Strikingly Long C···C Distances in 1,2-Disubstituted *ortho*-Carboranes and Their Dianions

Josep M. Oliva[a,b,*], Neil L. Allan[a], Paul v. R. Schleyer[c,*], Francesc Teixidor[d,*], and Clara Viñas[d]

[a]*School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*

[b]*Instituto de Química-Física "Rocasolano", CSIC, E-28006 Madrid, Spain*

(corresponding author: J.M.Oliva@iqfr.csic.es)

[c]*Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602 and Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany*

[d]*Institut de Ciència de Materials de Barcelona, CSIC, Campus de Bellaterra, Cerdanyola, E-08193 Barcelona, Spain*

SUPPLEMENTARY INFORMATION (SI)

All the calculations were performed with the program Gaussian98 [23].

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98* (Gaussian, Inc., Pittsburgh, PA, 1998).

B3LYP/6-31G* CALCULATIONS

Table S1. $C_c\cdots C_c$, C_c-B and B-B distances for 12-vertex icosahedral *o*-carboranes 1,2-R_2-1,2-$C_2B_{10}H_{10}$ and distance differences $\Delta d(R) = d(R) - d(H)$, as compared to original compound 1,2-$C_2B_{10}H_{12}$ in the substituted icosahedral *o*-carboranes. The notation d(R) means any of $C_c\cdots C_c$, C_c-B or B-B distances in 1,2-R_2-1,2-$C_2B_{10}H_{10}$; d(H) refers to the $C_c\cdots C_c$, C_c-B or B-B distances in the parent compound 1,2-$C_2B_{10}H_{12}$ – second column in Table S1. All distances in Ångstrom. B3LYP/6-31G* calculations.

Distance	d(H)	$\Delta d(CH_3)$	$\Delta d(NH_2)$	$\Delta d(OH)$	$\Delta d(F)$	$\Delta d(SiH_3)$	$\Delta d(PH_2)$	$\Delta d(SH)$	$\Delta d(Cl)$
C_1-C_2	1.624	0.039	0.236	0.142	0.039	0.053	0.065	0.179	0.068
C_1-B_3	1.720	0.006	-0.001	0.002	0.006	0.007	0.010	-0.002	0.014
C_1-B_4	1.699	0.014	0.015	-0.012	-0.008	0.012	0.012	-0.005	0.004
C_1-B_5	1.699	0.014	0.015	-0.006	-0.008	0.017	0.014	-0.005	0.004
C_1-B_6	1.720	0.006	-0.001	-0.010	0.006	0.004	-0.003	0.004	0.014
B_3-B_4	1.780	-0.011	-0.014	0.008	-0.001	0.000	0.001	0.016	0.005
B_3-B_7	1.780	-0.010	-0.015	0.004	-0.001	-0.003	0.000	0.015	0.005
B_3-B_8	1.764	-0.003	0.007	0.000	-0.007	0.007	0.006	0.012	0.000
B_4-B_5	1.785	-0.008	-0.005	-0.001	0.011	-0.009	-0.008	-0.005	0.005
B_4-B_8	1.781	-0.004	-0.005	-0.002	0.001	-0.005	-0.005	-0.007	-0.003
B_4-B_9	1.778	-0.002	0.000	-0.001	-0.001	0.001	-0.002	-0.001	-0.002
B_5-B_9	1.778	-0.002	0.000	-0.001	-0.001	-0.003	-0.003	-0.002	-0.002
B_5-B_{10}	1.781	-0.004	-0.005	-0.003	0.001	-0.006	-0.006	-0.006	-0.003
B_8-B_9	1.793	-0.004	0.000	0.000	-0.002	-0.002	-0.002	-0.001	-0.003
B_8-B_{12}	1.793	-0.004	0.001	-0.001	-0.002	-0.001	-0.003	-0.001	-0.003
B_9-B_{12}	1.784	-0.001	-0.013	-0.007	0.000	-0.005	-0.005	-0.013	-0.004

