Supporting Information

Flash-vacuum-pyrolytic reorganization of angular [4]phenylene

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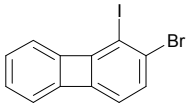
Spectral Data For New Compounds



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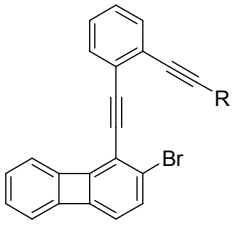
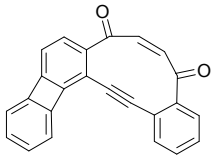
Pale yellow solid, m.p. 95–97 °C (CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (d, J = 7.2 Hz, 1 H), 6.88–6.80 (m, 3 H), 6.73–6.63 (m, 1 H), 6.45 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 150.9, 150.5, 148.5, 131.5, 129.8, 128.6, 127.5, 118.1, 117.9, 116.7, 87.7; MS (EI) *m/z* (%) 358 [(^{81}Br) M^+, 98], 356 [(^{79}Br) M^+, 100], 231 [(^{81}Br) M^+–I, 13], 229 [(^{79}Br) M^+–I, 13], 154, 150 [M^+–I–Br, 84]; HRMS (EI): calcd for $C_{12}H_6I^{79}Br$: 355.8698; found: 355.8696; UV/Vis (CH_3CN): λ_{max} (logε) = 263 (4.75), 336 (3.41), 352 (3.74), 368 (3.88); IR (KBr): $\tilde{\nu}$ = 3080, 1550, 1446, 1410, 1372, 1237, 1159, 808, 734 cm^{-1}.



R = $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2$

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60–7.50 (m, 2 H), 7.37–7.26 (m, 2 H), 7.05 (d, J = 7.6 Hz, 1 H), 6.87–6.82 (m, 1 H), 6.82–6.78 (m, 2 H), 6.71–6.67 (m, 1 H), 6.46 (d, J = 7.6 Hz, 1 H), 1.72 (hep, J = 6.8 Hz, 1 H), 0.94 (s, 6 H), 0.91 (d, J = 6.8 Hz, 6 H), 0.23 (s, 6 H).



