Supplementary data for article:

Baranac-Stojanović, M.; Stojanović, M. Magnetic Anisotropy of the C-C Single Bond. *Chemistry. A European Journal* **2013**, *19* (13), 4249–4254.

https://doi.org/10.1002/chem.201204267

CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Magnetic Anisotropy of the C−C Single Bond

Marija Baranac-Stojanović*[a] and Milovan Stojanović[b]

chem_201204267_sm_miscellaneous_information.pdf

Table of Contents:

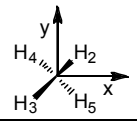
Tables with orbital contributions to proton shielding tensor
obtained by the NCS analysis……S2

Visualization of (de)shielding contributions.....……...S6

Colour versions of Figures 2-5, 7 and 8.....S7

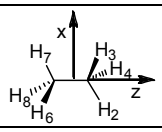
Absolute energies (atomic units) and x, y, z coordinates (Å)
of the optimized structures…….....S9

Table S1. Orbital contributions (ppm) to σ(H-2) in methane (T_d) obtained by the NCS analysis of proton shielding tensor.[a]

	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
C1-H2	25.22	25.22	25.22	25.22
C1-H3	2.78	2.78	0.87	2.14
C1-H4	2.78	0.87	2.78	2.14
C1-H5	0.87	2.78	2.78	2.14
core	0.08	0.08	0.08	0.08
total	31.74	31.74	31.74	31.74
CH_{other} total	6.43	6.43	6.43	6.43

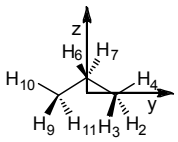
[a] σ_{xx}, σ_{yy}, σ_{zz} and σ_{iso} denote shielding contributions when magnetic field is applied along the x, y and z axis, respectively, and the average of all space orientations, $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

Table S2. Orbital contributions (ppm) to σ(H-2) in ethane (D_{3d}) obtained by the NCS analysis of proton shielding tensor.[a]

	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
C1-H2	28.50	24.49	24.73	25.91
C1-H3	2.83	1.29	2.15	2.09
C1-H4	2.83	1.29	2.15	2.09
C1-C5	0.04	1.70	1.04	0.92
C1-H6	-0.19	-0.34	0.72	0.06
C1-H7	-0.48	-0.83	0.62	-0.23
C1-H8	-0.19	-0.34	0.72	0.06
core C1	0.48	-0.03	-0.04	0.14
core C5	-0.06	-0.08	0.04	-0.03
total	33.75	27.15	32.13	31.01
$CH_{geminal}$ total	5.66	2.58	4.30	4.18
$CH_{vicinal}$ total	-0.87	-1.52	2.06	-0.11

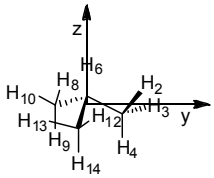
[a] σ_{xx}, σ_{yy}, σ_{zz} and σ_{iso} denote shielding contributions when magnetic field is applied along the x, y and z axis, respectively, and the average of all space orientations, $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

Table S3. Orbital contributions (ppm) to σ(H-6) in propane (C_{2v}) obtained by the NCS analysis of proton shielding tensor.[a]

	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
C1-H2	-0.54	-0.09	-0.09	-0.24
C1-H3	-0.21	0.12	0.45	0.12
C1-H4	0.07	0.25	0.24	0.19
C1-C5	0.44	0.26	1.92	0.87
C5-H6	27.80	25.21	26.32	26.44
C5-H7	2.32	3.29	0.60	2.07
C5-C8	0.44	0.26	1.92	0.87
C8-H9	-0.21	0.12	0.45	0.12
C8-H10	0.07	0.25	0.24	0.19
C8-H11	-0.54	-0.09	-0.09	-0.24
core C1	-0.08	0.00	-0.05	-0.04
core C5	0.55	0.05	0.10	0.23
core C8	-0.08	0.00	-0.05	-0.04
total	30.06	29.62	31.95	30.54
CC total	0.88	0.52	3.84	1.74
$CH_{vicinal}$ total	-1.36	0.56	1.20	0.14

