Transmission of Electronic Substituent Effects across the 1,12-Dicarba-*closo*-dodecaborane Cage: A Computational Study Based on Structural Variation, Atomic Charges, and ^{13}C NMR Chemical Shifts

Anna Rita Campanelli

Department of Chemistry, Sapienza – University of Rome, 00185 Rome, Italy

Aldo Domenicano

Department of Physical and Chemical Sciences, University of L'Aquila, 67100 L'Aquila, Italy

Drahomír Hnyk

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Husinec-Řež, Czech Republic

SUPPORTING INFORMATION

Table S1 Selected internal coordinates of the benzene ring and C–Ph bond distances in 12-substituted 1-phenyl-1,12-dicarba-*closo*-dodecaborane derivatives (**1**), from B3LYP/6-311++G** calculations[a,b,c]

Substituent	α	β	γ	δ	*a*	*r*(C–Ph)
H	118.31_2	120.82_9	120.37_5	119.28_0	1.3998	1.5165
Li	118.18_3	120.91_3	120.39_3	119.20_6	1.3999	1.5162
BH_2	118.32_7	120.82_2	120.36_5	119.30_1	1.4000	1.5155
BH_3^-	117.83_1	121.12_2	120.44_6	119.03_4	1.4009	1.5134
CH_2^+	118.62_7	120.55_4	120.18_3	119.89_9	1.4103	1.4969
CH_2^-	117.49_3	121.23_9	120.62_8	118.77_4	1.4047	1.5026
Me	118.31_8	120.82_9	120.37_5	119.27_3	1.3997	1.5160
CF_3	118.41_9	120.76_7	120.36_3	119.32_0	1.3997	1.5159
Ph	118.31_8	120.82_6	120.37_6	119.27_9	1.3999	1.5155
CHO	118.38_0	120.78_9	120.36_3	119.31_5	1.3999	1.5160
COMe	118.35_5	120.80_4	120.36_7	119.30_2	1.3998	1.5158
COCl	118.39_1	120.77_9	120.36_4	119.32_5	1.3999	1.5158
COO^-	117.90_3	121.08_0	120.43_1	119.07_6	1.4006	1.5144
COOH	118.36_9	120.79_6	120.36_6	119.30_6	1.3998	1.5158
COOMe	118.33_8	120.81_2	120.37_2	119.29_4	1.3999	1.5159
CCH	118.36_4	120.80_1	120.36_8	119.29_9	1.3998	1.5155
CN	118.43_6	120.75_4	120.36_1	119.33_4	1.3997	1.5157
NH^-	117.61_2	121.21_4	120.53_1	118.89_7	1.4026	1.5076
NH_2	118.29_1	120.84_6	120.37_1	119.27_7	1.3999	1.5158
NMe_2	118.28_6	120.84_8	120.37_2	119.27_4	1.3999	1.5154
NF_2	118.41_3	120.76_9	120.36_2	119.32_5	1.3997	1.5160
NH_3^+	118.81_6	120.51_1	120.32_1	119.51_9	1.3998	1.5161

Table S1, continued

NO_2	118.41_7	120.76_5	120.36_1	119.33_1	1.3998	1.5161
NC	118.41_7	120.76_8	120.36_2	119.32_5	1.3997	1.5157
N_2^+	118.89_7	120.44_4	120.29_8	119.62_0	1.4012	1.5118
O^-	117.61_5	121.23_3	120.49_0	118.93_9	1.4019	1.5101
OH	118.34_9	120.81_0	120.37_6	119.28_0	1.3997	1.5160
OMe	118.33_5	120.81_7	120.37_6	119.27_9	1.3998	1.5159
OH_2^+	118.83_0	120.49_9	120.32_2	119.52_8	1.3999	1.5166
F	118.36_5	120.80_0	120.37_0	119.29_6	1.3997	1.5162
Na	118.16_6	120.92_7	120.39_0	119.19_9	1.3999	1.5164
MgCl	118.34_8	120.81_4	120.36_7	119.29_0	1.3997	1.5163
SiH_3	118.35_0	120.81_1	120.37_0	119.28_9	1.3997	1.5162
$SiMe_3$	118.33_3	120.82_3	120.37_1	119.28_1	1.3997	1.5160
PH_2	118.34_8	120.81_2	120.36_7	119.29_4	1.3998	1.5160
PH_3^+	118.81_4	120.51_0	120.31_8	119.52_8	1.4000	1.5151
S^-	117.75_3	121.15_2	120.47_2	119.00_0	1.4017	1.5104
SH	118.37_6	120.79_4	120.37_2	119.29_3	1.3997	1.5158
Cl	118.37_8	120.79_2	120.36_7	119.30_4	1.3997	1.5159
ClO_3	118.47_9	120.72_6	120.35_6	119.35_7	1.3996	1.5170
Br	118.38_6	120.78_8	120.36_7	119.30_5	1.3997	1.5160
Range	1.40_4	0.79_5	0.44_5	1.12_5	0.0107	0.0201

[a] Bond angles are in degrees, bond distances in Å; they are labeled according to Figure 1.