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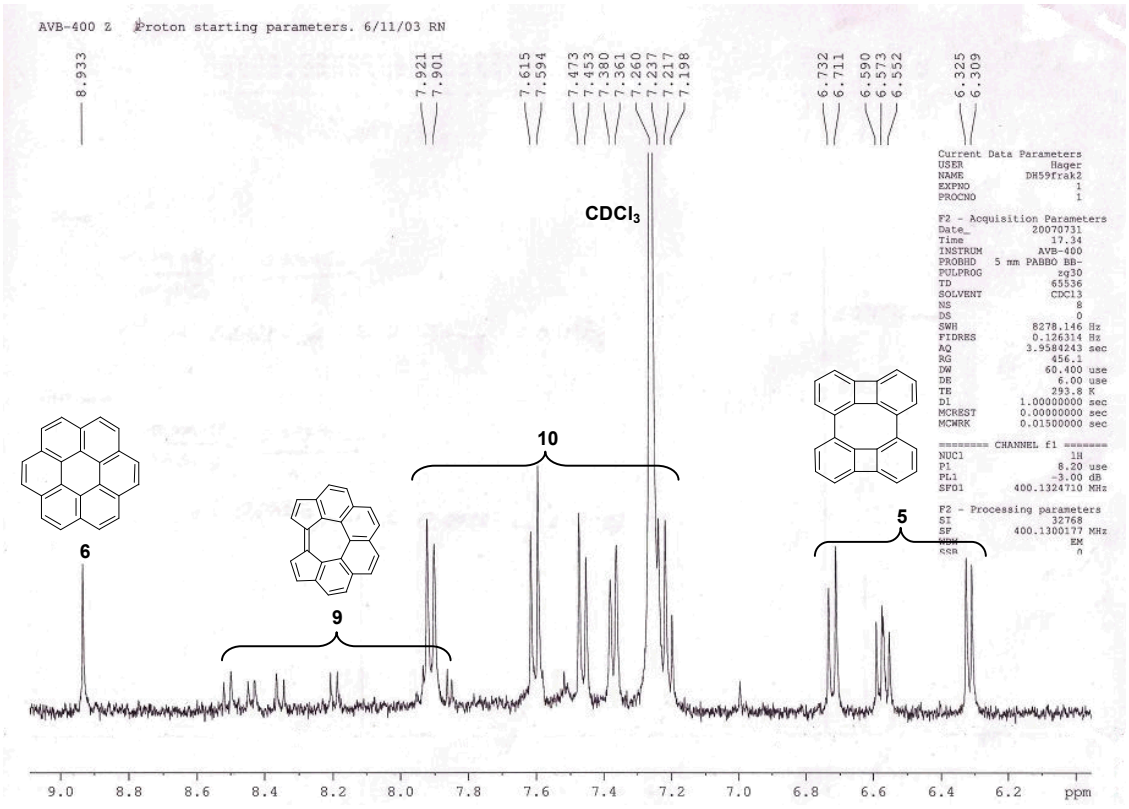
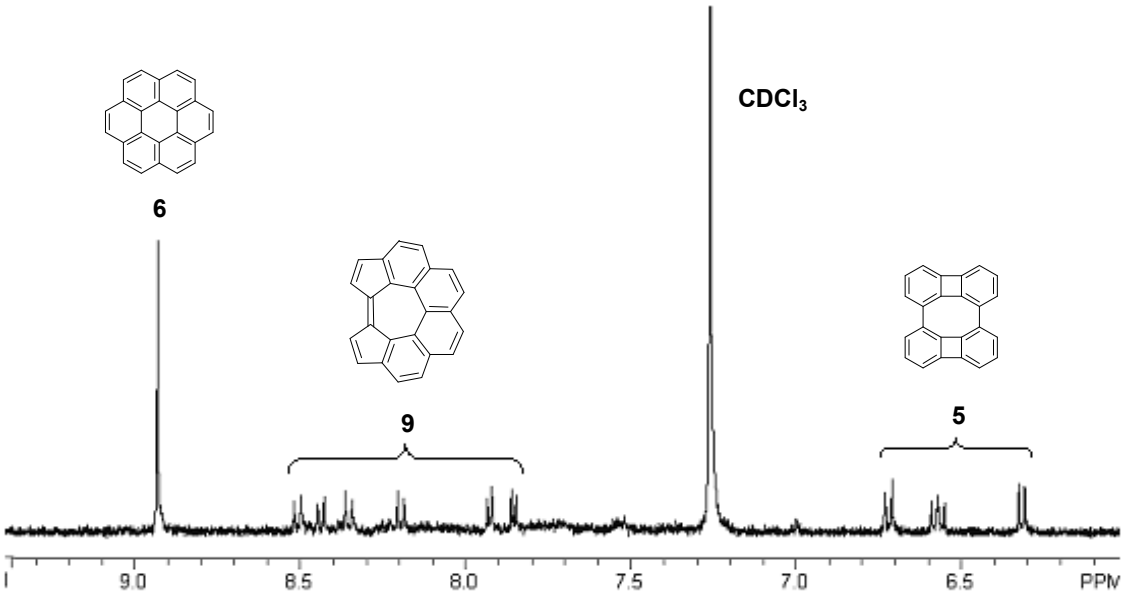
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.38 (m, 4 H), 7.01 (d, J = 7.2 Hz, 1 H), 6.96–6.84 (m, 3 H), 6.76 (d, J = 6.0 Hz, 1 H), 6.65 (d, J = 7.2 Hz, 1 H), 6.58 (s, 2 H); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.19 (dd, J = 2.5, 5.0 Hz, 1 H), 7.09 (dd, J = 2.5, 5.0 Hz, 1 H), 6.85–6.80 (m, 2 H), 6.76 (d, J = 7.5 Hz, 1 H), 6.68 (td, J = 1.0, 6.5 Hz, 1 H), 6.54–6.46 (m, 2 H), 6.34 (td, J = 1.0, 6.5 Hz, 1 H), 6.06 (d, J = 7.5 Hz, 1 H), 5.94 (AB quartet; simulated as 5.95 (d, J = 11.3 Hz, 1 H), 5.93 (d, J = 11.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 195.5, 154.2, 151.6, 149.5, 148.8, 142.7, 140.8, 136.6, 135.2, 131.0, 129.9, 129.8, 129.6, 129.4, 127.1 (2C), 120.4, 119.0, 118.8, 116.9, 109.3, 96.7, 93.3; ^{13}C NMR (125 MHz, C_6D_6): δ = 195.8, 194.6, 154.3, 152.1, 150.3, 149.6, 144.1, 142.1, 136.9, 135.4, 131.0, 130.2, 130.14, 130.05, 129.85, 129.83, 127.8, 121.1, 119.3, 119.1, 117.4, 110.5, 97.6, 94.1; MS (EI) *m/z* (%) 332 (M^+, 96), 304 [(M^+–CO), 100], 276 [(M^+–CO), 55]; HRMS (EI): calcd for $C_{24}H_{12}O_2$: 332.0837; found: 332.0837; UV/Vis (CH_3CN): λ_{max} (logε) = 299 (4.65), 336 (4.02), 403 (4.04); IR (KBr): $\tilde{\nu}$ = 2963, 1683, 1582, 1463, 1447, 1262, 1226, 1098, 1022, 801, 742 cm^{-1}.