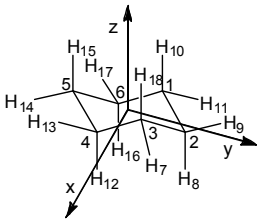
[a] σ_{xx}, σ_{yy}, σ_{zz} and σ_{iso} denote shielding contributions when magnetic field is applied along the x, y and z axis, respectively, and the average of all space orientations, $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

Table S4. Orbital contributions (ppm) to σ(H-6) in *i*-butane (C_{3v}) obtained by the NCS analysis of proton shielding tensor.[a]

	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
C1-H2	-0.18	0.41	0.42	0.21
C1-H3	-0.18	0.41	0.42	0.21
C1-H4	-0.84	0.19	0.00	-0.22
C1-C5	1.50	-0.03	1.24	0.90
C5-H6	25.59	25.59	28.88	26.69
C5-C7	0.35	1.12	1.24	0.90
C5-C11	0.35	1.12	1.24	0.90
C7-H8	0.27	-0.04	0.41	0.21
C7-H9	-0.07	-0.59	0.00	-0.22
C7-H10	0.25	-0.03	0.41	0.21
C11-H12	0.27	-0.04	0.41	0.21
C11-H13	0.25	-0.03	0.41	0.21
C11-H14	-0.07	-0.59	0.00	-0.22
core C1	-0.07	0.03	-0.07	-0.04
core C5	0.26	0.26	0.47	0.33
core C7	0.00	-0.05	-0.07	-0.04
core C11	0.00	-0.05	-0.07	-0.04
total	27.67	27.67	35.35	30.23
CC total	2.20	2.21	3.72	2.70
CH_{other} total	-0.30	-0.31	2.48	0.60

[a] σ_{xx}, σ_{yy}, σ_{zz} and σ_{iso} denote shielding contributions when magnetic field is applied along the x, y and z axis, respectively, and the average of all space orientations, $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

Table S5. Orbital contributions (ppm) to σ(H-8_{ax}) and σ(H-9_{eq}) in cyclohexane (D_{3d}) obtained by the NCS analysis of proton shielding tensor.[a]

	H_{ax}				H_{eq}			
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
C1-C2	0.86	1.58	1.45	1.30	-0.19	1.67	0.22	0.56
C1-C6	-0.27	0.18	0.33	**0.08**	-0.33	0.16	-0.62	**-0.26**
C1-H10	-0.18	-0.74	0.00	-0.30	0.19	0.36	-0.20	0.12
C1-H11	0.35	-0.27	0.15	0.07	0.31	0.49	-0.22	0.20
C2-C3	0.86	1.58	1.45	1.30	-0.19	1.67	0.22	0.56
C2-H8	25.39	25.60	28.96	26.65	3.56	1.09	1.56	2.07
C2-H9	2.62	0.49	1.72	1.61	24.76	28.40	26.10	26.42
C3-C4	-0.27	0.18	0.33	**0.08**	-0.33	0.16	-0.62	**-0.26**
C3-H7	0.35	-0.27	0.15	0.07	0.31	0.49	-0.22	0.20
C3-H18	-0.18	-0.74	0.00	-0.30	0.19	0.36	-0.20	0.12
C4-C5	-0.06	0.28	0.32	0.18	-0.08	0.18	0.18	0.09
C4-H12	-0.09	0.37	-0.59	-0.10	-0.03	0.15	-0.20	-0.03
C4-H13	0.01	0.27	-0.20	0.03	-0.03	0.11	-0.07	0.00
C5-C6	-0.06	0.28	0.32	0.18	-0.08	0.18	0.18	0.09
C5-H14	0.02	0.13	-0.09	0.02	0.00	0.09	-0.12	-0.01
C5-H15	-0.06	0.18	-0.11	0.00	-0.06	0.19	-0.20	-0.02
C6-H16	-0.09	0.37	-0.59	-0.10	-0.03	0.15	-0.20	-0.03
C6-H17	0.01	0.27	-0.20	0.03	-0.03	0.11	-0.08	0.00
core C1	0.02	-0.11	-0.07	-0.05	0.07	-0.06	-0.06	-0.01
core C2	-0.09	0.04	0.54	0.16	0.55	0.35	0.95	0.62
core C3	0.02	-0.11	-0.07	-0.05	0.07	-0.06	-0.06	-0.01
core C4	-0.04	-0.03	-0.13	-0.07	-0.04	-0.01	-0.09	-0.04
core C5	-0.07	0.00	-0.10	-0.06	-0.06	0.01	-0.09	-0.04
core C6	-0.04	-0.03	-0.13	-0.07	-0.04	-0.01	-0.09	-0.04
total	29.02	29.49	33.45	30.65	28.50	36.27	26.10	30.29

