Supplementary information to

"Deuterium isotope effects on ^{13}C NMR chemical shifts reflect the smaller steric size of CD_3 compared to CH_3 groups"

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^{1}H and ^{13}C NMR Data of Compounds **1**–**12**

^{1}H NMR spectra were obtained at an observation frequency of 400 MHz. The chemical shift reference was internal tetramethylsilane. The solvent for ^{1}H and ^{13}C NMR measurements was $CDCl_3$ unless mentioned otherwise. ^{13}C NMR spectra were obtained at 101 MHz using the solvent signal (δ = 77.05) as the chemical shift reference. Multiplicities given with the ^{13}C signals refer to the number of directly bonded hydrogens and were determined by the DEPT technique. All spectra were assigned as completely as possible by the use of H,H-COSY, C,H-HETCOR, C,H-COLOC and H{H} NOE difference experiments.

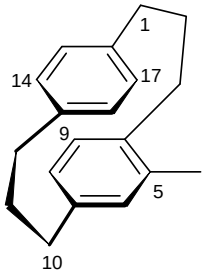
Compound 1 (protium isotopomer): 4-Methyl[2.2]paracyclophane

For ^{1}H and ^{13}C NMR data, see: L. Ernst, *Liebigs Ann.* **1995**, 13–17.

Compound 2 (protium isotopomer): 5-Methyl[3.3]paracyclophane

^{1}H NMR (110 °C, $C_2D_2Cl_4$): δ = 6.80 (dd, J_o and J_m, H-17), 6.79 (dd, J_o and J_m, H-14), 6.75, 6.60 (both dd, J_o and J_m, H-15,18), 6.58 (d, J = 7.9 Hz, H-9), 6.50 (dd, J_o and J_m, H-8), 6.49 (br. s, H-6), 2.87 (m, H-3$_{syn}$), 2.79–2.65 (m, 6 H, H-1,10,12), 2.54 (m, H-3$_{anti}$), 2.17–1.92 (m, 4 H, H-2,11), 2.22 (s, 3 H, CH_3); J_o = 7.5–8.0 Hz, J_m = 1.6–2.1 Hz.

^{13}C NMR, (110 °C, $C_2D_2Cl_4$): δ = 138.50, 138.36 (2 C), (both s, C-7,13,16), 136.40 (s, C-4), 134.48 (s, C-5), 131.34 (d, C-6), 130.90 (d, C-9), 129.89, 129.59 (both d, C-15,18), 129.37 (d, C-14), 127.73 (d, C-8), 126.67 (d, C-17), 36.06, 35.89, 35.56 (all t, C-1,10,12), 32.69 (t, C-3), 29.56 (t, C-11), 27.98 (t, C-2), 19.37 (q, CH_3).



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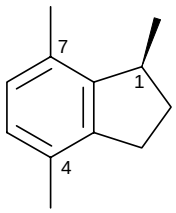
Compound 3 (protium isotopomer): 1,4,7-Trimethylindane

^{1}H NMR: δ = 6.87 (br. s, 2 H, H-5,6), 3.30 (dqd, *J* = 8.2, 7.0, 1.9 Hz, H-1), 2.89 (ddd, *J* = 16.0, 10.1, 7.9 Hz, H-3), 2.74 (ddd, *J* = 16.0, 9.1, 2.3 Hz, H-3), 2.27 (s, 7-CH_3), 2.21 (s, 4-CH_3), 2.20 (dddd, *J* = 12.6, 10.1, 9.1, 8.2 Hz, H-2), 1.75 (dddd, *J* = 12.6, 7.9, 2.3, 1.9 Hz, H-2), 1.15 (d, *J* = 7.0 Hz, 3 H, 1-CH_3).

^{13}C NMR: δ = 147.1 (s, C-7a), 141.8 (s, C-3a), 131.1 (s, C-4), 130.6 (s, C-7), 127.8 (d, C-6), 127.3 (d, C-5), 38.6 (d, C-1), 33.2 (t, C-2), 29.5 (t, C-3), 19.6 (q, 1-CH_3), 18.9 (q, 4-CH_3), 18.4 (q, 7-CH_3).