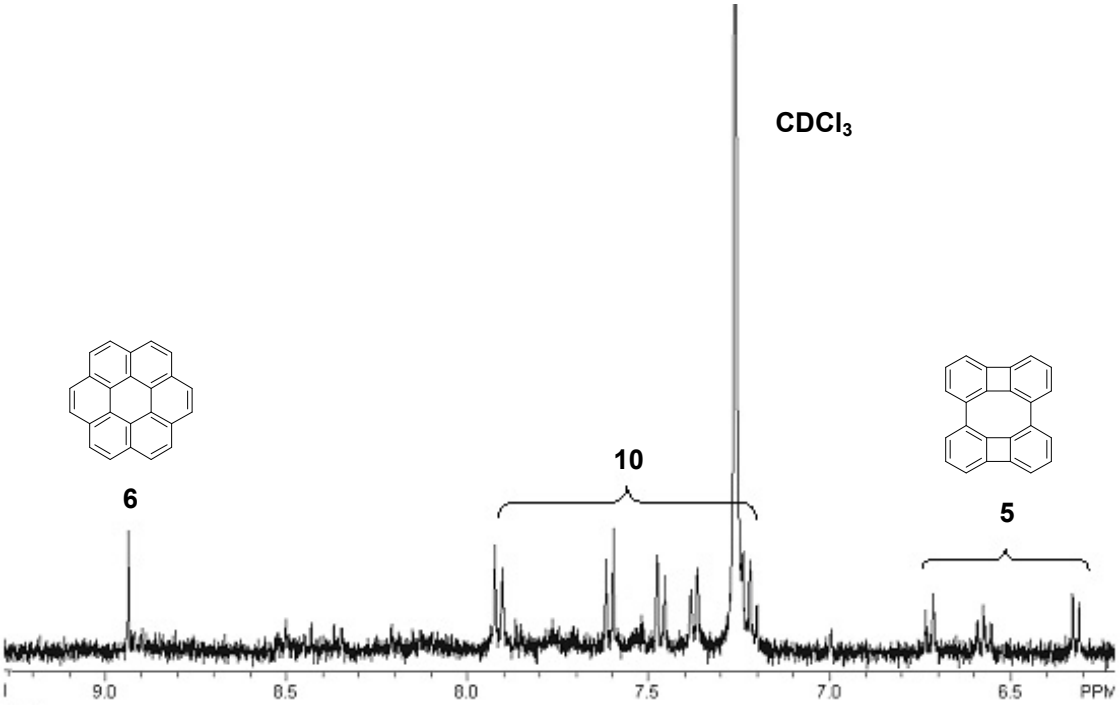
Selected ^{1}H NMR Spectra



^{1}H NMR (400 MHz, $CDCl_3$) of **9** and **10**, contaminated by residual **5** and **6**.



^{1}H NMR (400 MHz, $CDCl_3$) of proposed structure **9**, contaminated by residual **5** and **6**.



^{1}H NMR (400 MHz, $CDCl_3$) of unknown **10**, contaminated by residual **5** and **6**.

Computational Methods

Geometry optimizations and vibrational analyses were performed with B3LYP/6-31G*. Single point energies were then computed at the B3PW91/6-311+G** level. Structures were verified as minima by virtue of having zero imaginary vibrational frequencies. For purposes of computing NMR chemical shifts and coupling constants, geometries were optimized using BHandHLYP (BHLYP) and the 6-31G* basis set. Magnetic shieldings were determined at these geometries at the GIAO-B3LYP/6-311+G** level and compared with corresponding shieldings for tetramethylsilane to obtain proton chemical shifts. All calculations were performed with Gaussian 03.*

*Gaussian 03, Revision D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT, 2004.

Table S1. Absolute Energies and Zero Point Energies for Stationary Points

		B3LYP/6-31G*			B3PW91/6-311+G** //B3LYP/6-31G*
species	sym	E (au)	NIMAG	ZPE (kcal/mol)	E (au)
4	C_{2v}	–921.60746	0	172.16	–921.45252
5	D_{2d}	–921.68091	0	173.33	–921.52379
6	D_{6h}	–921.89789	0	175.91	–921.73749
7	C_s	–921.80102	0	175.17	–921.64588
9	C_{2v}	–921.80626	0	174.55	–921.64815
A	C_1	–921.62078	0	172.27	–921.46791
B	C_s	–921.66333	0	172.69	–921.50914
C	C_s	–921.68997	0	173.32	–921.53470
D	C_s	–921.69269	0	173.24	–921.53759
E	C_s	–921.74442	0	174.06	–921.58787
F	C_s	–921.75406	0	174.26	–921.59729
G	C_1	–921.68272	0	173.22	–921.52709
H	C_2	–921.69543	0	173.18	–921.54107
I	C_1	–921.66935	0	172.06	–921.51531
J	D_{2d}	–921.73261	0	173.36	–921.57731