Molecular Orbital Calculation on 1,2-Difuryl- and 1,2-Dithienyl-ethylenes and Their Photocyclisation Products the Benzodifuranes and Benzodithiophenes

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Es werden die HMO-Berechnungen der 1,2-Difuryl- und 1,2-Dithienyl-äthylene sowie die bei der photochemischen Cyclodehydrierung dieser Verbindungen entstehenden Benzodifurane und Benzodithiophene mitgeteilt. Die chemische Reaktivität dieser Verbindungen wird an Hand der berechneten Reaktivitätsindices vorausgesagt.

During the last year a series of publications has dealt with the photochemistry of 1,2-difuryl- and 1,2-dithienyl-ethylenes 1–3. These compounds undergo photochemical cis-trans isomerization 1 as well as

\[ E_\pi = \text{total } \pi\text{-energy for the ground state. } E_\pi^* = \text{total } \pi\text{-energy for the excited state.} \]

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1,2-Di-(3-furyl)-ethylene  
Benzo[1,2-b:4,3-b']-difuran

\[ E_{\pi} = 18.5549 \quad E_{\pi} = 17.2076 \]

1,3-Di-(2-thienyl)-ethylene  
Benzo[2,1-b:3,4-b']-dithiophene

\[ E_{\pi} = 15.1286 \quad E_{\pi} = 13.8420 \]

1,2-Di-(2-furyl)-ethylene  
Benzo[1,2-b:4,3-b']-difuran

\[ E_{\pi} = 18.5561 \quad E_{\pi} = 17.2985 \]

1,2-Di-(2-thienyl)-ethylene  
Benzo[1,2-b:4,3-b']-dithiophene

\[ E_{\pi} = 15.1392 \quad E_{\pi} = 13.9338 \]
photocyclisation. In presence of oxidizing agents, 1,2-dithienyl-ethylenes yield benzodithiophenes. Similarly, 1,2-di-(2-furyl)-ethylene results benzo[1,2-b:4,3-b']-dithiophene are unknown, are now available.

By means of this photocyclodehydrogenation the unsubstituted compounds of benzodifuranes and benzodithiophenes which besides the benzo[1,2-b:4,3-b']-dithiophene are unknown, are now available.

The present communication reports a theoretical study of some 1,2-difuryl- and 1,2-dithienyl-ethylenes in order to get some information about the mechanism of the photocyclisation. Furthermore we report the reactivity indices of the benzodifuranes and benzodithiophenes regarding substitution reactions as to predict the positions of electrophilic, nucleophilic and radical attack.

**Theoretical Approach**

In general the photocyclisation of 1,2-difuryl- and 1,2-dithienyl-ethylenes produces six possible isomers of benzodifuran as well as benzodithiophenes. From chemical argumentations accompanying the photocyclisation only the following isomers should be stable compounds: benzo[1,2-b:3,4-b']-difuran (1) and -dithiophene (1a), benzo[1,2-b:4,3-b']-difuran (2) and -dithiophene (2a) and the benzo[2,1-b:3,4-b']-difuran (3) and -dithiophene (3a). To these six molecules and the corresponding three difuryl- and dithienyl-ethylenes we applied the MO-theory within the framework of the Höcker 1 method. The assumption was made that all investigated molecules are planar. The empirical parameters used in the calculation are shown in table I.

<table>
<thead>
<tr>
<th>Ethylene-1,2-difuranes</th>
<th>Thiophenes</th>
<th>Benzodifuranes</th>
<th>Thiophenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>$\alpha + 0.02 \beta$</td>
<td>$\alpha + 0.02 \beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>$\alpha + 1.72 \beta$</td>
<td>$\alpha + 0.93 \beta$</td>
<td>$\alpha + 1.72 \beta$</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>$\beta - 0.04 \beta$</td>
<td>$\beta - 0.02 \beta$</td>
<td>$\beta - 0.04 \beta$</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1.02 $\beta$</td>
<td>1.02 $\beta$</td>
<td>All resonance integrals in the resulting benzene ring are equal to $\beta$</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>0.54 $\beta$</td>
<td>0.60 $\beta$</td>
<td>$\beta = 0.76 \beta$</td>
</tr>
<tr>
<td>$\beta_{34}$</td>
<td>0.76 $\beta$</td>
<td>0.50 $\beta$</td>
<td>$\beta_{34} = 0.64 \beta$</td>
</tr>
<tr>
<td>$\beta_{56}$</td>
<td>0.59 $\beta$</td>
<td>0.64 $\beta$</td>
<td>$\beta_{56} = 0.64 \beta$</td>
</tr>
</tbody>
</table>

Table I. Resonance and Coulomb Integrals. $\ast$ x = heteroatom.

