<table>
<thead>
<tr>
<th>Title</th>
<th>Addition reaction of alkyl radical to C-60 fullerene: Density functional theory study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Tachikawa, Hiroto; Kawabata, Hiroshi</td>
</tr>
<tr>
<td>Citation</td>
<td>Japanese Journal of Applied Physics (JJAP), 55(2)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2016-02</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/63833">http://hdl.handle.net/2115/63833</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2016 The Japan Society of Applied Physics</td>
</tr>
<tr>
<td>Type</td>
<td>article (author version)</td>
</tr>
<tr>
<td>File Information</td>
<td>Tachikawa-JJAP55(2).pdf</td>
</tr>
</tbody>
</table>

Hokkaido University Collection of Scholarly and Academic Papers: HUSCAP
Addition Reaction of Alkyl Radical to the $C_{60}$ Fullerene: 
Density Functional Theory (DFT) Study

Hiroto TACHIKAWA* and Hiroshi KAWABATA

Department of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, JAPAN

Abstract: Functionalized fullerenes are known as a high-performance molecule. In this study, the alkyl-functionalized fullerenes (denoted by R-$C_{60}$) have been investigated by means of density functional theory (DFT) method to elucidate the effects of functionalization on the electronic states of fullerene. Also, the reaction mechanism of alkyl radical with $C_{60}$ was investigated. The methyl, ethyl, propyl and butyl radicals (denoted by $n=1-4$, where $n$ means number of carbon atoms in alkyl radical) were examined as alkyl radicals. The DFT calculation showed that the alkyl radical binds to the carbon atom of $C_{60}$ in the on-top site, and a strong C-C single bond was formed. The binding energies of alkyl radicals to $C_{60}$ were distributed in the ranges 31.8-35.1 kcal mol$^{-1}$ at the CAM-B3LYP/6-311G(d,p) level. It was found that the activation barrier exists before the alkyl addition: the barrier heights were calculated to be 2.1-2.8 kcal mol$^{-1}$. The electronic states of R-$C_{60}$ complex were discussed on the basis of theoretical results.

KEYWORDS: radical addition; spin density; potential energy curve; absorption spectrum; hyperfine coupling constant

Corresponding author: Hiroto TACHIKAWA, FAX: +81-11-706-7897
E-mail: hiroto@eng.hokudai.ac.jp
1. Introduction

Functionalized fullerenes are known as a high-performance molecule. For example, methanofullerene ([6,6]-phenyl-C_{61}-butyric acid methyl ester: PCBM) is one of the most useful $n$-type organic semiconductors [1-7]. The interaction between organic radical and fullerene has recently attracted considerable interest because the electronic properties of carbon materials are drastically changed by the addition of radical [8-15]. Alkyl radical (C$_n$H$_{2n+1}$) is the simplest organic radical and is sometimes utilized in the surface modification of carbon materials such as diamond [16], graphene, and fullerene [17]. The radical influences strongly electronic conductivity and the band gap in the semi-conductor. Also, the fullerene and graphene materials have a possibility as a radical storage medium. Therefore, the elucidation of an electronic state and the formation mechanism of radical added carbon materials are an important theme to develop the high performance materials.

The interaction of hydrogen atom with fullerenes has been investigated as radical added fullerenes. Using density functional theory (DFT) calculations, Tokunaga et al. have investigated electronic states of mono- and di-hydrated fullerene, C$_{60}$H and C$_{60}$H$_2$. [18] They found that energy of C$_{60}$H radical is smaller than the summation of energy of the fullerene and that of hydrogen atom. They also calculated cationic states of C$_{60}$H, C$_{60}$H$^+$, and found that dipole moment of C$_{60}$H becomes significantly larger in cationic state.

In case of graphene-hydrogen atom system, Novoselov and co-workers showed experimentally that the electronic property of graphene is drastically changed: the highly conductive graphene is converted from a semimetal into an insulator [19]. The reaction with hydrogen was reversible.
Raman studies revealed that the hydrogenation interrupts the delocalized \( \pi \)-bonding system of graphene through the formation of \( sp^3 \) carbon–hydrogen bonds \[20\]. From the transmission electron microscopy, it was found that the hydrogenation is reversible through annealing, thereby restoring the conductivity and structure of graphene. This reversibility also creates the possibility of hydrogen storage.