[a] σ_{xx}, σ_{yy}, σ_{zz} and σ_{iso} denote shielding contributions when magnetic field is applied along the x, y and z axis, respectively, and the average of all space orientations, $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

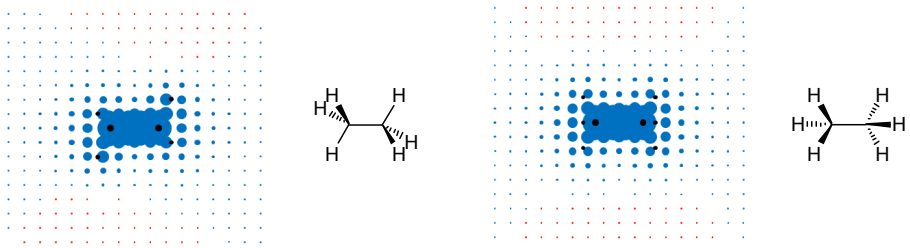


Figure S1. Visualization of total anisotropic effects of ethane: view in the plane containing HCCH bonds (left) and in the plane perpendicular to it (right). Blue and red points denote shielding and deshielding effects, respectively. The radius of points is proportional to the absolute value of the contribution (the points merge into one another near the bond). Positions of carbon and hydrogen nuclei are marked by black points.

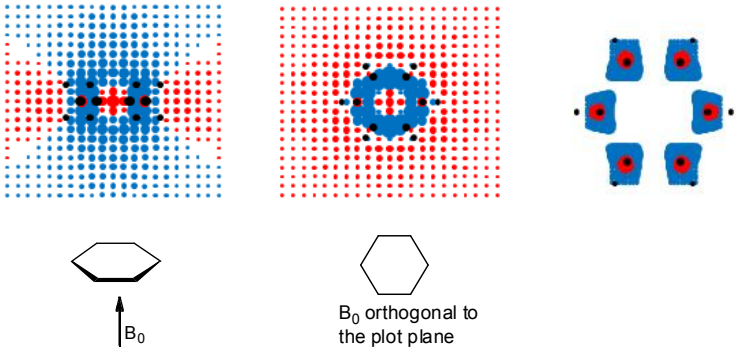


Figure S2. Visualization of (de)shielding contributions of cyclohexane (D_{6h}) CC framework for a magnetic field applied perpendicularly to the ring plane: the first view is in the σ_v plane and the second view is in the plane of the carbon nuclei. The shielding pattern near the carbon nuclei calculated with the use of a finer grid, with a step width of 0.1 Å is shown at the right. Other details are the same as for Figure S1.

Colour versions of Figures 2-5, 7 and 8

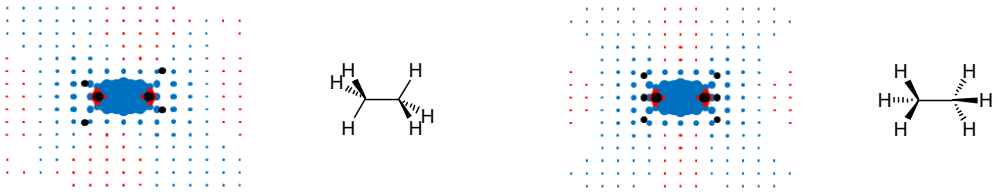


Figure 2. Visualization of anisotropic effects of the C–C single bond in ethane: view in the plane containing the HCCH bonds (left) and in the plane perpendicular to it (right). Blue and red points denote shielding and deshielding effects, respectively. The radius of points is proportional to the absolute value of the contribution (the points merge into one another near the bond). Positions of carbon and hydrogen nuclei are marked by black points.

