observation that the mixed endo/exohedral addition patterns lead to energetically favorable products.

Supporting Information available:

Tables of the data presented in Figures 2–4, and of single-point B3LYP energies with 6-311G* and 6-311G(2d,p) basis sets of the endo- and exohedral additions of H and F atoms to (n,n) SWCNTs.

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Rydberg – Valence Interactions in Monoolefins: Dispersing Electronic Properties in 1,1′-Bicyclohexylidene


Functionalized oligo(cyclohexylidene) form an attractive class of molecular building blocks for the development of organic materials for (opto)electronic applications because of their long-range electron transfer properties over several molecular units. The compounds are built from 1,4-linked cyclohexylidene units bridging an electron donating and accepting moiety via an alternating ψ–π–ψ orbital topology. The photoinduced electron transfer process in oligo(cyclohexylidene)s is related to their orbital topology has been the subject of various studies. 1,1′-Bicyclohexylidene (BCH), and its end-functionalized derivatives have shown that through-
bond interactions between the π-system of the exocyclic carbon–carbon bond and the α-orbitals of the sp²-hybridized carbon atoms, of appropriate energy and symmetry, in the cyclohexyl rings are the driving force for the charge separation. Time-resolved measurements of photoinduced currents in a system of self-assembled monolayers of the α,ω-bisulfide derivative of BCH on a gold surfaces and CdSe quantum dots corroborate this conclusion: Strong coupling between the two interfaces is provided by the organic spacer bisulfides.

Although significant progress has been made in the study of the electron-transfer and conductive properties of BCH derivatives, much of their spectroscopy and electronic structure has remained elusive. One of the particularly distressing aspects concerns the character and properties of the lower electronically excited singlet states of BCH itself. A priori, one expects that the absorption spectrum of BCH—similar to that of ethene—would simply exhibit one strong absorption band associated with the ππ* valence state. The gas-phase UV absorption spectrum of BCH shows, in striking contrast, two equally intense bands with maxima at 5.95 and 6.82 eV and oscillator strengths f of 0.19 and 0.26, respectively. These two bands remain discernible both in solution and the solid state, an observation that has been interpreted as giving evidence for their valence character. Efforts to assign the two low-lying "valence" excitations have led to widely varying assignments. Elucidation of the nature and properties of these excited states is important for various reasons. On the one hand, it is crucial for a rational design of novel materials with user-defined (non)linear optical properties, as has become amply clear, for example, from attempts to model the (non)linear optical properties of donor/acceptor systems like push–pull stilbenes. On the other hand, studies of other monoolefins—ranging from tetramethylethene to steroids—suggest the presence of two low-lying valence-like states in these molecules as well. Hence, unraveling the electronic structure of BCH has far-reaching implications for our understanding of the electronic structure of the entire class of monoolefinic compounds.

In order to settle these issues, we have recently performed an excited-state PES study of the excited singlet states of isolated BCH in the gas phase. Surprisingly, no indication was found for the presence of a state around 6.82 eV with any of the previously proposed valence characters. Instead, states were observed that took place between the ππ* valence and the Rydberg manifold as a function of the diffuseness of the basis set employed and the effect of this mixing on the electronic properties of the excited states. The calculations have been performed with the Gaussian 98 suite of programs using the MP2/6-31G* optimized structure of anti-BCH. We are well aware that considerably higher levels of calculation exist, but the size of the bicyclohexyldiene system precludes the use of them in the present study. For the spectroscopic properties of the parent molecule ethene, the CIS level has been shown to be adequate, and we may therefore be confident that for BCH this will also be the case.

To take the Rydberg character in the description of the excited states appropriately into account necessitates the use of highly diffuse basis sets. The influence of the diffuseness of the basis set has been established by calculation of vertical excitation energies and oscillator strengths for the anti-conformer of BCH with the a) 6-31G, b) 6-311G*, c) 6-311(+)G*, d) 6-311(2→+G), and e) 6-311(2→,2→+G**) basis sets. In Figure 1 the CIS-predicted vertical excitation energies are plotted as a function of the basis set. Similar to conclusions reached in an earlier ab initio study on ethene, the vertical excitation energies appear to be converged using either one of the two largest basis sets (6-311(2→+G* and 6-311(2→,2→+G**).