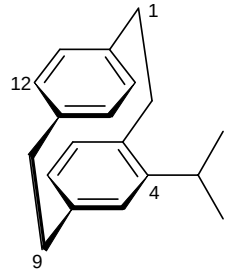


3

Compound 4 (protium isotopomer): 4-(Prop-2-yl)[2.2]paracyclophane

^{1}H NMR: δ = 6.54 (ddd, *J* = 7.8, 1.8, 0.4 Hz, H-15), 6.50 (dd, *J* = 7.8, 1.8 Hz, H-12), 6.47 (ddt, *J* = 7.8, 1.8, 0.6 Hz, H-13), 6.41–6.36 (m, 3 H, H-7,8,16), 6.22 (br. s, H-5), 3.41 (ddd, *J* = 13.5, 10.2, 2.0 Hz, H-2_{syn}), 3.15–2.93 (m, 6 H, H-1,9,10), 2.87 (sept, *J* = 6.8 Hz, *i*Pr-CH), 2.81 (dddd, *J* = 13.5, 10.7, 6.2, 0.3 Hz, H-2_{anti}), 1.31 (d , *J* = 6.8 Hz, 3 H, CH_3), 1.01 (d, *J* = 6.8 Hz, 3 H, CH_3).

^{13}C NMR: δ = 146.7 (s, C-4), 139.8 (s, C-6), 139.49 (s, C-14), 139.47 (s, C-11), 137.1 (s, C-3), 135.1 (d, C-8), 133.4 (d, C-12), 132.9 (d, C-13), 132.2 (d, C-16), 130.4 (d, C-7), 129.7 (d, C-15), 129.1 (d, C-5), 35.5 (t, C-10), 35.4 (t, C-9), 34.5 (t, C-1), 33.6 (t, C-2), 30.2 (d, CH), 25.6 (q, CH_3), 20.0 (q, CH_3).

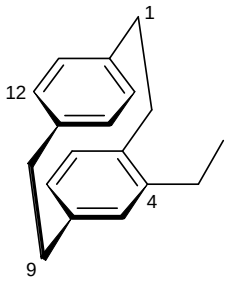


4

Compound 5 (protium isotopomer): 4-Ethyl[2.2]paracyclophane

^{1}H NMR: δ = 6.66 (dd, *J* = 7.8, 2.0 Hz, H-15), 6.51 (dd, *J* = 7.8, 2.0 Hz, H-12), 6.45 (dd, *J* = 7.8, 2.0 Hz, H-13), 6.42–6.37 (m, 2 H, H-7,8), 6.37 (dd, *J* = 7.8, 2.0 Hz, H-16), 6.13 (br. s, H-5), 3.33 (ddd, *J* = 13.5, 10.1, 2.0 Hz, H-2$_{syn}$), 3.14–2.89 (m, 6 H, H-1,9,10), 2.77 (ddd, *J* = 13.5, 10.7, 6.2 Hz, H-2$_{anti}$), 2.60 (dq, *J* = 14.8, 7.4 Hz, 1 H, CH_2), 2.30 (dq, *J* = 14.8, 7.4 Hz, 1 H, CH_2), 1.08 (t, *J* = 7.4 Hz, CH_3).

^{13}C NMR: δ = 143.3 (s, C-4), 139.8 (s, C-6), 139.4 (s, 2 C, C-11,14), 137.3 (s, C-3), 134.6 (d, C-8), 133.5 (d, C-5), 133.3 (d, C-12), 133.2 (d, C-13), 132.1 (d, C-16), 130.1 (d, C-7), 128.7 (d, C-15), 35.4 (t, C-10), 35.2 (t, C-9), 34.3 (t, C-1), 33.4 (t, C-2), 27.0 (t, CH_2), 14.3 (q, CH_3).