[b] The geometry of the benzene ring has been made consistent with C_{2v} symmetry by averaging appropriate bond distances and angles.

[c] The small intervals of values spanned by the ring angles and the correlation introduced by geometrical constraints make it necessary to present bond angles with three decimal figures.

Table S2 Selected geometrical parameters of the *para*-carborane cage in 12-substituted 1-phenyl-1,12-dicarba-*closo*-dodecaborane derivatives (**1**), from B3LYP/6-311++G** calculations[a]

Substituent	$r(C\cdots C)_1$	α_1	a_1
H	3.1066	62.97	1.7054
Li	3.1776	61.70	1.7168
BH_2	3.1419	62.33	1.7204
BH_3^-	3.1910	61.52	1.7239
CH_2^+	3.1232	62.67	1.7444
CH_2^-	3.2795	59.98	1.7762
Me	3.1457	62.23	1.7181
CF_3	3.1251	62.62	1.7201
Ph	3.1594	61.98	1.7266
CHO	3.1195	62.73	1.7146
COMe	3.1360	62.43	1.7202
COCl	3.1247	62.64	1.7210
COO^-	3.1526	62.22	1.7159
COOH	3.1254	62.64	1.7188
COOMe	3.1263	62.61	1.7188
CCH	3.1393	62.39	1.7257
CN	3.1226	62.69	1.7232
NH^-	3.2855	59.76	1.7810
NH_2	3.1495	62.19	1.7217
NMe_2	3.1768	61.67	1.7352
NF_2	3.1124	62.88	1.7174

Table S2, continued

NH_3^+	3.0822	63.40	1.7066
NO_2	3.0972	63.17	1.7116
NC	3.1226	62.70	1.7217
N_2^+	3.0750	63.61	1.7300
O^-	3.2924	59.60	1.7880
OH	3.1314	62.51	1.7166
OMe	3.1419	62.32	1.7220
OH_2^+	3.0472	64.07	1.6971
F	3.1016	63.08	1.7077
Na	3.1742	61.78	1.7138
MgCl	3.1533	62.12	1.7167
SiH_3	3.1427	62.30	1.7192
$SiMe_3$	3.1590	61.99	1.7230
PH_2	3.1413	62.34	1.7187
PH_3^+	3.1032	63.04	1.7213
S^-	3.2207	61.06	1.7443
SH	3.1348	62.47	1.7191
Cl	3.1157	62.84	1.7137
ClO_3	3.0638	63.77	1.7016
Br	3.1162	62.85	1.7140
Range	0.2452	4.47	0.0909

[a] The $r(C\cdots C)_1$ parameter (Å) is the non-bonded distance between C1 and C12; α_1 (degrees) is the mean valuee of the five B–C–B angles at C12; a_1 (Å) is the mean value of the five C12–B bond distances.

Table S3 ^{13}C and ^{11}B NMR chemical shifts (ppm) of the carbon and boron atoms of the para-carborane cage in 12-substituted 1-phenyl-1,12-dicarba-*closo*-dodecaborane derivatives (**1**), from GIAO-B3LYP/II//B3LYP//6-311++G** calculations[a,b]

