Evidence for string-like behaviour in all-trans octatetraene.

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Evidence of Stringlike Behavior in all-trans-Octatetraene

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The versatile nature of polyenes, H(CH)nH, makes them prototypes of biologically active molecules and of polyacycylene, a polymer of fundamental importance in materials science. In the polymer, electron transport has long been modeled in terms of solitons which appear in the dynamics of a linear string of bodies.1 In the pioneering model of polyacycylene,2 the string was described by π electrons that were treated as quantized, with a tight binding scheme, whereas the σ electrons and nuclei were simulated by classical harmonic oscillators. No allowance was made for potential energy functions of bending and out-of-plane motions or for the hybridization of the carbon atoms that forms angles of ∼120°. Although the quasi-particles can appear in high-level calculations, the simplicity and success of the original model indisputably captures the fundamental aspects of the macroscopic phenomena, and the “experimental” detection of stringlike behavior in any polyene would sanction the generality of this ingenious scheme.

To detect the signature of stringlike behavior from experimental data, we selected all-trans-octatetraene, a highly studied polyene.3-7 For alternant hydrocarbons,8 such as octatetraene, a host of information can be obtained on the basis of pseudoparity quantum numbers.9,10 Of interest for the detection of stringlike behavior is that pseudoparity considerations require that the vibronic interaction between electronic states of different pseudoparity be most effective for couplings via bending vibrations.11 This requirement finds strong experimental support in the dipole-forbidden S0(1 1 A(g)) → S1(2 1 A(g)) spectrum of octatetraene where the most intense band is associated with the lowest-frequency in-plane bending vibration of CCC character.4,6,7 This vibrational band owes its intensity to the coupling of S1(2 1 A(g)) with S2(1 1 B(u)).13 Because of this context, it is natural to focus on bending motions of CCC character. If octatetraene were linear, a degenerate counterpart would be associated with each in-plane CCC bending mode. This counterpart is an out-of-plane CCC motion in the real molecule. Stringlike behavior would consequently imply similar roles for in- and out-of-plane motions of CCC character. When one considers the coupling of S0(2 1 A(g)) and S2(1 1 B(u)), the activity of out-of-plane motions would seem forbidden on symmetry arguments. In fact, the out-of-plane vibrations are divided into a and b symmetry and do not have the correct symmetry to mix the two states. But do they not? A combination of any two out-of-plane modes of different symmetry does indeed fulfill the symmetry requirements. Interestingly, if octatetraene becomes a string, the two electronic states still have different symmetries whereas only the a mode, becomes the counterpart of the b in-plane mode. In the real molecule, the remaining b mode can be seen as a helping vibration whose function merely is to “dress” the molecular deformation of octatetraene with the proper symmetry.

To determine the presence of stringlike behavior in octatetraene, one must therefore compare the coupling between S0(2 1 A(g)) and S2(1 1 B(u)) induced by CCC bending vibrations of b symmetry and by the combination of a and b CCC modes. Previously, we have employed quantum-chemical modeling to simulate the first-order vibronic activity in the S0 → S1 → S2 excitation spectrum of all-trans-octatetraene.4,12 The calculated first-order vibronic couplings, are shown in Table 1. Notice that a two-state model gives excellent agreement with the full-scale calculations for the three CCC bending vibrations, νa8, νb7, and νc8. For instance, for the induced transition moment of νc8 it predicts an induced moment of 0.0913 e.Å versus 0.0851 e.Å obtained in our previous calculations.4 We can conclude that in case of the CCC bending modes the vibronically induced intensities are predominantly determined by the S1–S2 couplings, and that pseudoparity rules are almost perfectly obeyed.

The second-order couplings for combinations of out-of-plane modes are shown in Table 2. It is clear that the magnitudes of (12) Vibrationally induced intensities of the b3 false origins were obtained by displacing the molecular geometry along the b3 normal coordinates. From the study of the influence of basis set, electron correlation, and Duschinsky mixing, it was concluded that calculations based on a 6-31G* basis, full CI in the space of 47r and 47*r ground state SCF MOs, and CASSCF/6-31G* force fields could simulate the experimental data satisfactorily.4 The same numerical approach is used to obtain the mixing of the electronic states induced by the vibrational motions. A computer program was therefore written on the basis of the theory developed in ref 13 to calculate by numerical differentiation of the electronic wave functions the vibronic coupling matrix elements.14 Calculation of the first-order couplings was performed using a step size of ∆Q = 0.03 amu1/2 Å, while numerical stability was obtained for second-order couplings with step sizes of ∆Q = ∆Q = 0.025 amu1/2 Å. The accuracy of the calculations was checked by comparison of each matrix element with its transpose.