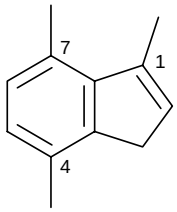


5

Compound 6 (protium isotopomer): 3,4,7-Trimethyl-1*H*-indene

^{1}H NMR: δ = 6.94 (d, *J* = 7.6 Hz, H-5), 6.88 (d, *J* = 7.6 Hz, H-6), 6.15 ("sext", "*J*" ≈ 1.7 Hz, H-2), 3.12 ("quint", "*J*" = 2.2 Hz, H-1), 2.56 (s, 4-CH_3), 2.34 (td, *J* = 2.3, 1.5 Hz, 3-CH_3), 2.29 (s, 7-CH_3). NOEs (irradiated signal → enhanced signal): 4-CH_3 → H-5; 3-CH_3 → H-2, 4-CH_3; 7-CH_3 → H-1, H-6.

^{13}C NMR: δ = 144.0 (s, C-7a), 142.9 (s, C-3a), 141.8 (s, C-3), 130.5 (s, C-7), 129.5 (d, C-2), 129.1 (d, C-5), 128.6 (s, C-4), 125.7 (d, C-6), 36.2 (t, C-1), 19.6 (q, 4-CH_3), 18.2 (q, 7-CH_3), 17.6 (q, 3-CH_3).

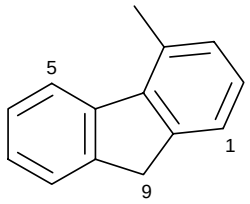


6

Compound 7 (protium isotopomer): 4-Methylfluorene

^{1}H NMR: δ = 7.91 (br. d, *J* = 7.7 Hz, H-5), 7.54 (br. d, *J* = 7.4 Hz, H-8), 7.40–7.35 (m, 2 H, H-1,6), 7.29 (td, *J* = 7.5, 1.1 Hz, H-7), 7.20 (t, *J* ≈ 7.4 Hz, H-2), 7.13 (br. d, *J* = 7.5 Hz, H-3), 3.88 (s, 2 H, H-9), 2.72 (s, 3 H, CH_3).

^{13}C NMR: δ = 143.7 (s, C-8a), 143.6 (s, C-9a), 142.7 (s, C-4b), 139.8 (s, C-4a), 133.1 (s, C-4), 129.0 (d, C-3), 126.6 (d, C-6), 126.4 (d, C-2), 126.0 (d, C-7), 124.9 (d, C-8), 123.1 (d, C-5), 122.5 (d, C-1), 37.1 (t, C-9), 21.1 (q, CH_3).

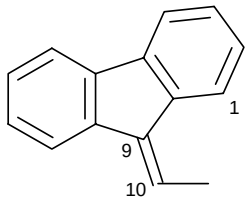


7

Compound 8 (protium isotopomer): 9-Ethylidenefluorene

^{1}H NMR: δ = 7.79 (br. d, *J* = 7.1 Hz, H-1), 7.67 (m, H-4), 7.62 (m, H-5), 7.54 (m, H-8), 7.28 (m, H-3), 7.24 (m, 2 H, H-2,6), 7.20 (m, H-7), 6.72 (q, *J* = 7.6 Hz, H-10), 2.26 (d, *J* = 7.6 Hz, 3 H, 10-CH_3). NOEs (irradiated → enhanced signals): 10-CH_3 → H-1, H-10; H-10 → H-8, 10-CH_3.

^{13}C NMR: δ = 140.7 (s, C-4a), 139.3 (s, C-8a), 138.5 (s, C-4b), 137.7 (s, C-9a), 136.5 (s, C-9), 127.5 (d, C-3), 127.3 (d, C-6), 126.81 (d, C-2), 126.79 (d, C-7), 125.0 (d, C-1), 124.8 (d, C-10), 119.74 (d, C-4), 119.58 (d, C-8), 129.4 (d, C-5), 15.2 (q, 10-CH_3).