Substituent	C1	B2, B5	B3, B4	B6	C12	B7, B9	B10, B11	B8
H	96.8	–13.5	–15.0	–18.1	67.4	–17.3	–18.9	–18.9
Li[c]	100.2	–10.3	–11.9	–15.0	87.3	–13.9	–15.4	–15.4
BH_2	101.8	–12.3	–13.8	–16.9	83.6	–16.8	–16.2	–14.7
BH_3^-	83.1	–14.5	–14.7	–17.2	112.3	–10.1	–13.1	–13.9
CH_2^+	129.1	–5.7	–13.3	–18.2	118.5	–4.8	–11.2	–15.9
CH_2^-	41.9	–10.3	–19.8	–30.2	95.9	3.7	–15.6	–25.9
Me	90.0	–14.1	–14.7	–17.0	85.0	–13.0	–16.0	–16.7
CF_3	97.2	–15.0	–15.3	–17.5	86.0	–15.2	–17.9	–18.5
Ph	92.9	–12.8	–15.9	–18.9	92.9	–12.8	–15.9	–18.9
CHO	97.2	–13.6	–14.9	–18.4	90.8	–14.6	–19.1	–19.5
COMe	95.7	–13.4	–15.4	–19.4	93.7	–14.8	–17.9	–17.8
COCl	97.3	–14.0	–15.6	–19.2	91.9	–14.5	–16.9	–17.8
COO^-	84.5	–15.4	–16.8	–20.2	110.0	–13.8	–15.7	–15.9
COOH	96.4	–13.5	–15.7	–19.1	83.7	–14.7	–17.2	–17.3

Table S3, continued

COOMe	95.8	–13.7	–15.8	–19.4	85.4	–14.9	–17.1	–17.5
CCH	93.5	–13.9	–15.5	–18.4	73.7	–13.3	–14.9	–14.8
CN	97.9	–13.6	–15.3	–18.2	65.1	–14.3	–15.9	–15.9
NH^-	45.8	–15.2	–19.5	–25.4	130.5	–2.9	–12.1	–20.3
NH_2	82.8	–15.9	–16.1	–17.4	102.6	–15.4	–15.0	–13.5
NMe_2	85.6	–16.9	–16.1	–18.2	112.8	–16.7	–14.7	–18.2
NF_2	94.2	–16.0	–16.2	–18.3	110.9	–16.0	–18.2	–19.3
NH_3^+	96.7	–12.9	–13.7	–16.0	82.8	–16.4	–19.6	–20.3
NO_2	92.4	–14.8	–17.0	–20.2	116.3	–15.5	–17.5	–18.5
NC	90.8	–14.8	–16.4	–19.2	85.1	–13.9	–15.5	–15.5
N_2^+	113.4	–11.3	–14.1	–17.1	71.0	–12.9	–14.9	–15.3
O^-	47.8	–18.5	–19.9	–23.3	142.6	–10.4	–12.4	–12.4
OH	81.2	–14.9	–17.5	–20.3	117.1	–14.1	–16.9	–17.2
OMe	83.1	–15.2	–17.6	–21.1	123.1	–16.2	–15.6	–20.5
OH_2^+	91.5	–14.3	–15.7	–17.1	124.1	–19.4	–20.0	–20.0
F	82.4	–16.3	–17.7	–20.5	129.0	–16.5	–18.1	–17.9
Na[c]	99.6	–10.1	–11.6	–14.6	92.1	–13.4	–14.9	–14.8

Table S3, continued

MgCl[c]	104.0	–10.6	–12.2	–15.2	71.2	–15.2	–16.8	–16.7
SiH_3	99.2	–12.5	–13.2	–15.5	69.2	–13.4	–16.4	–17.1
$SiMe_3$	99.6	–12.8	–13.6	–16.0	79.3	–14.6	–17.0	–17.3
PH_2	94.0	–13.2	–13.7	–15.8	76.6	–12.6	–15.9	–13.6
PH_3^+	110.4	–11.1	–11.6	–13.7	50.8	–14.0	–18.1	–19.6
S^-	58.3	–15.0	–16.5	–20.0	129.4	–7.6	–9.6	–9.5
SH	89.9	–13.3	–14.8	–18.0	85.8	–11.3	–14.4	–17.7
Cl	88.0	–14.4	–15.9	–18.7	97.5	–13.6	–15.2	–15.1
ClO_3	89.2	–16.9	–16.6	–18.4	154.3	–16.0	–19.0	–19.5
Br	89.4	–14.0	–15.4	–18.2	94.9	–13.2	–14.8	–14.7

[a] See text (Section 2) for additional information.

[b] Atoms are numbered according to the IUPAC numbering scheme, see Figure 1 of ref 1.

[c] For the elements Li, Na, and Mg Pople's basis set 6-31++G** was used for magnetic properties calculations.

