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Arene–Perfluoroarene Interactions in Crystal Engineering 9: Structural Preferences in Polyfluorinated Tolans†

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Details of the spectroscopic characterisation of 4b-k:

Compound **4b**: R = Et. Yield: 0.225 g, 89%. m.p. 49–50°C. ^{1}H NMR (200 MHz): δ 1.44 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, O-CH_2-CH_3), 4.36 (q, $^{3}J_{HH}$ = 7.1 Hz, 2H O-CH_2-CH_3), 7.39 (m, 3H, ArH), 7.57 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.3 (m, 2F), -157.8 (m, 2F). ^{13}C-{^{1}H} NMR (100 MHz): δ 15.4 (*C*H_3), 71.1 (*C*H_2-O), 74.1 (*C*≡C), 98.1 (m, C_{Ar}-O), 100.2 (*C*≡C), 122.0 (C_{ipso} of phenyl ring), 128.5 (C_{Ar}-H) 129.1 (C_{Ar}-H), 131.8 (C_{Ar}-H), 138.3 (m, C_{ispo} of fluoroaryl ring), 141.1 (d of m, C_{Ar}-F, J_{CF} = 240 Hz), 147.3 (d of m, C_{Ar}-F J_{CF} = 250 Hz). MS (EI) m/z (relative intensity): 294 (M^+, 29), 266 (M^+-C_2H_4, 100). Elemental analysis calculated for $C_{16}H_{10}F_4O$: C 65.31, H 3.43; found: C 64.98, H 3.41.

Compound **4c**: R = ^{n}Pr. Yield: 0.243 g, 85%, m.p. 75–75.5°C. ^{1}H NMR (200 MHz): δ 1.05 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3-), 1.83 (apparent sext, $^{3}J_{HH}$ = 7.0 Hz, 2H, CH_2-), 4.25 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H, O-CH_2), 7.40 (m, 3H, ArH), 7.60 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.5 (m, 2F), -157.8 (m, 2F). ^{13}C-{^{1}H} NMR (63 MHz): δ 10.0, 23.2 (alkyl), 74.2 (*C*≡C), 77.1 (*C*H_2-O), 98.1 (m, C_{Ar}-O), 100.1 (*C*≡C), 122.0 (C_{ipso} of phenyl ring) 128.4 (C_{Ar}-H), 129.2 (C_{Ar}-H), 131.8 (C_{Ar}-H), 138.2 (m, C_{ipso} of fluoroaryl ring) 141.1 (d of m, C_{Ar}-F, J_{CF} = 250 Hz), 147.3 (d of m, C_{Ar}-F, J_{CF} = 260 Hz). MS (EI) m/z (relative intensity): 308 (M^+, 13), 266 (M^+-C_3H_6, 100). Elemental analysis calculated for $C_{17}H_{12}F_4O$: C 66.23, H 3.92; found: C 65.99, H 3.91.

Compound **4d,** R = ^{i}Pr. Yield: 0.211 g, 74%. m.p. 64.2–64.7°C. ^{1}H NMR (300 MHz): δ 1.32 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$), 4.54 (sep, $^{3}J_{HH}$ = 6.0 Hz, 1H, C*H*Me$_2$), 7.31 (m, 3H, ArH), 7.51 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.5 (m, 2F), -156.1 (m, 2F). (MS (EI) m/z : 308 (M^+, 5), 293 (M^+-Me, 2), 266 (M^+-C_3H_6, 100). Elemental analysis calculated for $C_{17}H_{12}F_4O$: C 66.23, H 3.92; found: C 66.08, H 3.82.

Compound **4e,** R = ^{n}Bu. Yield: 0.229 g, 76%. m.p. 31.2–32°C. ^{1}H NMR (200 MHz): δ 0.98 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_3-), 1.51 (apparent sext, $^{3}J_{HH}$ = 7.3 Hz, 2H, -CH_2-CH_3), 1.78 (apparent qn, $^{3}J_{HH}$ = 7.3 Hz, 2H, CH_2-CH_2-CH_3), 4.27 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, -OCH_2), 7.38 (m, 3H, ArH), 7.57 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.5 (m, 2F), -157.9 (m, 2F). ^{13}C-{^{1}H} NMR (63 MHz): δ 13.6, 18.7, 31.9 (alkyl), 74.2(*C*≡C), 75.2 (*C*H_2-O), 97.8 (m, C_{Ar}-O), 100.1 (*C*≡C), 122.0 (C_{ipso} of phenyl ring), 128.4 (C_{Ar}-H), 129.2 (C_{Ar}-H), 131.8 (C_{Ar}-H), 138.3 (m, C_{ispo} of fluoroaryl ring), 141.1 (d of m, C_{Ar}-F, J_{CF} = 248 Hz), 147.4 (d of m, C_{Ar}-F, J_{CF} = 254 Hz). MS (EI) m/z (relative intensity): 322 (M^+, 10), 266 (M^+ - C_4H_8, 100). Elemental analysis calculated for $C_{18}H_{14}F_4O$: C 67.08, H 4.38; found: C 66.79, H 4.42.