A similar choice of parameter has been given by Sappenfield and Kreevoy for furan and thiophene. We calculated the $\pi$-bond orders, the $\pi$-electron densities, the free valence indices and the total $\pi$-energy of the molecules for the ground and the excited state. The results are presented in the molecular diagrams showing the starting 1,2-disubstituted ethylene and the resulting photocyclodehydrogenation product. All numbers in brackets refer to the excited state. The charge densities are multiplied by 1000. The numbers at the end of the arrows represent the free valence indices. For the seek of simplicity the numbering of the atoms in our skeletal structures is somewhat different. We always count the ethylenic carbon atoms in the difuryl- and dithienyl-ethylenes as 1 and 2, the heteroatom in the rings as 3 and 8 respectively, and the numbering of the remaining ring carbon atoms is going clockwise upward. The same numbering is applied to the photocyclodehydrogenation product.

**Discussion**

The mechanism of the photocyclisation reaction of cis-stilbenes is not completely cleared as yet. Several authors assume that the photochemical part of the reaction proceeds from the excited state of the cis-compound to the ground state of the cyclisation product. An other discussed mechanism suggests that the photochemical ring closure proceeds via vibrationally excited ground state levels of the cis-compound which are reached in a fast $S_1 \rightarrow S_0$ deactivation process from the short living excited singlet state of the cis-compound (Lewis isomerism) in a study of the photocyclisation.
of para- and meta-substituted cis-stilbenes we were able to show that the quantum yield of the photocyclisation \(^{11}\) is going linear with a reactivity index \(q_{st}\), being the product of the electron densities of the reacting \(o,o'\)-positions in the ground state \(^{10}\). Applying this criterion to the photocyclisation of the difuryl- and dithienyl-ethylenes i.e. multiplying the excited and ground state \(\pi\)-electron densities of the reacting positions we obtain the following results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrophilic</th>
<th>Nucleophilic</th>
<th>Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1</td>
<td>6, 11 &gt; 2*</td>
<td>12, 7 &gt; 1</td>
<td>6 ≥ 7, 11, 12</td>
</tr>
<tr>
<td>cis-1a</td>
<td>5, 11 &gt; 1, 2</td>
<td>4, 12 &gt; 1, 2</td>
<td>4, 12 ≥ 5, 11</td>
</tr>
<tr>
<td>cis-2</td>
<td>6, 10 &gt; 1, 2</td>
<td>7, 9 &gt; 1, 2</td>
<td>6, 10 ≥ 7, 9</td>
</tr>
<tr>
<td>cis-3</td>
<td>5, 11 &gt; 1, 2</td>
<td>4, 12 &gt; 1, 2</td>
<td>4, 12 ≥ 5, 11</td>
</tr>
<tr>
<td>cis-3a</td>
<td>6, 10 &gt; 1, 2</td>
<td>7, 9 &gt; 1, 2</td>
<td>7, 9 ≥ 6, 10</td>
</tr>
</tbody>
</table>

Table II. \(q_{st}\)-values for difuryl- and dithienyl-ethylenes.

The \(q_{st}^+\) and \(q_{st}^-\) values predict a photocyclisation probability in the order of \(cis-2 > cis-2a > cis-3 > cis-3a\), \(cis-1 > cis-3\) and \(cis-2 > cis-2a > cis-1 > cis-3 > cis-3a\), respectively. According to the experimental data \(^{2,3}\) the \(cis-2\), \(cis-1a\), \(cis-2a\) and \(cis-3a\)-compounds undergo photocyclisation. With the exception of \(3a\) the oxidation products \(2a\) (90%), \(2\) (24%) and \(1a\) (47%) have been isolated \(^{2,3}\) (yield in parenthesis). In \(cis-3a\) the abstraction of hydrogen leads to a \(\beta\)-thio-substituted radical which undergoes very rapid elimination of the sulfur as thyl radical \(^{**}\). From our theoretical data we can expect that \(1\) can be obtained by photocyclodehydrogenation and \(3\) probably not. On the contrary to the HMO-calculations for the photocyclisation of mono-substituted \(cis\)-stilbenes \(^{10}\) the results of the HMO-calculation for the photocyclisation of 1,2-difuryl- and dithienyl-ethylenes give no distinction whether the photocyclisation proceeds via the excited or the ground state of the \(cis\)-compound. Although the predicted order of the \(q_{st}\)-values (ground state) fits better the experimental data than the \(q_{st}^+\)-values, we feel that the small differences between the \(q_{st}^+\) and \(q_{st}^-\) values do not permit a discrimination on the mechanism of the photocyclisation.

In predicting the chemical reactivities shown in table III we have followed the isolated molecule approximation \(^{12}\) from which we can expect a correla-

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