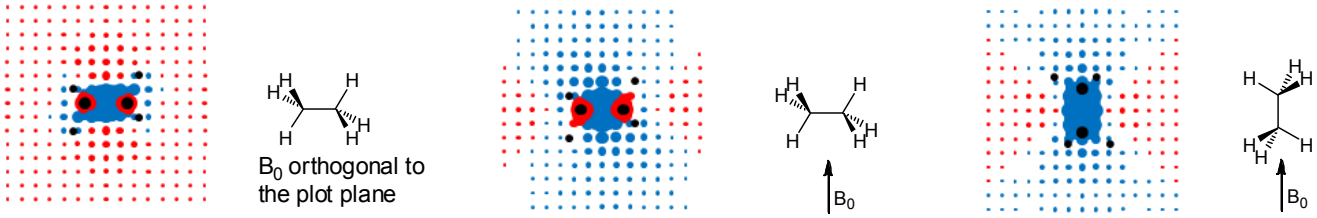


Figure 3. Visualization of anisotropic effects of the C–C single bond in ethane, in the plane containing the HCCH bonds: when direction of magnetic field is orthogonal to the plot plane and the C–C bond (left), when magnetic field is parallel to the HCCH plane and orthogonal to the C–C bond (middle) and when magnetic field is parallel to the C–C bond (right). Other details are the same as for Figure 2.

Figure 4. Visualization of (de)shielding contributions of the H3–C1–C2–H6 bonds assuming magnetic field applied perpendicularly to the plot plane (left) and of H4(H5)–C1–C2–H7(H8) bonds in the shown field direction (right). Other details are the same as for Figure 2.

Figure 5. Visualization of anisotropic effects of the C–C single bond in the eclipsed conformation of ethane: view in the plane containing the HCCH bonds (left) and in the plane perpendicular to it (right). Other details are the same as for Figure 2.

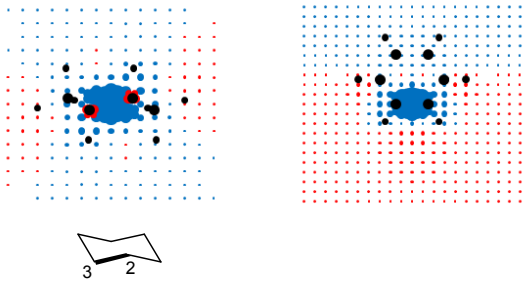


Figure 7. Visualization of anisotropic effects of the single C2–C3 bond in cyclohexane (D_{3d}): in the plane including the bond, parallel to the C_3 symmetry axis (left) and in the plane orthogonal to the C_3 symmetry axis, passing through the bonds (right). Other details are the same as for Figure 2.

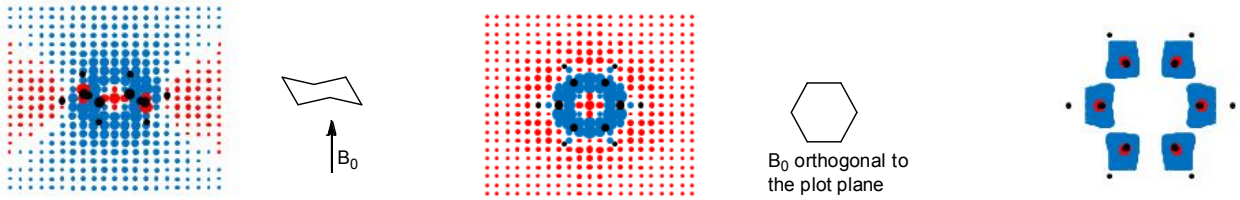


Figure 8. Visualization of (de)shielding contributions of cyclohexane (D_{3d}) CC framework for a magnetic field applied along the C_3 symmetry axis: the first view is in the σ_v plane (left) and the second view is in the plane orthogonal to the first, passing through the bonds (middle). The shielding pattern near the carbon nuclei calculated with the use of a finer grid, with a step width of 0.1 Å is shown at the right. Other details are the same as for Figure 2.