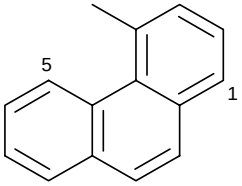


8

Compound 9 (protium isotopomer): 4-Methylphenanthrene

^{1}H NMR: δ = 8.95–8.91 (m, H-5), 7.94–7.90 (m, H-8), 7.79–7.75 (m, H-1), 7.72 (br. s, 2 H, H-9,10), 7.66–7.58 (m, 2 H, H-6,7), 7.52–7.47 (m, 2 H, H-2,3), 3.16 (s, 3 H, CH_3).

^{13}C NMR: δ = 135.6 (s, C-4), 133.8 (s, C-10a), 133.5 (s, C-8a), 131.7 (s, C-4b), 131.2 (d, C-3), 130.1 (s, C-4a), 128.7 (d, C-8), 128.0 (d, C-10), 127.6 (d, C-1), 127.5 (d, C-5), 127.1 (d, C-9), 125.9 (d, C-2), 125.8 (d, C-7), 125.6 (d, C-6), 27.4 (q, CH_3).

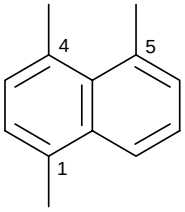


9

Compound 10 (protium isotopomer): 1,4,5-Trimethylnaphthalene

^{1}H NMR: δ = 7.82 (dd, *J* = 8.4, ≈0.7 Hz, H-8), 7.30 (dd, *J* = 8.4, 7.0 Hz, H-7), 7.23 (br. d, *J* = 7.0 Hz, H-6), 7.11 (br. s, 2 H, H-2,3), 2.89 (s, 5-CH_3), 2.85 (s, 4-CH_3), 2.60 (s, 1-CH_3).

^{13}C NMR: δ = 136.0 (s, C-5), 134.4 (s, C-8a), 133.6 (s, C-4), 133.2 (s, C-4a), 132.9 (s, C-1), 129.3 (d, C-6), 129.0 (d, C-3), 126.2 (d, C-2), 124.9 (d, C-7), 123.4 (d, C-8), 26.3 (q, 5-CH_3), 26.2 (q, 4-CH_3), 20.4 (q, 1-CH_3).



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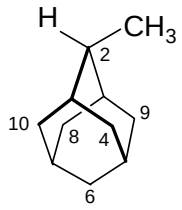
Compound 11 (protium isotopomer): 2-Methyladamantane

^{1}H NMR: δ = 1.93 (d, *J* = 12.4 Hz, 2 H, H-4$_{ax}$,9$_{ax}$), 1.85 (br., H-7), 1.84 (m, H-2), 1.82 (d, *J* = 12.4 Hz, 2 H, H-8,10), 1.77 (br. H-5), 1.74 (d, *J* = 12.4 Hz, 2 H, H-8,10), 1.71 (m, 2 H, H-6), 1.58 (m, 2 H, H-1,3), 1.48 (d, *J* = 12.4 Hz, 2 H, H-4$_{eq}$,9$_{eq}$), 1.03 (d, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR: δ = 39.4 (t, 2 C, C-8,10), 39.0 (d, C-2), 38.6 (t, C-6), 33.7 (d, 2 C, C-1,3), 31.3 (t, 2 C, C-4,9), 28.4, 28.1 (both d, C-5 and C-7), 18.9 (q, CH_3).



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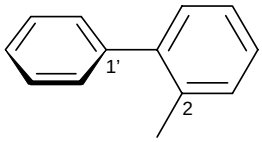
Compound 12 (protium isotopomer): 2-Methylbiphenyl

^{1}H NMR: δ = 7.41–7.37 (m, 2 H, H-3',5'), 7.33–7.28 (m, 3 H, H-2',4',6'), 7.26–7.21 (m, 4 H, H-3,4,5,6), 2.26 (s, 3 H, CH_3).

^{13}C NMR: δ = 141.99 (s, C-1'), 141.96 (s, C-1), 135.3 (s, C-2), 130.3 (d, C3), 129.8 (d, C-6), 129.2 (d, 2 C, C-2',6'), 128.1 (d, 2 C, C-3',5'), 127.3 (d, C-4), 126.8 (d, C-4'), 125.8 (d, C-5), 20.5 (q, CH_3).



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