The interaction between graphene surface and hydrogen atom have been investigated by means of DFT calculation. \[21-26\] Casolo et al. investigated the adsorption of hydrogen atom to a 5x5 surface unit cell of graphene using the DFT method \[21\]. The binding energies per one hydrogen atom were calculated in the range 0.8-1.9 eV and a barrier to sticking in the range 0-0.15 eV. It was suggested that the change of hybrid orbital from \( sp^2 \) to \( sp^3 \) is important in the addition of H atom to graphene. Thus, the electronic states of H atom on graphene and C\textsubscript{60} surfaces are understood theoretically. However, interaction of organic radical with C\textsubscript{60} is not clearly understood. Especially, the addition process of alkyl radicals to C\textsubscript{60} surface is scarcely known.

In the present study, the addition reaction of simple alkyl radicals (R) to the C\textsubscript{60} surface was investigated by means of DFT method. We focus our attention mainly on the mechanism of addition process of alkyl radical to the C\textsubscript{60} surface. We have searched the transition state structure of radical addition to the C\textsubscript{60} surface. Also, potential energy curve of alkyl radical approaching to the surface was investigated.

2. Method of calculation

All DFT calculations were carried out using Gaussian 09 program package.\[15\] The geometries of free C\textsubscript{60} and complexes of C\textsubscript{60} with alkyl radical (R) (expressed by R-C\textsubscript{60}), were fully optimized at the CAM-B3LYP/6-31G(d) and CAM-B3LYP/6-311G(d,p)
levels. Previous works showed that these levels of theory give reasonable electronic structures of graphene systems [28-30]. To confirm the stabilities of molecules at the stationary points along the reaction coordinate, the harmonic vibrational frequencies were calculated at the CAM-B3LYP/6-31G(d) level. The barrier height at the transition state and binding energy were also calculated at the CAM-B3LYP/6-31G(d,p) level. Potential energy curve for the approach of alkyl radical to C_{60} were calculated at the CAM-B3LYP/6-31G(d) level. The electronic states of R-C_{60} were obtained by natural population analysis and natural bond orbital (NBO) methods at the CAM-B3LYP/6-31G(d,p) level. The binding energy of alkyl radical to C_{60}, E_{\text{bind}}(n), is defined by

\[ E_{\text{bind}}(n) = E_{R(n)-C_{60}} - [E_{R(n)} + E(C_{60})]. \]

where, \( E_{R(n)-C_{60}} \) means total energy of the R-C_{60} complex with \( n \). \( E_{R(n)} \) and \( E(C_{60}) \) are total energies of alkyl radical and C_{60}, respectively.

3. Results

3.1 Binding structures

The optimized structures of the R-C_{60} system are illustrated in Figure 1. We discuss the structures and electronic states of R-C_{60} using the results of the most sophisticated calculation (CAM-B3LYP/6-311G(d,p) level). In case of n=4 (butyl radical), two conformers exist as structural form: normal butyl (4n) and tertiary butyl (4t) radicals. The calculations showed that all alkyl radicals can bind to the on-top site of C_{60}.

In case of ethyl radical (n=2, C_{2}H_{5}), the C_{0}-C_{1} bond distance was calculated to be R_{1}=1.554 Å, which was slightly longer than that of methyl radical (1.543 Å, n=1). The planar structure of methylene moiety of ethyl radical was changed to a bent form after the binding to the C_{60} surface. The bending angle was calculated to be \( \theta_1 = <C_0-C_1-C_2 = \)
114.9°. The C1-H bond distance was 1.093 Å, which was slightly elongated from that of free ethyl radical (1.082 Å). The C0-C1 bond distances were almost constant in \( n=2, 3, \) and 4n (~1.554 Å). On the other hand, the distance in \( n=4t \) (1.588 Å) was longer than those of \( n=1-4n \) (~1.554 Å). This elongation was due to the steric hindrance between methyl group of 4t and C\(_{60}\) surface.

