TETRAHYDROPHTHALIC ANHYDRIDES AS ADDITION CURING POLYIMIDE END CAPS: THERMAL ISOMERIZATION OF METHYLENDIANILINE 3,6-DIPHENYLTETRAHYDROPHTHALIC BISIMIDES

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Abstract

In-depth NMR studies confirm that heating a 1:2 mixture of \( \text{cis, cis, cis}\) 3,6-diphenyltetrahydrophthalic anhydride (end cap 9\(\text{c}\)) with methylenedianiline at 316 °C initially yields the corresponding highly congested \( \text{cis, cis, cis}\) 3,6-diphenyltetrahydrophthalic bisimide 11, which is converted at this temperature to the observed product, the less hindered \( \text{trans, cis, trans}\) isomer 12.

Introduction

Over the past decade, we have explored the mechanism of the thermal oxidative degradation of addition-curing polyimides, and have shown that it is the end cap which is responsible for much of the observed weight-loss.\(^1\),\(^2\),\(^3\) Further exploration focused on a variety of new end caps in the hope that they would prolong the useful lifetime of polyimide materials.\(^4\),\(^5\) We recently reported in this journal\(^6\) on our reevaluation of tetrahydrophthalic anhydrides 3 as such an end cap. In particular, the preferred Diels-Alder endo-addition of butadienes 1 with maleic anhydride 2 conveniently yields these anhydrides (3) in a \( \text{cis, cis, cis}\) configuration.\(^7\),\(^8\) When this anhydride is heated with methylenedianiline (MDA) to 204 °C, the primary product at this stage was bisimide 5, accompanied by a small amount (<2%) of the intermediate/precursor monoimide 4. Further heating of the bisimide to 371 °C in the presence of air, results in competitive crosslinking and aromatization. (Scheme 1). Under inert conditions, aromatization is inhibited and crosslinking is favored.

Scheme 1
We noted\textsuperscript{6} *en passant* that in the case of the 3,6-diphenyl analog 9c (equivalent to 3: R=R''=Ph; R'=H in general Scheme 1), bisimidization with MDA is slowed by steric hindrance; indeed, the bisimide was the primary product only when the reaction mixture was heated to 316 °C. Noteworthy, however, is the fact the vinyl (H-4 and H-5) and bridgehead (H-1 and H-2) hydrogens in anhydride 9c and monoimide 10 resonate at 6.52±0.03 and 3.67±0.07 ppm, respectively (see Scheme 2). However, after heating to 316 °C, they are observed in the corresponding bisimide ca. 0.5 ppm upfield, at 6.01 and 3.18 ppm, respectively (see Scheme 2 and Table 1). These observations led us to suggest\textsuperscript{6} that this shift corresponds to a conversion of the initially formed highly congested *cis, cis, cis* bisimide 11 (with the phenyls and anhydride rings on the same face) to the less hindered *trans, cis, trans* isomer 12 (Scheme 2); this isomerization will, in turn, affect the diamagnetic anisotropy felt by the aforementioned hydrogens. We report herein several pieces of evidence which confirm this scenario.

Scheme 2

**Experimental**

Solution NMR spectra were obtained on a Bruker DMX-600 spectrometer, in CDCl\textsubscript{3} with TMS as the internal standard. Assignments were facilitated by COSY, NOESY, HMQC and HMBC experiments. The carbon numbering of the various compounds used in the spectral assignments is shown in Scheme 2. Infrared absorptions were determined with a Nicolet 510P FTIR. High-resolution mass spectra (HRMS) were run on a VG-Fison AutoSpecE High Resolution Spectrometer. The synthesis and spectral data for anhydride 9c, monoimide 10 and bisimide 12 have been previously reported.\textsuperscript{6}
Cis, Cis, Cis Methyleneedianiline 3,6-Diphenyltetrahydrophthalic Bisimide (11). The title compound was prepared by refluxing trans, trans-1,4-diphenyl-1,3-butadiene (8, Aldrich, 1.55 g, 7.5 mmol) and 1,1'--(methylene-4,1-phenylene)bismaleimide (13, Aldrich, 1.07 g, 3 mmol) in p-xylene (25 mL) under nitrogen. The reaction was followed by TLC eluting with a 1:1 ethyl acetate/n-hexane solution. Rf values – 8: 0.675 (fluorescent); 11: 0.61; 12: 0.53; 13: 0.1. After 20 h of reflux, essentially all the bisimide had reacted. On cooling to room temperature, a small amount of precipitation was observed, which increased upon the addition of hexane (25 mL). After standing overnight in the refrigerator, the reaction mixture was filtered to yield a yellow solid (1.7 g, 2.2 mmol, 74% yield), which NMR showed to be a mixture of cis, cis, cis bisimide 11 and its trans, cis, trans isomer 12 in a 20:1 ratio. Pure product was obtained via column chromatography (silica, 50:1) eluting with a 1:1 ethyl acetate/n-hexane solution. The NMR resonances appear in Table 1; some splitting constants appear in Table 2, note e.