Table 1 reports the CIS-predicted vertical excitation energies and oscillator strengths of the transitions to the twelve lower excited singlet states of anti-BCH obtained with the five different basis sets. The results clearly show that increasing the diffuseness of the basis set concomitantly leads to a sharp decrease of

![Figure 1. Dependence of CIS excitation energies on basis set for anti-1,1'-bicyclohexyldiene (BCH). a) 6-31G, b) 6-311G*, c) 6-311(+)G*, d) 6-311(2→+G* and e) 6-311(2→,2→+G**.](image-url)
the oscillator strength of the \( 1B_\alpha(\pi\pi^*) \) valence state transition and an increase of the oscillator strength of the transition to another excited singlet state of \( B_u \) symmetry, located about 0.5–1.0 eV above the \( 1B_\alpha(\pi\pi^*) \) valence state. For the two largest basis sets, it is noteworthy that the transition to the \( 51B_\alpha \), instead of the \( 21B_\alpha \), state obtains the largest oscillator strength. Although the absolute oscillator strengths should be regarded with caution, the calculated ratio of the oscillator strength of the transition to the \( 21B_\alpha \) and \( 51B_\alpha \) states (0.79 and 0.68 for 6-311G* and 6-311(2+G** basis sets, respectively) is in excellent agreement with the experimentally determined ratio of 0.73. [28] The behavior of the oscillator strengths gives compelling evidence for configuration mixing between the \( \pi\pi^* \) state and the Rydberg manifold. Addition of diffuse sp functions on the carbon atoms strongly decreases the vertical excitation energies of the Rydberg states and leads to a diminishing energy gap between the unperturbed \( 1B_\alpha(\pi\pi^*) \) valence state and the Rydberg states. As a result, Rydberg–valence mixing is enhanced and the electronic characteristics of the unperturbed states are shared.

Configuration mixing also prominently appears from the electron density distribution in the excited states. Figure 2 shows contour plots of the primary natural orbital of the excited electron from the CIS/6-311G* wave function of the twelve lower excited singlet states of anti-BCH. For the four lower states a Rydberg character in terms of a hydrogenlike orbital is easily deduced; they are assigned as states with 3s and 3p character. For higher excited states this becomes more difficult, because mixing occurs not only between the \( \pi\pi^* \) valence state and the Rydberg manifold but also between the Rydberg states themselves. Nevertheless, the plots definitely show that it is the \( (n,3d) \) Rydberg manifold that engages in configuration interaction with the \( \pi\pi^* \) valence state.

Due to the Rydberg–valence mixing, the electronic radial spatial extent \( \langle R^2 \rangle \) of the interacting states is affected. Since in the triplet manifold the energy gap between the \( 2\pi\pi^* \) valence and the triplet Rydberg states is much larger, Rydberg–valence mixing is even more pronounced.

### Table 1. CIS calculated vertical excitation energies [eV] and oscillator strengths (f) of the twelve lower excited singlet states of anti-BCH as a function of the basis set.

