.5(5) | 0.1 | 6.2 |
| $u_8$ | C(1)···H(9) | 338.9(2) | 9.6(12) | 0.7 | 9.6 |
| $u_{16}$ | C(2)···H(12) | 340.2(2) | 9.7(tied to $u$8) | 0.6 | 9.6 |
| $u_{14}$ | C(2)···F(10) | 361.9(1) | 6.6(3) | 0.2 | 6.3 |
| $u_{15}$ | C(2)···H(11) | 388.4(2) | 7.2(24) | 0.5 | 9.5 |
| $u_9$ | C(1)···F(10) | 407.8(2) | 6.8(6) | 0.1 | 6.4 |
| $u_{22}$ | H(8)···H(12) | 427.8(3) | 13.1(fixed) | 0.8 | 13.1 |
| $u_{18}$ | F(7)···H(9) | 451.1(2) | 9.0(17) | 0.5 | 10.8 |
| $u_{21}$ | H(8)···H(11) | 496.4(3) | 11.9(fixed) | 0.7 | 11.9 |
| $u_{19}$ | F(7)···F(10) | 542.0(3) | 7.6(9) | 0.0 | 6.8 |

[a] Values in parentheses are the uncertainties on the last digits.

**Table S4** Least-squares correlation matrix (×100) from the refinement of 1,4-difluorobenzene.[a]

| | $p_2$ | $p_3$ | $p_4$ | $p_5$ | $p_6$ | $p_7$ | $p_8$ | $p_9$ | $p_{10}$ | $p_{11}$ | $p_{12}$ | $p_{13}$ | $p_{14}$ | $p_{15}$ | $p_{16}$ | $p_{17}$ | $p_{18}$ | $p_{19}$ | $p_{20}$ | $p_{22}$ | $p_{23}$ | $u_4$ | $u_{14}$ | $k_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $p_1$ | –52 | –68 | –54 | | | | | | | | | | | | | | | 64 | | | | –50 | | |
| $p_2$ | | | | | 74 | | | | | | | | | | | | | | | | –56 | | | |
| $p_3$ | | | | 56 | | | | | | | | | | | | | | –93 | | | | 59 | | |
| $p_4$ | | | | | | –65 | –70 | 70 | 74 | –67 | –65 | 63 | 82 | 59 | 73 | –62 | –69 | | | 51 | | | | |
| $p_5$ | | | | | –65 | | | | | | | | | | | | | –63 | | | | | | |
| $p_6$ | | | | | | | | | | | | | | | | | | | | | –54 | | | |
| $p_7$ | | | | | | | | –81 | | 76 | | –76 | –53 | –71 | | 72 | | | | | | | | |
| $p_8$ | | | | | | | | | –76 | | 69 | | –81 | | –78 | | 76 | | | | | | | |
| $p_9$ | | | | | | | | | | –82 | | 82 | 58 | 76 | | –77 | | | 53 | | | | | |
| $p_{10}$ | | | | | | | | | | | –72 | | 84 | | 79 | | –75 | | | | | | | |
| $p_{11}$ | | | | | | | | | | | | –77 | –55 | –72 | | 74 | | | | | | | | |
| $p_{12}$ | | | | | | | | | | | | | –75 | | –71 | | 68 | | | | | | | |
| $p_{13}$ | | | | | | | | | | | | | | 72 | | –73 | | | 51 | | | | | |
| $p_{14}$ | | | | | | | | | | | | | | | 84 | –51 | –80 | | | | | | | |
| $p_{15}$ | | | | | | | | | | | | | | | | –68 | | | | | | | | |
| $p_{16}$ | | | | | | | | | | | | | | | | | –78 | | | | | | | |
| $p_{19}$ | | | | | | | | | | | | | | | | | | | | | | –55 | | |
| $u_4$ | | | | | | | | | | | | | | | | | | | | | | | 52 | 60 |

[a] Only elements with absolute values ≥ 50% are shown; $k_2$ is a scale factor.

**Table S5** Cartesian coordinates in Å for the final refined structure ($r_{h0}$) of 1,4-difluorobenzene.

| | *x* | *y* | *z* |
|---|---|---|---|
| C(1) | –1.3671 | 0.0000 | 0.0000 |
| C(2) | –0.6968 | 1.2150 | 0.0000 |
| C(3) | 0.6968 | 1.2150 | 0.0000 |
| C(4) | 1.3671 | 0.0000 | 0.0000 |
| C(5) | 0.6968 | –1.2150 | 0.0000 |
| C(6) | –0.6968 | –1.2150 | 0.0000 |
| F(7) | –2.7103 | 0.0000 | 0.0000 |
| H(8) | –1.2585 | 2.1368 | 0.0000 |
| H(9) | 1.2585 | 2.1368 | 0.0000 |
| F(10) | 2.7103 | 0.0000 | 0.0000 |
| H(11) | 1.2585 | –2.1368 | 0.0000 |
| H(12) | –1.2585 | –2.1368 | 0.0000 |

**Figure S1** Experimental and difference (experimental minus theoretical) molecular-scattering intensity curves for 1,4-difluorobenzene.