(14) Ab initio calculations of CI wave functions have been performed with the GAMESS-DAKOTA package: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. QCPE Bull. 1990, 10, 52.
frequencies of the $a_u$ and $b_g$ vibrations in the $2 \, 1 \, A_g$ state. It has furthermore been shown that the relevant bands in the reported excitation spectrum derive from the all-trans-isomer and not from cis–trans or cis–cis isomers. Finally, the possibility raised in ref 6 that all-trans-octatetraene might not be planar has been discarded since the $2 \, 1 \, A_g$ state has been shown to be planar at all levels of ab initio theory (see, for example, refs 4, 17, and 18).

The couplings due to CCC bending vibrations are underlined. The numbers in brackets give the accuracy of the last digits of the calculated value. Entries which have a numerical error larger than the value itself are indicated by #.

### Table 3. Calculated Intensities of Second-Order Vibronic Coupling Induced $1 \, A_g \rightarrow 2 \, 1 \, A_g$ Transitions

<table>
<thead>
<tr>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
<th>$\nu_7$</th>
<th>$\nu_9$</th>
<th>$\nu_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>2.4</td>
<td>0.7</td>
<td>0.1</td>
<td>0.5</td>
<td>3.9</td>
<td>2.0</td>
</tr>
<tr>
<td>147</td>
<td>536.2</td>
<td>817.5</td>
<td>1061.0</td>
<td>2.7</td>
<td>1.0</td>
<td>12.1</td>
</tr>
<tr>
<td>271</td>
<td>27.0</td>
<td>31.3</td>
<td>1.0</td>
<td>3.3</td>
<td>22.5</td>
<td>1.1</td>
</tr>
<tr>
<td>329</td>
<td>1477.8</td>
<td>1498.7</td>
<td>1670.9</td>
<td>1.6</td>
<td>1.8</td>
<td>12.9</td>
</tr>
<tr>
<td>375</td>
<td>870.5</td>
<td>1415.7</td>
<td>34.4</td>
<td>0.9</td>
<td>11.0</td>
<td>0.7</td>
</tr>
<tr>
<td>790</td>
<td>1477.8</td>
<td>1498.7</td>
<td>1670.9</td>
<td>1.6</td>
<td>1.8</td>
<td>12.9</td>
</tr>
<tr>
<td>812</td>
<td>1061.0</td>
<td>1787.5</td>
<td>1834.1</td>
<td>1.6</td>
<td>1.8</td>
<td>12.9</td>
</tr>
</tbody>
</table>

### Table 2. Second-Order Vibronic Coupling Matrix Elements 100 (2 $1 \, A_g$–$|\partial^{2}Q|\partial Q_{1}\partial Q_{2}|2 \, 1 \, B_u$) for Combinations of $a_u$ and $b_g$ Vibrations Expressed in Dimensionless Coordinates $Q$

<table>
<thead>
<tr>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
<th>$\nu_7$</th>
<th>$\nu_9$</th>
<th>$\nu_{10}$</th>
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<tr>
<td>0.545</td>
<td>0.623</td>
<td>1.019</td>
<td>0.886</td>
<td>0.446</td>
<td>0.030</td>
<td>0.460</td>
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<tr>
<td>0.033</td>
<td>1.328</td>
<td>0.313</td>
<td>0.342</td>
<td>0.601</td>
<td>0.946</td>
<td>1.167</td>
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<tr>
<td>0.041</td>
<td>1.699</td>
<td>1.307</td>
<td>0.254</td>
<td>0.432</td>
<td>0.493</td>
<td>0.383</td>
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<tr>
<td>0.359</td>
<td>0.107</td>
<td>0.341</td>
<td>1.017</td>
<td>1.198</td>
<td>0.645</td>
<td>0.968</td>
</tr>
<tr>
<td>0.948</td>
<td>0.680</td>
<td>1.369</td>
<td>0.776</td>
<td>1.289</td>
<td>0.196</td>
<td>0.400</td>
</tr>
<tr>
<td>0.158</td>
<td>0.162</td>
<td>0.680</td>
<td>0.840</td>
<td>0.030</td>
<td>0.156</td>
<td>0.793</td>
</tr>
<tr>
<td>0.504</td>
<td>0.772</td>
<td>0.537</td>
<td>1.031</td>
<td>0.008</td>
<td>0.374</td>
<td>1.514</td>
</tr>
<tr>
<td>0.811</td>
<td>0.835</td>
<td>0.591</td>
<td>0.117</td>
<td>1.074</td>
<td>0.896</td>
<td>1.351</td>
</tr>
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</table>

### Acknowledgment.
We gratefully acknowledge Dr. M. C. van Hemert (University of Leiden) for helpful discussions.

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