<table>
<thead>
<tr>
<th>state</th>
<th>6-31G energy</th>
<th>f state</th>
<th>6-311G* energy</th>
<th>f state</th>
<th>6-311(2+G*) energy</th>
<th>f state</th>
<th>6-311(2+2+G**) energy</th>
<th>f state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'B_\alpha</td>
<td>7.64</td>
<td>1.0177</td>
<td>1'B_\alpha</td>
<td>7.29</td>
<td>0.9185</td>
<td>1'B_\alpha</td>
<td>6.61</td>
<td>0.2004</td>
</tr>
<tr>
<td>1'B_\beta</td>
<td>9.08</td>
<td>0.0000</td>
<td>2'B_\beta</td>
<td>8.45</td>
<td>0.0955</td>
<td>2'B_\beta</td>
<td>7.02</td>
<td>0.0000</td>
</tr>
<tr>
<td>1'A_\alpha</td>
<td>9.79</td>
<td>0.0361</td>
<td>2'A_\alpha</td>
<td>8.76</td>
<td>0.0000</td>
<td>1'A_\alpha</td>
<td>7.29</td>
<td>0.0000</td>
</tr>
<tr>
<td>2'A_\beta</td>
<td>9.84</td>
<td>0.0000</td>
<td>1'B_\alpha</td>
<td>8.94</td>
<td>0.0000</td>
<td>2'B_\alpha</td>
<td>7.30</td>
<td>0.5757</td>
</tr>
<tr>
<td>3'A_\gamma</td>
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<td>0.0000</td>
<td>3'B_\alpha</td>
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<td>0.0713</td>
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<tr>
<td>3'B_\alpha</td>
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<td>0.0000</td>
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<td>7.89</td>
<td>0.0151</td>
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<tr>
<td>4'A_\delta</td>
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<td>4'A_\delta</td>
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<td>0.0000</td>
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<tr>
<td>3'B_\gamma</td>
<td>11.04</td>
<td>0.0266</td>
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<tr>
<td>1'A_\beta</td>
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<td>2'A_\gamma</td>
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<tr>
<td>4'B_\alpha</td>
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<td>3'B_\alpha</td>
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<td>0.0000</td>
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<td>8.67</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**Figure 2.** Contour plots (left: 0.001 a.u.; right: 0.01 a.u.) of the primary natural orbital of the excited electron from the CIS/6-311G* wave function of the twelve lower excited singlet states of anti-BCH.
mixing should be reduced considerably in this manifold. Another way to quantify the effect of Rydberg–valence mixing is therefore provided by comparing \( R^2 \) values for corresponding states in the two manifolds. Table 2 gives the vertical excitation energies and the \( R^2 \) values of the twelve lower excited singlet and triplet states of anti-BCH. The results demonstrate unambiguously that the \( 1^1B_u \) state is significantly more diffuse than its triplet counterpart and the electronic ground state. The \( 5^1B_u \) state, on the other hand, is less diffuse than its triplet analog.

In Table 3, these values have been obtained from RPA calculations with the Gaussian98 package.\[23\]

![Table 2](image)

<table>
<thead>
<tr>
<th>State</th>
<th>Singlet Manifold Energy ( (R^2) )</th>
<th>Triplet Manifold Energy ( (R^2) )</th>
<th>( (R^2) - (R^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1^1B_u )</td>
<td>6.30 + 58 6.27 + 50 – 8</td>
<td>( 2^1A_g )</td>
<td>6.49 + 63 6.43 + 58 – 5</td>
</tr>
</tbody>
</table>

[a] Expectation values of the electronic radial spatial extent \( R^2 \) expressed as the difference between the values for each of the excited states minus that of the electronic ground state for \( S_0 \) \( (R^2) = 2639[a] \) at the MP2/6-31G* level.

More advanced RPA calculations confirm the conclusions reached from the CIS calculations (Table 3). Here, extensive mixing with similar consequences on oscillator strengths and \( R^2 \) values is observed as well, albeit slightly less than predicted by the CIS calculations.

The present results have been obtained for the isolated molecule in the gas phase. Since Rydberg states are noticeably more diffuse than valence states, they are more susceptible to external perturbations than valence states. Nevertheless, since the relevant Rydberg states are still of low principal quantum number \( n \), one expects that the energy difference between the \( \pi^* \) valence state and these Rydberg states will not be affected to such an extent that their interaction is changed significantly.\[24\]

The present conclusions are therefore expected to hold for the nonisolated molecule as well.