The binding energies of alkyl radicals to C\(_{60}\) (E\(_{\text{bind}}\)) are given in Table 1. The binding energies of R for \( n=1, 2, 3, 4n, \) and 4t were calculated to be +35.1, +31.8, +32.2, +32.1, and +24.1 kcal mol\(^{-1}\), respectively, indicating that the binding energy decreases with increasing \( n \). The binding energy for \( n=4t \) was significantly smaller than that of \( n=4 \) (24.1 vs. 32.1 kcal mol\(^{-1}\)). This is due to the steric hindrance of methyl groups in tertiary butyl radical. The similar results were obtained from the CAM-B3LYP/6-31G(d) calculations. The NPA charges on moieties of C\(_{60}\) and R were -0.1 and +0.1, respectively. These values indicate that the alkyl part behaves as a slight electron donor in R-C\(_{60}\). The result indicates that an electron transfer takes place from alkyl radical to C\(_{60}\) after the addition: \( R + C_{60} \rightarrow (R)^{\delta+} (C_{60})^{\delta-} \).

The van der Waals (vdW) structures of R--C\(_{60}\) were obtained at the entrance region in the binding reaction of R to C\(_{60}\). The optimized distances between C\(_0\) and C\(_1\) are given in Table 2 together with the binding energies of vDW (E\(_{\text{vdW}}\)). The distances of alkyl radicals from C\(_{60}\) surface were calculated to be 3.56-3.68 Å. The structures of alkyl radicals were close to those of free alkyl radicals.

### 3.2. Potential energy curve (PEC)

Potential energy curve (PEC) for the approach of butyl radical (\( n=4n \)) to the C\(_{60}\) surface is plotted in Figure 2 as a function of C\(_0\)-C\(_1\) distance (\( r_1 \)). All geometrical
parameters of the R-C\textsubscript{60} system except for \( r_1 \) were optimized at each point of \( r_1 \).

When the butyl radical approaches to the C\textsubscript{60} surface, the first energy minimum was found at \( r_1=r(C_0-C_1)=3.636 \text{ Å} \). This is due to a vdW complex composed of R and C\textsubscript{60}. After that, the energy barrier was found at \( r_1=2.438 \text{ Å} \). This point corresponds to a transition state of R addition to C\textsubscript{60}. The barrier height of TS was calculated to be 2.10 kcal mol\(^{-1}\) at the CAM-B3LYP/6-311G(d,p) level. The potential energy decreased significantly after TS and it reaches the lowest energy point corresponding to a bound state of R-C\textsubscript{60} radical (PD).

### 3.3 Structures of transition state

The transition state (TS) structures of R--C\textsubscript{60} are given in Figure 3. In the transition state of methyl radical addition, the distance of CH\textsubscript{3} from the surface was \( r_1=r(C_0-\text{CH}_3) = 2.424 \text{ Å} \), and the angle of C\textsubscript{0}-C-H was \( \theta_1=97.9^\circ \). An imaginary frequency corresponding to the CH\textsubscript{3} dissociation coordinate was detected by the vibrational analysis. The value was calculated to be 302 \( i \text{ cm}^{-1}\). This indicates that the structure of TS in fig. 3 corresponds to the true transition state and saddle point for the CH\textsubscript{3} dissociation and addition reactions. In alkyl radical additions of \( n=2-4 \), the distances \( (r_1) \) were 2.439, 2.437, and 2.438 Å, respectively. Also, the angles \( (\theta_1) \) were 106.7\(^\circ \) (\( n=2 \)), 106.4\(^\circ \) (\( n=3 \)), and 107.2\(^\circ \) (\( n=4 \)). These results indicate that the structures in TS are very similar to each other. This is due to the fact that the interaction of alkyl radical with C\textsubscript{60} is localized in 2p-orbital of alkyl radical. The chain part of alkyl radical behaves as a spectator in the alkyl radical addition.

The activation energies for the radical addition reaction are given in Table 3. The barrier heights of TS from the dissociation limit (C\textsubscript{60} + R) were 2.8 kcal mol\(^{-1}\) (\( n=1 \)) and
2.1 kcal mol$^{-1}$ (n=2-4n), indicating that the activation energy is saturated in n=2-3. This is caused by the similarity of the TS structure in n=2-4.