Table S2. $C_c \cdots C_c$, C_c-B and B-B distance differences $\Delta d(R^-) = d(R^-) - d(H)$, for dianions of 12-vertex icosahedral *o*-carboranes 1,2-$(R^-)_2$-1,2-$C_2B_{10}H_{10}$ as compared to the original neutral compound 1,2-$C_2B_{10}H_{12}$. The notation $d(R^-)$ means any of $C_c \cdots C_c$, C_c-B or B-B distances in 1,2-$(R^-)_2$-1,2-$C_2B_{10}H_{10}$; d(H) and $d(e^-)$ refers respectively to the $C_c \cdots C_c$, C_c-B or B-B distances in the parent neutral compound 1,2-$C_2B_{10}H_{12}$ and dianion thereof by proton removal on the C_c's $(1,2\text{-}C_2B_{10}H_{10})^{2-}$. All distances in Ångstrom. B3LYP/6-31G* calculations.

Distance	$\Delta d(e^-)$	$\Delta d(CH_2^-)$	$\Delta d(NH^-)$	$\Delta d(O^-)$	$\Delta d(SiH_2^-)$	$\Delta d(PH^-)$	$\Delta d(S^-)$
C_1-C_2	0.199	1.014	0.849	0.500	0.416	0.706	0.572
C_1-B_3	-0.039	0.715	0.500	0.069	0.003	0.027	0.038
C_1-B_4	0.013	-0.018	0.020	0.006	-0.022	-0.047	-0.031
C_1-B_5	0.013	0.001	-0.012	0.006	-0.022	-0.043	-0.031
C_1-B_6	-0.039	-0.138	-0.110	0.069	0.003	0.014	0.036
B_3-B_4	0.007	0.111	0.042	0.004	0.027	0.065	0.027
B_3-B_7	0.007	0.026	0.077	0.004	0.027	0.063	0.027
B_3-B_8	0.075	-0.013	0.006	0.013	0.055	0.056	0.042
B_4-B_5	-0.046	0.051	0.018	0.006	-0.019	-0.004	0.003
B_4-B_8	-0.010	0.060	-0.042	-0.011	-0.015	-0.010	-0.013
B_4-B_9	0.011	0.073	-0.046	0.003	0.004	0.003	0.005
B_5-B_9	0.011	-0.053	0.047	0.003	0.004	0.000	0.005
B_5-B_{10}	-0.010	-0.033	0.036	-0.011	-0.015	-0.013	-0.014
B_8-B_9	-0.001	-0.013	0.009	-0.004	-0.004	0.002	-0.007
B_8-B_{12}	-0.001	0.005	-0.007	-0.004	-0.004	0.003	-0.007
B_9-B_{12}	-0.012	0.001	-0.009	-0.007	-0.021	-0.021	-0.016

Table S3. $C_c\cdots C_c$, C_c-B and B-B distances for 6-vertex octahedral *o*-carboranes 1,2-R_2-1,2-$C_2B_4H_4$ and distance differences $\Delta d(R) = d(R) - d(H)$, as compared to original compound 1,2-$C_2B_4H_6$ in the substituted octahedral *o*-carboranes. The notation d(R) means any of $C_c\cdots C_c$, C_c-B or B-B distances in 1,2-R_2-1,2-$C_2B_4H_4$; d(H) refers to the $C_c\cdots C_c$, C_c-B or B-B distances in the parent compound 1,2-$C_2B_4H_6$ – second column in Table S3. All distances in Ångstrom. B3LYP/6-31G* calculations.

Distance	d(H)	$\Delta d(CH_3)$	$\Delta d(NH_2)$	$\Delta d(OH)$	$\Delta d(F)$	$\Delta d(SiH_3)$	$\Delta d(PH_2)$	$\Delta d(SH)$	$\Delta d(Cl)$
C_1-C_2	1.544	0.007	0.122	0.066	0.000	0.029	0.051	0.070	0.007
C_1-B_3	1.620	0.006	-0.018	-0.009	0.011	0.004	-0.003	-0.005	0.011
C_1-B_4	1.630	0.006	0.010	-0.004	-0.020	0.020	0.010	0.008	-0.006
C_1-B_5	1.620	0.006	-0.018	-0.005	0.011	0.008	-0.003	-0.009	0.011
B_3-B_4	1.734	-0.013	0.018	0.004	-0.003	-0.002	0.005	0.014	-0.001
B_3-B_6	1.734	-0.013	0.018	0.009	-0.003	-0.003	0.005	0.010	-0.001
B_4-B_6	1.707	0.003	0.045	-0.020	0.007	-0.010	-0.018	-0.028	0.000