Absolute energies (atomic units) and x, y, z coordinates (Å) of the optimized structures

CH_4 (T_d)

E = -40.5339325 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.629674	0.629674	0.629674
3	1	0	-0.629674	-0.629674	0.629674
4	1	0	-0.629674	0.629674	-0.629674
5	1	0	0.629674	-0.629674	-0.629674

C_2H_6 (D_{3d})

E = -79.8565414 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.765447
2	1	0	0.000000	1.018733	1.163771
3	1	0	0.882249	-0.509367	1.163771
4	1	0	-0.882249	-0.509367	1.163771
5	6	0	0.000000	0.000000	-0.765447
6	1	0	0.882249	0.509367	-1.163771
7	1	0	0.000000	-1.018733	-1.163771
8	1	0	-0.882249	0.509367	-1.163771

C_2H_6 (D_{3h})

E = -79.8522256 a.u.; imaginary frequency: 297.3 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.772317
2	1	0	0.000000	1.014704	1.177751
3	1	0	0.878759	-0.507352	1.177751
4	1	0	-0.878759	-0.507352	1.177751
5	6	0	0.000000	0.000000	-0.772317
6	1	0	0.000000	1.014704	-1.177751
7	1	0	-0.878759	-0.507352	-1.177751
8	1	0	0.878759	-0.507352	-1.177751

C_3H_8 (C_{2v})

E = -119.1810826 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.277201	-0.259659
2	1	0	-0.883042	1.322183	-0.905531
3	1	0	0.883042	1.322183	-0.905531
4	1	0	0.000000	2.174164	0.366468
5	6	0	0.000000	0.000000	0.585850
6	1	0	0.875760	0.000000	1.245003
7	1	0	-0.875760	0.000000	1.245003
8	6	0	0.000000	-1.277201	-0.259659
9	1	0	0.883042	-1.322183	-0.905531
10	1	0	0.000000	-2.174164	0.366468
11	1	0	-0.883042	-1.322183	-0.905531

i-C_4H_{10} (C_{3v})

E = -158.5064273 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.461711	-0.095690
2	1	0	0.884254	1.995678	0.265422
3	1	0	-0.884254	1.995678	0.265422
4	1	0	0.000000	1.520298	-1.190012
5	6	0	0.000000	0.000000	0.371680
6	1	0	0.000000	0.000000	1.469839
7	6	0	-1.265879	-0.730856	-0.095690
8	1	0	-2.170435	-0.232052	0.265422
9	1	0	-1.316617	-0.760149	-1.190012
10	1	0	-1.286181	-1.763626	0.265422
11	6	0	1.265879	-0.730856	-0.095690
12	1	0	2.170435	-0.232052	0.265422
13	1	0	1.286181	-1.763626	0.265422
14	1	0	1.316617	-0.760149	-1.190012

C_6H_{12} (D_{3d})

E = -235.9448094 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.270269	0.733390	0.228186
2	6	0	0.000000	1.466780	-0.228186
3	6	0	1.270269	0.733390	0.228186
4	6	0	1.270269	-0.733390	-0.228186
5	6	0	0.000000	-1.466780	0.228186
6	6	0	-1.270269	-0.733390	-0.228186
7	1	0	2.160398	1.247306	-0.149994
8	1	0	0.000000	1.538437	-1.324085
9	1	0	0.000000	2.494613	0.149994
10	1	0	-1.332325	0.769218	1.324085
11	1	0	-2.160398	1.247306	-0.149994
12	1	0	1.332325	-0.769218	-1.324085
13	1	0	2.160398	-1.247306	0.149994
14	1	0	0.000000	-2.494613	-0.149994
15	1	0	0.000000	-1.538437	1.324085
16	1	0	-1.332325	-0.769218	-1.324085
17	1	0	-2.160398	-1.247306	0.149994
18	1	0	1.332325	0.769218	1.324085