Compound **4f,** R = *n*-C_5H_{11}. Yield: 0.312 g, 68%. m.p. 27–27.5°C. ^{1}H NMR (200 MHz): δ 0.94 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3-), 1.41 (m, 4H, -CH_2-CH_3 and CH_2-CH_2-CH_3), 1.80 (m, 2H, CH_2-CH_2-CH_2-CH_3), 4.27 (t, $^3J_{HH}$ = 6.5 Hz, 2H, O-CH_2), 7.38 (m, 3H, ArH), 7.57 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.5 (m, 2F), -157.8 (m, 2F). ^{13}C-{^{1}H} NMR (63 MHz): δ 13.9, 22.7, 27.6, 29.6 (alkyl), 74.16 (*C*≡C), 75.46 (*C*H_2-O), 98.0 (m, C_{Ar}-O), 100.1 (*C*≡C), 122.0 (C_{ipso} of phenyl ring), 128.4 (C_{Ar}-H), 129.2 (C_{Ar}-H), 131.8 (C_{Ar}-H), 138.2 (m, C_{ispo} of fluoroaryl ring), 141.2 (d of m, C_{Ar}-F, J_{CF} = 248 Hz) 147.2 (d of m, C_{Ar}-F, J_{CF} = 263 Hz). MS (EI) m/z (relative intensity): 336 (M^+, 7), 266 (M^+ - C_5H_{10}, 100). Elemental analysis calculated for $C_{19}H_{16}F_4O$: C 67.85, H 4.79; found: C 68.05, H 4.89.

Compound **4g,** R = $PhCH_2$ (Bz). Gentle heat was applied (40°C water bath for 1.5 h) to drive the reaction to completion. Yield: 0.204 g, 61%. m.p. 126.5–128°C. ^{1}H NMR (200 MHz): δ 5.30 (s, 2H, -CH_2O), 7.37-7.42 (m, 8H, ArH), 7.56 (m, 2H, ArH). ^{19}F-{^{1}H} (188 MHz): δ -138.3 (m, 2F), -156.6 (m, 2F). ^{13}C-{^{1}H} NMR (63 MHz): δ 74.1 (CH_2-O), 77.2 (*C*≡C), 98.6 (m, C_{Ar}-O), 100.4 (*C*≡C), 121.9 (C_{ipso} of phenyl ring), 128.3 (C_{Ar}-H), 128.4 (C_{Ar}-H), 128.7 (C_{Ar}-H), 128.9 (C_{Ar}-H), 129.2 (C_{Ar}-H), 131.8 (C_{Ar}-H), 135.3 (C_{ipso} of phenyl ring), 137.2 (m, C_{ispo} of fluoroaryl ring), 141.3 (d of m, C_{Ar}-F, J_{CF} = 246 Hz), 147.1 (d of m, C_{Ar}-F, J_{CF} = 258 Hz). MS (EI) m/z (relative intensity): 356 (M^+, 3), 265 (M^+-CH_2Ph, 3), 91 ($PhCH_2^+$, 100). Elemental analysis calculated for $C_{21}H_{12}F_4O$: C 70.79, H 3.39; found: C 71.11, H 3.48.

Compound **4h,** R = $Ph(CH_2)_2$. Yield: 0.188 g, 55%. m.p. 72–73°C. ^{1}H NMR (200 MHz): δ 3.12 (t, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2Ph), 4.49 (t, $^3J_{HH}$ = 7.0 Hz, 2H, O-CH_2), 7.25 – 7.40 (m, 7H, Ar-H), 7.55 – 7.60 (m, 3H, Ar-H). ^{19}F-{^{1}H} NMR (188 MHz): δ -138.3 (m, 2F), -158.6 (m, 2F). ^{13}C-{^{1}H} NMR (63 MHz): δ 36.4 (*C*H_2-Ph), 74.0 (*C*≡C), 75.5 (*C*H_2-O), 98.1 (m, C_{Ar}-O), 100.2 (*C*≡C), 121.9 (C_{ipso} of phenyl ring), 126.8 (C_{Ar}-H), 128.4 (C_{Ar}-H), 128.6 (C_{Ar}-H), 128.9 (C_{Ar}-H), 129.3 (C_{Ar}-H), 131.8 (C_{Ar}-H), 137.0 (C_{ipso} of phenyl ring), 137.9 (m, C_{ipso} of fluoroaryl ring), 140.9 (d of m, C_{Ar}-F, J_{CF} = 258 Hz), 147.4 (d of m, C_{Ar}-F, J_{CF} = 264 Hz**)**. MS (EI) m/z (relative intensity): 370 (M^+, 100), 266 (M^+ - CH_2CHPh, 35), 105 ($PhCH_2CH_2^+$, 92). Elemental analysis calculated for $C_{22}H_{14}F_4O$: C 71.35, H 3.81; found: C 70.88, H 3.80.