3.4 Spin density along the reaction coordinate

The spatial distributions of spin density along the reaction coordinate are given in Figure 4. The spin density was only localized in the alkyl radical at longer separation, r(C$_0$-C)=3.636Å (vdW state). Especially, the unpaired electron was mainly localized in the 2p orbital of the carbon atom of butyl radical (C$_1$). The spin density on the butyl radical was calculated to be 0.992. At the TS position, the spin was widely distributed around R and a part of the C$_{60}$ surface. The spin density on R was 0.832.

At the binding structure (PD), i.e., the optimized structure of the R-C$_{60}$ system, the spin density was fully distributed around the C$_{60}$ surface. The spin density on R was changed to 0.04. This result indicates that the unpaired electron on alkyl radical (spin density) is fully transferred to the C$_{60}$ surface by the radical addition.

3.5 Electronic states of alkyl functionalized fullerenes

The electronic states of carbon atom in the binding site (C$_0$) will be changed by the addition of alkyl radical. To elucidate the electronic state of the C$_0$ atom, the natural bond orbital (NBO) analysis was carried out for the R-C$_{60}$ system. The NBO of the C$_0$-C$_1$ bond of free C$_{60}$ was expressed by

$$\sigma_{C=C} = 0.707(sp^{2.15})_{C_0} + 0.707(sp^{2.15})_{C_5}$$  \hspace{1cm} (1)$$

where, C$_0$ and C$_5$ mean the carbon atom in addition center and neighbor positioned carbon atom, respectively. After the alkyl radical addition to C$_{60}$, the NBO was changed to be
\[ \sigma_{e-C} = a(sp^m)_{C_0} + b(sp^l)_{C_1} \]  

(2)

The values of \( m \) and \( l \) obtained by NBO analysis are given in Table 4. Before the addition, the carbon atom in the addition site (C \(_0\)) has a hybrid orbital composed of \( sp^2\)-type. After the addition of R, the configuration was changed from \( sp^{2.15}\) to \( sp^{3.0}\). This value indicates that the carbon atom (C\(_0\)) is changed from \( sp^2\) to \( sp^3\) hybrid orbitals after the radical addition.

### 3.6 Hyperfine coupling constants of R-C\(_{60}\)

Hyperfine coupling constant (hfcc) of radical species provides important information on the electronic states and structure of radical. In the present study, proton-hfccs of free alkyl radicals and R-C\(_{60}\) (n=1-4) were calculated at the CAM-B3LYP/6-311G(d,p) level. The results are given in Table 5. In case of free alkyl radicals, hfccs of \( \alpha\)- and \( \beta\)-protons (denoted by H\(_1\) and H\(_2\), respectively) were significantly larger than the others. This result indicates that the unpaired electron was localized on C\(_1\) and C\(_2\) carbon atoms of free radical.

In vDW state, the hfccs were slightly decreased: for example, the hfccs of H\(_1\) in R-C\(_{60}\) (n=4) were changed from -22.13 G (free radical) to -21.91 G (vdW). At the transition state (TS), the value of H\(_1\) was further decreased to -16.44 G. The change was caused by the dissipation of unpaired electron from the alkyl radical to C\(_{60}\). In final state (PD formation), the hfccs of H\(_1\) and H\(_2\) were close to zero (-0.97G and -0.08G, respectively). This result indicates that almost all unpaired electron is transferred from the radical to C\(_{60}\). These significant changes suggest that the alkyl radical addition to C\(_{60}\) takes place together with the transfer of unpaired electron.
3.7 Absorption spectra of alkyl functionalized C\textsubscript{60} fullerenes

Simulated absorption spectra of C\textsubscript{60} and R-C\textsubscript{60} are given in Figure 5. The C\textsubscript{60} molecule showed a very weak peak: the absorption maximum was peaked at 4.50 eV. In vdw state, the peak was red-shifted to 3.83 eV, and the intensity of peak was about 100 times larger than that of C\textsubscript{60}. The product CH\textsubscript{3}-C\textsubscript{60} has two peaks at 2.13 and 3.50 eV.