Table S4 Total atomic charges of the carbon and boron atoms of the para-carborane cage in 12-substituted 1-phenyl-1,12-dicarba-*closo*-dodecaborane derivatives (**1**), from NAO calculations[a]

Substituent	C1	B2, B5	B3, B4	B6	C12	B7, B9	B10, B11	B8
H	–0.500	0.007	–0.012	–0.021	–0.690	–0.007	–0.007	–0.008
Li	–0.505	0.013	–0.007	–0.016	–0.994	–0.034	–0.034	–0.036
BH_2	–0.496	0.014	–0.007	–0.015	–0.885	0.004	0.000	–0.003
BH_3^-	–0.515	0.003	–0.017	–0.025	–0.670	0.001	0.000	–0.002
CH_2^+	–0.486	0.021	–0.010	–0.024	–0.644	0.061	0.016	–0.014
CH_2^-	–0.515	0.004	–0.036	–0.062	–0.425	–0.019	–0.026	–0.039
Me	–0.498	0.011	–0.009	–0.017	–0.509	0.000	–0.002	–0.003
CF_3	–0.495	0.010	–0.010	–0.018	–0.630	0.004	0.002	0.001
Ph	–0.496	0.013	–0.008	–0.018	–0.496	0.013	–0.008	–0.018
CHO	–0.497	0.013	–0.009	–0.015	–0.627	0.014	–0.007	0.000
COMe	–0.496	0.013	–0.010	–0.016	–0.603	0.013	–0.010	0.000
COCl	–0.494	0.010	–0.010	–0.018	–0.633	0.018	0.003	0.002
COO^-	–0.513	0.002	–0.019	–0.027	–0.601	0.007	0.002	–0.002
COOH	–0.496	0.010	–0.012	–0.020	–0.627	0.014	0.004	0.003

Table S4, continued

COOMe	–0.497	0.009	–0.011	–0.020	–0.616	0.013	0.005	0.004
CCH	–0.496	0.007	–0.015	–0.024	–0.570	0.017	0.016	0.015
CN	–0.493	0.008	–0.014	–0.024	–0.628	0.020	0.019	0.018
NH^-	–0.518	–0.004	–0.036	–0.049	–0.143	–0.032	–0.054	–0.038
NH_2	–0.498	0.005	–0.011	–0.021	–0.292	–0.014	0.003	–0.015
NMe_2	–0.496	0.006	–0.008	–0.018	–0.257	–0.032	–0.001	–0.017
NF_2	–0.496	0.006	–0.012	–0.020	–0.389	0.002	0.006	–0.002
NH_3^+	–0.484	0.022	0.001	–0.008	–0.386	–0.006	–0.007	–0.008
NO_2	–0.495	0.009	–0.012	–0.022	–0.412	0.014	0.005	–0.002
NC	–0.495	0.006	–0.016	–0.026	–0.335	0.015	0.014	0.013
N_2^+	–0.476	0.012	–0.012	–0.023	–0.462	0.037	0.034	0.032
O^-	–0.518	–0.013	–0.034	–0.044	0.115	–0.063	–0.064	–0.067
OH	–0.500	0.008	–0.013	–0.028	–0.121	–0.014	–0.005	–0.036
OMe	–0.499	0.008	–0.012	–0.029	–0.114	–0.018	–0.003	–0.044
OH_2^+	–0.486	0.019	0.001	–0.012	–0.246	–0.016	0.007	–0.010
F	–0.500	0.005	–0.016	–0.025	–0.012	–0.018	–0.019	–0.020
Na	–0.508	0.012	–0.009	–0.018	–0.907	–0.032	–0.033	–0.035

Table S4, continued

MgCl	–0.500	0.017	–0.004	–0.014	–1.040	–0.024	–0.025	–0.026
SiH_3	–0.498	0.014	–0.006	–0.014	–0.952	–0.002	–0.006	–0.009
$SiMe_3$	–0.498	0.016	–0.004	–0.013	–0.971	–0.011	–0.010	–0.013
PH_2	–0.498	0.012	–0.009	–0.015	–0.814	–0.001	–0.005	0.000
PH_3^+	–0.481	0.021	0.001	–0.008	–0.920	0.009	0.002	–0.002
S^-	–0.513	–0.006	–0.028	–0.038	–0.613	–0.005	–0.006	–0.008
SH	–0.498	0.010	–0.012	–0.023	–0.674	0.008	–0.001	–0.005
Cl	–0.498	0.007	–0.015	–0.024	–0.541	0.008	0.006	0.005
ClO_3	–0.499	0.011	–0.008	–0.016	–0.652	0.003	0.002	0.001
Br	–0.498	0.007	–0.014	–0.024	–0.619	0.009	0.007	0.006

[a] Charges are in electrons. They have been obtained by NAO analysis[13,14] at the B3LYP/6-31G* level of theory, based on B3LYP/6-311++G** geometries. Atoms are numbered according to the IUPAC numbering scheme, see Figure 1 of ref 1.