Compound **4i,** R = 4-$CH_3C_6H_4$. Yield: 0.272 g, 82%. m.p. 85–86.5°C. ^{1}H NMR (200 MHz): δ 2.56 (s, 3H, Ph-CH_3), 6.82 (m, 2H, ArH), 7.56 (m, 2H, ArH), 7.50 – 7.55 (m, 5H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -137.3 (m, 2F), -154.9 (m, 2F). ^{13}C-{^{1}H} NMR (100 MHz): δ 20.6 (*C*H_3), 73.8 (*C*≡C), 100.8 (m, C_{Ar}-O), 101.2 (*C*≡C), 115.5 (C_{Ar}-H), 121.8 (C_{ipso} of phenyl ring), 128.5 (C_{Ar}-H), 129.5 (C_{Ar}-H), 130.2 (C_{Ar}-H), 131.9 (C_{Ar}-H), 133.5 (C_{Ar}-Me), 134.4 (m, C_{ipso} of fluoroaryl ring), 141.6 (d of m, C_{Ar}-F, J_{CF} = 250 Hz), 147.4 (d of m, C_{Ar}-F,

J_{CF} = 240 Hz**)**, 155.1 (C_{Ar}-O). MS (EI) m/z (relative intensity): 356 (M^+, 100), 265 (M^+ - C_6H_4Me, 21), 91 ($C_6H_4Me^+$, 80). Elemental analysis calculated for $C_{21}H_{12}F_4O$: C 70.79, H 3.39; found: C 70.68, H 3.67.

Compound **4j,** R = 4-EtC_6H_4. Yield: 0.276 g, 80%. m.p. 99.5-101 °C. ^{1}H NMR (200 MHz): δ 1.23 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2-CH_3), 2.63 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2-CH_3), 6.91 (m, 2H, ArH), 7.16 (m, 2H, ArH), 7.41 (m, 3H, ArH), 7.60 (m, 2H, ArH). ^{19}F-{^{1}H} NMR (188 MHz): δ -137.3 (m, 2F), -154.9 (m, 2F). ^{13}C-{^{1}H} NMR (100 MHz): δ 15.6, 28.0 (alkyl), 73.8 (*C*≡C), 100.7 (m, C_{Ar}-O), 101.3 (*C*≡C), 115.5 (C_{Ar}-H), 121.8 (C_{ipso} of phenyl ring), 128.5 (C_{Ar}-H), 129.1 (C_{Ar}-H), 129.5 (C_{Ar}-H), 131.9 (C_{Ar}-H), 134.4 (m, C_{ipso} of fluoroaryl ring), 139.4 (C_{Ar}-Et), 141.6 (d of m, C_{Ar}-F, J_{CF} = 240 Hz), 147.4 (d of m, C_{Ar}-F, J_{CF} = 240 Hz**)**, 155.2 (C_{Ar}-O). MS (EI) m/z (relative intensity): 370 (M^+, 82), 355 (M^+ - CH_3, 100), 265 (M^+ - PhEt and -H, 19). Elemental analysis calculated for $C_{22}H_{14}F_4O$: C 71.35, H 3.81; found: C 71.76, H 4.24.