To assign the peaks appearing at low- and high-energy regions in CH\textsubscript{3}-C\textsubscript{60}, the molecular orbitals (MOs) contributing to the electronic excitations were analyzed. Three MOs were illustrated in Figure 6. The MOs contributing to the lower excitation were 182 and 185: the excitation from 182 to 185 shows the peak (c), where 182 and 185 are orbital numbers in CH\textsubscript{3}-C\textsubscript{60}. HOMO and LUMO correspond to 184 and 185, respectively. The excitation from 178 to 185 contributes to the peak (d). These results indicate that both electronic excitation bands (peaks c and d) are composed of charge transfer (CT) bands from C\textsubscript{60} from CH\textsubscript{3} moiety of CH\textsubscript{3}-C\textsubscript{60}.

3.8 Potential energy diagram for the reaction

As a summary of the present study, potential energy diagrams of alkyl radical addition reaction to C\textsubscript{60} surface is illustrated in Figure 7. The values indicate relative energies (in kcal mol\textsuperscript{-1}) along the reaction coordinate, and the zero level means total energy of C\textsubscript{60} plus alkyl radical (RC). In the entrance region of the reaction, a weakly bound complex exists as a vdw complex. Before the addition to C\textsubscript{60}, there is a transition state barrier. However, the barrier heights are very low (about 2.1 kcal mol\textsuperscript{-1}). The alkyl radicals were strongly bound to the C\textsubscript{60} surface with the binding energy of ~35 kcal mol\textsuperscript{-1}.
4. Conclusion

The present calculations can be summarized as follows: (1) the alkyl radicals can react with a $C_{60}$ surface and binds directly to the carbon atom ($C_0$), and $C_0$-$C_1$ strong single bond is formed. The binding energies of alkyl radical to $C_{60}$ surface were calculated to be 31.8-35.1 kcal mol$^{-1}$ at the CAM-B3LYP/6-311G(d,p) level. (2) Low activation barrier exists in the approach of alkyl radical to the $C_{60}$ surface. This barrier was caused by a re-organization from sp$^2$ to sp$^3$ hybridization of carbon atom in the binding site ($C_0$ atom). The barrier heights were 2.1-2.8 kcal mol$^{-1}$ at the CAM-B3LYP/6-311G(d,p) level, and (3) the spin density of alkyl radical is widely distributed over the $C_{60}$ surface after the binding.

Acknowledgment. The author acknowledges partial support from JSPS KAKENHI Grant Number 15K05371 and MEXT KAKENHI Grant Number 25108004.
References

[27] Ab-initio calculation program: Gaussian 09, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery,


Figure captions

Figure 1. (color online). Optimized structure of alkyl radical-fullerene complexes (R-C_{60}) calculated at the CAM-B3LYP/6-311G(d,p) level. The values indicate the bond distance in Å.

Figure 2. (color online). Potential energy curve (PEC) for the addition of butyl radical (n=4n) to C_{60}.

Figure 3. (color online). Optimized structures of R-C_{60} at transition state (TS). Bond lengths and angles are in Å and in degrees, respectively.

Figure 4. (color online). Spatial distributions of spin densities on R(n=4)-C_{60} system at van der Waals (vdW) state, TS, and addition complex (PD) with the binding structure.

Figure 5. (color online). Simulated absorption spectra of C_{60} and C_{60}-R complexes (vdW and PD states).

Figure 6. (color online). Molecular orbitals contributing to the electronic excitations.

Figure 7. (color online) Potential energy diagrams of alkyl radical addition reaction to C_{60} surface. The values indicate relative energies (in kcal mol\(^{-1}\)) along the reaction coordinate.
Table 1. Binding energies ($E_{\text{bind}}$ in kcal mol$^{-1}$) of alkyl radicals to C$_{60}$.