Table S4. $C_c\cdots C_c$, C_c-B and B-B distance differences $\Delta d(R^-) = d(R^-) - d(H)$, for dianions of 6-vertex octahedral *o*-carboranes 1,2-$(R^-)_2$-1,2-$C_2B_4H_4$ as compared to the original neutral compound 1,2-$C_2B_4H_6$. The notation $d(R^-)$ means any of $C_c\cdots C_c$, C_c-B or B-B distances in 1,2-$(R^-)_2$-1,2-$C_2B_4H_4$; d(H) and $d(e^-)$ refers respectively to the $C_c\cdots C_c$, C_c-B or B-B distances in the parent neutral compound 1,2-$C_2B_4H_6$ and dianion thereof by proton removal on the C_c's $(1,2\text{-}C_2B_4H_4)^{2-}$. All distances in Ångstrom. B3LYP/6-31G* calculations.

Distance	$\Delta d(e^-)$	$\Delta d(CH_2^-)$	$\Delta d(NH^-)$	$\Delta d(O^-)$	$\Delta d(SiH_2^-)$	$\Delta d(PH^-)$	$\Delta d(S^-)$
C_1-C_2	0.245	0.639	1.555	0.326	0.082	0.490	0.150
C_1-B_3	-0.008	0.004	1.072	0.041	0.005	0.005	0.010
C_1-B_4	0.057	0.038	-0.004	0.037	0.020	0.002	0.013
C_1-B_5	-0.008	0.004	-0.102	0.041	-0.004	-0.009	0.010
B_3-B_4	0.016	0.081	-0.046	0.003	-0.007	0.048	-0.009
B_3-B_6	0.016	0.081	0.137	0.003	-0.014	0.053	-0.009
B_4-B_6	-0.037	-0.114	0.162	-0.036	-0.013	-0.082	-0.017

MP2/6-31G* CALCULATIONS

Table S5. $C_c\cdots C_c$ distances (Å), and topological properties of the density at bond-critical points: $\rho(\boldsymbol{r}_c)$ ($e\cdot$Å^{-3}) and the Laplacian of the density $L(\mathbf{r}_c) = -\nabla^2\rho(\boldsymbol{r}_c)$ ($e\cdot$Å^{-5}). These were determined at the MP2/6-31G* optimised geometries of icosahedral 1,2-R_2-1,2-$C_2B_{10}H_{10}$ and octahedral 1,2-R_2-1,2-$C_2B_4H_4$ *o*-carboranes (R = {H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl}). Results for ethane, ethylene, *cis*-*n*-butane, *cis*-1,2-diaminoethane and *cis*-1,2-diaminoethene are included for comparison purposes.

Molecule	$C_c\cdots C_c$	$\rho(\boldsymbol{r}_c)$	$L(\boldsymbol{r}_c)$
Ethane	1.526	1.71	16.04
Ethylene	1.337	2.36	26.41
cis-*n*-butane	1.530	1.73	16.29
cis-1,2-diaminoethane	1.523	1.78	17.62
cis-1,2-diaminoethene	1.344	2.36	26.65
Icosahedral			
1,2-$C_2B_{10}H_{12}$	1.620	1.30	6.22
1,2-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$	1.648	1.25	5.36
1,2-$(NH_2)_2$-1,2-$C_2B_{10}H_{10}$	1.775	1.00	2.00
1,2-$(OH)_2$-1,2-$C_2B_{10}H_{10}$	1.726	1.10	3.51
1,2-F_2-1,2-$C_2B_{10}H_{10}$	1.652	1.28	6.31
1,2-$(SiH_3)_2$-1,2-$C_2B_{10}H_{10}$	1.658	1.19	4.41
1,2-$(PH_2)_2$-1,2-$C_2B_{10}H_{10}$	1.668	1.19	4.44
1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$	1.743	1.04	2.46
1,2-Cl_2-1,2-$C_2B_{10}H_{10}$	1.673	1.20	4.78
Octahedral	$C_c\cdots C_c$	$\rho(\boldsymbol{r}_c)$	$L(\boldsymbol{r}_c)$
1,2-$C_2B_4H_6$	1.535	1.53	8.23
1,2-$(CH_3)_2$-1,2-$C_2B_4H_4$	1.537	1.54	8.40
1,2-$(NH_2)_2$-1,2-$C_2B_4H_4$	1.620	1.33	4.84
1,2-$(OH)_2$-1,2-$C_2B_4H_4$	1.588	1.42	6.62
1,2-F_2-1,2-$C_2B_4H_4$	1.532	1.60	9.97
1,2-$(SiH_3)_2$-1,2-$C_2B_4H_4$	1.561	1.44	6.53
1,2-$(PH_2)_2$-1,2-$C_2B_4H_4$	1.579	1.41	6.13
1,2-$(SH)_2$-1,2-$C_2B_4H_4$	1.588	1.39	5.79
1,2-Cl_2-1,2-$C_2B_4H_4$	1.538	1.54	8.60