Compound **4k***,* OR = (1R, 2S, 5R)-(-)-menthoxy: Initially obtained as colourless oil, which solidified over extended period of time. Yield: 0.287 g, 76%. m.p 48-49 ^{o}C. ^{1}H NMR (300 MHz): δ 0.86 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH(CH_3)$_2$), 0.91 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH(CH_3)$_2$), 0.97 (d, $^3J_{HH}$ = 4.8 Hz, 3H, CH_3), 1.06 (br d, J_{HH} = 12.8 Hz, 1H H_{ring}), 1.14 (br d, J_{HH} = 8.2 Hz, 1H, H_{ring}), 1.25 (br s, 1H, H_{ring}), 1.57 (br t, J_{HH} = 8.8 Hz, 1H, H_{ring}), 1.68 (br s, 1H, H_{ring}), 1.71 (br s, 1H, H_{ring}), 1.76 (apparent q, J_{HH} = 2.4 Hz, H_{ring}), 1.92 (br d, J_{HH} = 7.8 Hz, 1H, H_{ring}), 2.39 (apparent sept of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, C*H*(CH_3)$_2$), 4.20 (apparent t of d, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, CH-O), 7.38 (m, 3H, ArH), 7.58 (m, 2H, ArH) (assigned with the help of ref. 24) ^{19}F-{^{1}H} NMR (188 MHz): δ -138.7 (m, 2F), -156.3 (m, 2F). ^{13}C-{^{1}H} NMR (100 MHz): δ 15.9, 20.9, 22.0, 23.1, 25.7, 31.4, 34.1, 40.6, 48.4 (alkyl), 74.3 (*C*≡C), 84.6 (*C*H-O), 98.1 (m, C_{Ar}-O), 100.1 (*C*≡C), 122.0 (C_{ipso} of phenyl ring), 128.4 (C_{Ar}-H), 129.2 (C_{Ar}-H), 131.8 (C_{Ar}-H), 137.0 (m, C_{ipso} of fluoroaryl ring), 141.7 (d of m, C_{Ar}-F, J_{CF} = 240 Hz), 147.2 (d of m, C_{Ar}-F, J_{CF} = 260 Hz**)**, MS (EI) m/z (relative intensity): 404 (M^+, <1), 293 (M^+ - C_3H_7, 2) 266 (M^+ - $C_{10}H_{18}$, 100). Elemental analysis calculated for $C_{24}H_{24}F_4O$: C 71.27, H 5.98; found: C 71.51, H 6.16.

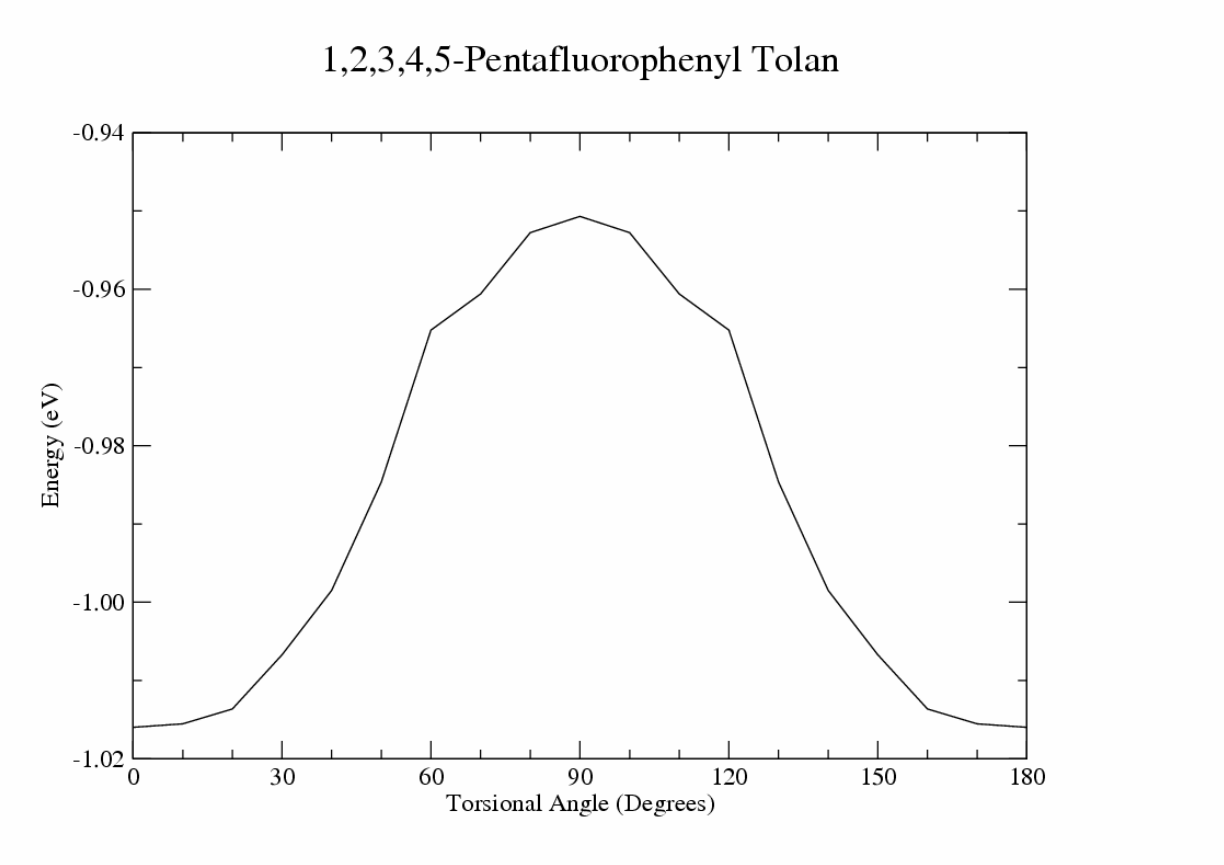

Figure S1: Energy as a function of inter-ring torsion angle in 1,2,3,4,5-pentafluoro tolan.