In conclusion, we have shown that Rydberg–valence mixing provides an explanation for the observation of two intense bands in the UV spectrum of 1,1'-bicyclohexylidene. Due to this coupling, the electronic properties of the unperturbed states are changed, leading for the \( \pi^* \) valence state to a gain in Rydberg character and vice versa for the interacting Rydberg states. Concurrently, the transitions to two or more states with the same symmetry as the \( \pi^* \) state obtain an appreciable oscillator strength. An important consequence of our results is that Rydberg–valence mixing is expected to be a major player in the spectroscopy and photophysics of other monooxins as well. Indeed, for such compounds there is experimental evidence for the presence of more than one state with valence-like properties.\[1, 12\]

\[22\] At room temperature, BCH is present in nearly equal amounts in the anti- and syn-conformations, which rapidly interconvert. Calculations as
A Photochromic Liquid Crystal System

Michel Frigoli and Georg H. Mehl[a]

KEYWORDS:
liquid crystals • molecular switches • photochromism • self-assembly

Understanding the folding behaviour of molecules or supramolecular entities of either synthetic or biological origin is of fundamental importance in a number of disciplines.[1] In this context, the light-induced folding and unfolding of molecules due to the reversible formation and cleavage of covalent bonds is a particularly attractive area of research, as not only is the spatial structure of the molecular entities changed, but other physical properties are modulated as well. These range from electromagnetic absorption behaviour to self-assembly properties, thus making these materials not only highly functional but also potentially very useful as molecular switches. Photochromic organic compounds are very promising systems for achieving these important scientific goals.

The great potential of liquid crystalline systems to be used as optical switches has been recognised: Research has concentrated predominantly on azo groups as the photoactive groups. However, there are reports of other photochromic groups being used, particularly in macromolecular systems,[2,3] but, due to questions associated with the stability of such systems, they have not yet been included in optical switching devices. Hence, finding a reliable class of systems that have liquid crystalline phase behaviour close to ambient temperature, and which are structurally compatible with current liquid crystal systems and technology, is a very promising and necessary area of research.

The use of photochromic groups of modified diarylethene structures, where the photochromism is due to a reversible electrolytisation reaction, has recently been advanced.[4] The thermal stability and versatility of such systems, particularly of heteroazolyl systems, has been demonstrated for a large number of systems.[5] Efforts to synthesise systems which are miscible with liquid crystals have been made by number of researchers.[7]

Our approach is modular, and makes use of a photochromic core, a 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene system connected (using ether linkages, which are known to be beneficial for forming mesomorphic behaviour) to two cyanobiphenyl groups (the mesogens), via spacers of ten methylene groups. The system is shown in Scheme 1. The versatility of this new concept is apparent, and should lead to the systematic investigation of the influence of the photochromic group, the spacer lengths and the mesogens on the properties of such systems.[6]

The synthetic path to the photochromic liquid crystal 1, which can switch to 1a in an electrolytisation reaction, is shown in Scheme 2.[6] The synthesis is convergent in the sense that the mesogenic groups are attached to the phenol groups of the photochromic core 6 in an etherification reaction in the final reaction step. The core, whose synthesis and structure has not yet been reported, was obtained in four reaction steps, starting from 6-methoxybenzothiophene, 2, where the phenol function is protected as a methoxy group. Methylolation at the 2-position of the aromatic ring system, using n-butyllithium at −50 to −40 °C (see Scheme 2), followed by the addition of methyliodide at −78 °C resulted in 3. Bromination at the 3-position using bromine in chloroform resulted in compound 4, and introduced the functionality required for the assembly of the photochromic skeleton. Treating 4 in THF with n-butyllithium at −78 °C, followed by the addition of a semiquivalent amount of octafluorocyclopentene yielded 5. The subsequent reaction of the methoxy groups with boron tribromide resulted in the new functional photochrome 6 (1,2-bis(6-hydroxy-2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene). Following this scheme, compound 1 was synthesised on a gram scale, in an overall yield of 34% based on the starting material 2.

The photochromic properties of compounds 5, 6 and the liquid crystal 1 were investigated in a manner described elsewhere, and the results are listed in Table 1.[9]