Table S6. $C_c\cdots C_c$ distances (Å), and topological properties of the density at bond-critical points: $\rho(\boldsymbol{r}_c)$ (e/Å^{-3}) and the Laplacian of the density $L(\mathbf{r}_c) = -\nabla^2\rho(\boldsymbol{r}_c)$ (e/Å^{-5}). These were determined at the MP2/6-31G* optimised geometries of icosahedral 1,2-(R^-)-1,2-$C_2B_{10}H_{10}$ and octahedral 1,2-(R^-)-1,2-$C_2B_4H_4$ dianions of *o*-carboranes (R^- = {e^-, CH_2^-, NH^-, O^-, SiH_2^-, PH^-, S^-}). The dianions obtained by proton removal of ending groups in *cis*-*n*-butane, *cis*-1,2-diaminoethane and *cis*-1,2-diaminoethene are included for comparison purposes.

Dianions	$C_c\cdots C_c$ (Å)	$\rho(\boldsymbol{r}_c)$	$L(\boldsymbol{r}_c)$
(*cis*-*n*-butane – $2H^+$)$^{2-}$	1.597	1.54	13.25
(*cis*-1,2-diaminoethane – $2H^+$)$^{2-}$	1.615	1.52	13.09
(*cis*-1,2-diaminoethene – $2H^+$)$^{2-}$	1.395	2.11	20.55
Icosahedral dianions			
(1,2-$C_2B_{10}H_{10}$)$^{2-}$	1.807	0.89	0.22
1,2-(CH_2^-)$_2$-1,2-$C_2B_{10}H_{10}$	2.515[a]	0.26	-2.70
1,2-(NH^-)$_2$-1,2-$C_2B_{10}H_{10}$	2.250[a]	0.46	-2.86
1,2-(O^-)$_2$-1,2-$C_2B_{10}H_{10}$	2.072[a]	0.59	-1.86
1,2-(SiH_2^-)$_2$-1,2-$C_2B_{10}H_{10}$	1.789	0.93	1.06
1,2-(PH^-)$_2$-1,2-$C_2B_{10}H_{10}$	2.311[a]	0.48	-3.31
1,2-(S^-)$_2$-1,2-$C_2B_{10}H_{10}$	2.104[a]	0.57	-2.27
Octahedral dianions	$C_c\cdots C_c$ (Å)	$\rho(\boldsymbol{r}_c)$	$L(\boldsymbol{r}_c)$
(1,2-$C_2B_4H_6$)$^{2-}$	1.748	1.04	0.55
1,2-(CH_2^-)$_2$-1,2-$C_2B_4H_4$	2.206[a]	0.54	-4.77
1,2-(NH^-)$_2$-1,2-$C_2B_4H_4$	2.106[a]	0.58	-4.53
1,2-(O^-)$_2$-1,2-$C_2B_4H_4$	1.799	0.93	-0.12
1,2-(SiH_2^-)$_2$-1,2-$C_2B_4H_4$	1.600	1.35	5.13
1,2-(PH^-)$_2$-1,2-$C_2B_4H_4$	1.961[a]	0.73	-3.21
1,2-(S^-)$_2$-1,2-$C_2B_4H_4$	1.640	1.25	3.91

[a] Ring critical point (3, +1).