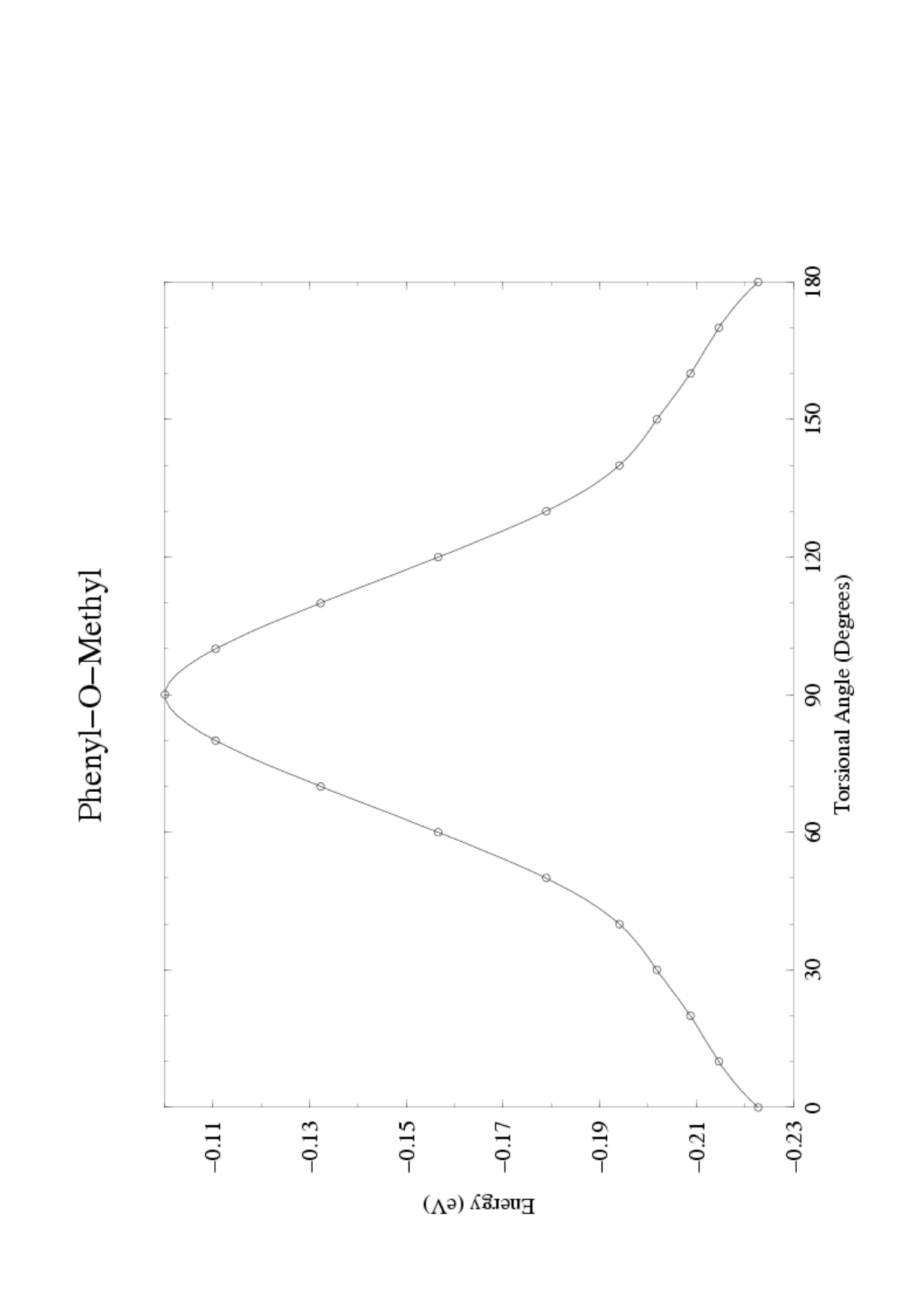

Figure S2: Energy as a function of C(Ph)-C(Ph)-O-C(Me) torsion angle in Ph-O-Me.