Supporting Information

Shorter Still: Compressing C—C Single Bonds

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Group A

1 $C_{20}H_{18}$

2 C_8H_6

3 $C_{16}H_{14}$

4 $C_{23}H_{30}$

5 $C_{20}H_{24}$

6 $C_{17}H_{18}$

7 $\text{C}_{14}\text{H}_{12}$

8 $\text{C}_{20}\text{H}_{18_2}$

9 $\text{C}_{23}\text{H}_{12}$

10 $\text{C}_{12}\text{H}_{10}$

11 $\text{C}_{11}\text{H}_{12}$

12 $\text{C}_{17}\text{H}_{18_2}$

13 C₈F₆

14 C₁₇F₁₉

15 C₈Si₆H₁₂

16 C₁₉H₁₄

17 C₁₆B₃H₁₁

18 C₁₆N₃H₁₁

19 C₁₆O₃H₈

20 C₁₆S₂H₈

Group B

21 C_2H_6

22 C_4H_{10}

23 C_8H_{14}

24 $\text{C}_{10}\text{H}_{18}$

25 $\text{C}_{12}\text{H}_{22}$

26 $\text{C}_{10}\text{H}_{10}$

27 C_6H_{10}

28 C_6H_6

29 C₄H₆

30 C₄H₂

31 C₁₂H₁₀

Figure 1: Structures of the systems included in groups A and B.

Table S.1: Bond lengths, and bond orders for the short bonds in Group A, plus the orbital compositions and bond angle data employed in the main text. The symbols used in the graphs are included.*

	Molecules	Symbol*	Bond Length	Bond Order	%s Composition	Angle
1	C ₂₀ H ₁₈	◇	1.350	0.98	27.8	110.7
2	C ₈ H ₆	o	1.426	1.04	41.2	144.8
3	C ₁₆ H ₁₄	o	1.475	1.02	35.2	125.8
4	C ₂₃ H ₃₀	*	1.421	1.02	40.5	144.1
5	C ₂₀ H ₂₄	*	1.397	1.02	40.6	143.2
6	C ₁₇ H ₁₈	*	1.360	0.98	39.8	140.8
7	C ₁₄ H ₁₂	*	1.313	0.95	38.4	136.3
8	C ₂₀ H ₁₈ (2)	*	1.345	0.95	38.6	138.6
9	C ₂₃ H ₁₂	*	1.330	0.96	39.2	139.0
10	C ₁₂ H ₁₀	o	1.456	1.03	37.0	129.4
11	C ₁₁ H ₁₂	△	1.440	0.88	18.4	79.4
12	C ₁₇ H ₁₈ (2)	◇	1.366	0.95	30.9	114.8
13	C ₈ F ₆	o	1.415	1.07	43.6	145.8
14	C ₁₇ F ₁₈	◇	1.377	0.94	31.0	115.0
15	C ₈ Si ₆ H ₁₂	*	1.370	1.03	41.3	142.7
16	C ₁₉ H ₁₄	◇	1.366	0.95	32.3	114.3
17	C ₁₆ B ₃ H ₁₁	◇	1.387	0.95	32.5	115.2
18	C ₁₆ N ₃ H ₁₁	◇	1.358	0.95	31.5	112.5
19	C ₁₆ S ₃ H ₈	◇	1.384	0.97	33.0	117.9
20	C ₁₆ O ₃ H ₈	◇	1.341	0.94	30.3	111.8

* See Tables in the main text. The symbols indicate the basic structural motif of the molecules: The simple bipolyhedryl systems (o), the backstrapped bitetrahedryl (*) and bicubyl or (open/truncated) bicubyl derived (◇) systems, and a low symmetry adamantane type structure (△). The ordering in the table follows the ordering of the structures in Table S.1.

Table S.2: Computed bond lengths obtained at the B3LYP and MP2(full) levels for the short C-C bonds in structures 1 and 4, two of the most competitive structures, in group A.

	6-311G	6-311++G**	cc-pVTZ	cc-pVQZ
B3LYP				
(1) C ₂₀ H ₁₈	1.350	1.351	1.345	1.347
(4) C ₁₄ H ₁₂	1.313	1.314	1.310	1.309
MP2(full)				
(1) C ₂₀ H ₁₈	1.346	1.347	1.338	
(4) C ₁₄ H ₁₂	1.297	1.298	1.286

Figure S.2: Representations of the main types of molecular orbitals of the bitetrahedryl $C_{14}H_{12}$ system (7) that control the bonding in the short C-C bond.

Table S.3: Overlap populations and the reduced overlap population (ROP) (in *electron* units) for four bitetrahedryl based structures (4 - 7) with very short C(1)-C(2) bonds. Ethane is included for comparison.

C_2H_6 (Ethane; Structure 21)				
$C(1)$	$C(2)$			
	$2s$	$2p_x$	$2p_y$	$2p_z$
$2s$	0.08	0.00	0.00	0.15
$2p_x$	0.00	0.00	0.00	0.00
$2p_y$	0.00	0.00	0.00	0.00
$2p_z$	0.15	0.00	0.00	0.37
Overall ROP	0.75			
$C_{23}H_{30}$ (Structure 4)				
$C(1)$	$C(2)$			
	$2s$	$2p_x$	$2p_y$	$2p_z$
$2s$	0.18	0.00	0.00	0.20
$2p_x$	0.00	0.04	0.00	0.00
$2p_y$	0.00	0.00	0.04	0.00
$2p_z$	0.20	0.00	0.00	0.24
Overall ROP	0.90			
$C_{20}H_{24}$ (Structure 5)				
$C(1)$	$C(2)$			
	$2s$	$2p_x$	$2p_y$	$2p_z$
$2s$	0.19	0.00	0.00	0.20
$2p_x$	0.00	0.05	0.00	0.00
$2p_y$	0.00	0.00	0.05	0.00
$2p_z$	0.20	0.00	0.00	0.25
Overall ROP	0.93			
$C_{17}H_{18}$ (Structure 6)				
$C(1)$	$C(2)$			
	$2s$	$2p_x$	$2p_y$	$2p_z$
$2s$	0.19	0.00	0.00	0.20
$2p_x$	0.00	0.06	0.00	0.00
$2p_y$	0.00	0.00	0.06	0.00
$2p_z$	0.20	0.00	0.00	0.26
Overall ROP	0.98			

$C_{14}H_{12}$ (Structure 7)				
$C(1)$	$C(2)$			
	$2s$	$2p_x$	$2p_y$	$2p_z$
$2s$	0.20	0.0	0.0	0.21
$2p_x$	0.0	0.08	0.0	0.0
$2p_y$	0.0	0.0	0.08	0.0
$2p_z$	0.21	0.0	0.0	0.28
Overall ROP	1.06			