<table>
<thead>
<tr>
<th>n</th>
<th>6-31G(d)</th>
<th>6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.1</td>
<td>35.1</td>
</tr>
<tr>
<td>2</td>
<td>33.7</td>
<td>31.8</td>
</tr>
<tr>
<td>3</td>
<td>34.1</td>
<td>32.2</td>
</tr>
<tr>
<td>4n</td>
<td>34.0</td>
<td>32.1</td>
</tr>
<tr>
<td>4t</td>
<td>25.7</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Table 2. Optimized geometrical parameters (R(C$_0$-C$_1$) in Å) and binding energies ($E_{\text{vdW}}$ in kcal mol$^{-1}$) of vdW complexes, R—C$_{60}$. The calculation was carried out the CAM-B3LYP/6-311G(d,p) level.

<table>
<thead>
<tr>
<th>n</th>
<th>R(C$_0$-C$_1$) / Å</th>
<th>$E_{\text{vdW}}$ / kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.684</td>
<td>-0.4</td>
</tr>
<tr>
<td>2</td>
<td>3.667</td>
<td>-0.6</td>
</tr>
<tr>
<td>3</td>
<td>3.639</td>
<td>-0.6</td>
</tr>
<tr>
<td>4n</td>
<td>3.636</td>
<td>-0.5</td>
</tr>
<tr>
<td>4t</td>
<td>3.560</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

Table 3. Activation energies ($E_{\text{act}}$ in kcal mol$^{-1}$) of addition of alkyl radicals to C$_{60}$.

<table>
<thead>
<tr>
<th>n</th>
<th>6-31G(d)</th>
<th>6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.96</td>
<td>2.81</td>
</tr>
<tr>
<td>2</td>
<td>1.28</td>
<td>2.10</td>
</tr>
<tr>
<td>3</td>
<td>1.16</td>
<td>2.08</td>
</tr>
<tr>
<td>4n</td>
<td>1.23</td>
<td>2.12</td>
</tr>
</tbody>
</table>
Table 4. Coefficients of equation (2) obtained from the NBO analysis

<table>
<thead>
<tr>
<th>n</th>
<th>a</th>
<th>b</th>
<th>m</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.706</td>
<td>0.708</td>
<td>2.83</td>
<td>2.02</td>
</tr>
<tr>
<td>2</td>
<td>0.709</td>
<td>0.705</td>
<td>2.86</td>
<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>0.710</td>
<td>0.705</td>
<td>2.87</td>
<td>1.95</td>
</tr>
<tr>
<td>4n</td>
<td>0.707</td>
<td>0.708</td>
<td>2.88</td>
<td>2.01</td>
</tr>
<tr>
<td>4t</td>
<td>0.705</td>
<td>0.710</td>
<td>2.90</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table 5. Hyperfine coupling constants (hfccs) of protons in the alkyl radicals along the reaction coordinate calculated at CAM-B3LYP/6-311G(d,p)

<table>
<thead>
<tr>
<th>n</th>
<th>position</th>
<th>alkyl radical</th>
<th>vdW</th>
<th>TS</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H1</td>
<td>-22.56</td>
<td>-23.04</td>
<td>-17.61</td>
<td>-0.06</td>
</tr>
<tr>
<td>2</td>
<td>H1</td>
<td>-22.35</td>
<td>-22.09</td>
<td>-16.51</td>
<td>-0.98</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>+26.03</td>
<td>+25.95</td>
<td>+19.41</td>
<td>+0.17</td>
</tr>
<tr>
<td>3</td>
<td>H1</td>
<td>-22.13</td>
<td>-21.80</td>
<td>-16.44</td>
<td>-0.97</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>+11.05</td>
<td>+10.85</td>
<td>+7.06</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>+0.70</td>
<td>+0.78</td>
<td>+1.29</td>
<td>+0.29</td>
</tr>
<tr>
<td>4</td>
<td>H1</td>
<td>-22.13</td>
<td>-21.91</td>
<td>-16.44</td>
<td>-0.97</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>+11.28</td>
<td>11.18</td>
<td>+7.21</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>-1.41</td>
<td>-1.40</td>
<td>-0.99</td>
<td>+0.07</td>
</tr>
<tr>
<td></td>
<td>H4</td>
<td>+0.16</td>
<td>0.15</td>
<td>+0.20</td>
<td>+0.02</td>
</tr>
</tbody>
</table>
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.