IR (KBr) 1778 and 1709 (imide C=O), 1602, 1508 (Ar) cm⁻¹; HRMS (DCl, CH₄) calcd (C₅₃H₄₂N₂O₄, M⁺) 770.3144, obsd 770.3110.

Isomerization of Cis, Cis, Cis Bisimide 11. A sample (70 mg, 0.091 mmol) of the above prepared bisimide 11, containing 5% 12, was dissolved in a dioxane solution (14 mL) containing conc. HCl (30% by volume) and stirred for 4 days. The progress of the isomerization was followed by TLC, eluting as above with a 1:1 ethyl acetate/n-hexane solution. The dioxane was diluted with CHCl₃ (10 mL) and water (10 mL), and solid K₂CO₃ was slowly added with stirring until the water phase turned basic. The organic phase was separated and washed with sat. NaCl solution, dried and rotary evaporated. The residue (60 mg, 0.078) was analyzed by NMR to reveal that the 11:12 ratio decreased from 20:1 to 5:1. The bisimides were accompanied
by a few percent of impurities, but these could not be identified. The 11:12 ratio similarly decreased when crude 11 was chromatographed on silica.

**Results and Discussion**

We prepared the *cis, cis, cis* isomer of 11 via a Diels-Alder reaction between diphenylbutadiene 8 and MDA bismaleimide 13 in refluxing p-xylene. The vinyl (H-4 and H-5) and bridgehead (H-1 and H-2) hydrogens in the bisimide 11 formed indeed resonate, as observed for the *cis, cis, cis* anhydride 9c and monoimide 10, at 6.49 and 3.59 ppm – suggesting that 11 too shares the *cis, cis, cis* configuration. Heating a sample of 11 to 316 °C for 30 minutes, converts it completely to bisimide 12.

Further evidence as to the geometry of bisimides 11 and 12 comes from the NMR data, but here the argument is less straightforward. We had initially expected that the geometries and, hence vicinal $^{3}J_{HH}$ coupling constants for a *cis, cis, cis* configuration would be very different from that of its *trans, cis, trans* isomer. To our surprise, however, the multiplets for the relevant protons in the *cis, cis, cis* configured 9c and 11, as well as in (what we maintain to be) the *trans, cis, trans* 12, are actually quite similar, suggesting similar coupling constants.

In order to obtain some basic idea as to what to properly expect, we felt it useful to carry out *ab initio* calculations on models for 11 and 12, namely the *cis, cis, cis* anhydride 9c and its *trans, cis, trans* isomer 9t, respectively (eq. 1).
Gaussian 03 \textit{ab initio} calculations\textsuperscript{9} (performed at the B3LYP level using 6-31G* basis set) for the two anhydrides indicated that in each case the lowest energy structures are not symmetrical – but rather are a pair of enantiomeric conformers. However, each of these molecules should quickly flip back and forth between the two low energy enantiomeric conformers, providing a seemingly symmetrical NMR system at room temperature. (We note in this regard that the energy barrier for the equivalent interconversion process in cyclohexene\textsuperscript{10} is only 5.3 kcal/mol). Relevant dihedral angles from the \textit{ab initio} calculations are provided in Table 2. Very similar geometries were then obtained with molecular mechanics calculations\textsuperscript{11} (see Table 2), which can then be used in turn to predict NMR coupling constants. The latter were then compared to the data extracted from the observed spectra.

We note, however, that the actual vicinal proton-proton coupling constants \((J_{HH})\) are not trivial to determine from the spectrum, as the cyclohexene ring protons form an AA'MM'XX' spin system, with second-order multiplets. But since coupling constants between the bridgehead H-1,2 and the olefinic H-4,5 are expected to be small, the H-1,2 multiplets can be analyzed as part of a \textit{pseudo}-AA'XX' system.\textsuperscript{12}

The aforementioned similarity in the observed splittings for the different configurations can be understood as follows. For \textit{9c}, \textit{9t} and \textit{11}, the values of the vicinal coupling constants between
the bridgehead hydrogens H-1 and H-2 ($^3J_{1,2}$) are in excellent agreement with the calculated dihedral angle of ca. 40° (Table 2 and note e).\textsuperscript{13} Interestingly, the individual vicinal coupling constants ($^3J_{1,6}$ and $^3J_{2,3}$) between the bridgehead hydrogens (H-1 and H-2) and the corresponding adjacent benzylic ones (H-3 and H-6) are actually quite different (respectively, 8.5 and 6.5 Hz in 9c, and 11.3 and 0.5 Hz in 9f). However, because of the rapid flipping described above, all we observe is their averages, which turn out to be quite similar (7.0 and 5.9 Hz) – and in good agreement with experimental results (6.5 and 5.7 Hz).

The other coupling constants involved ($^5J_{3,6}$ and the averages of $^4J_{1,3}$ and $^4J_{2,6}$) are close to zero (0.0±0.3 Hz) in all cases, as expected.

As noted above, the chemical shift of the olefinic protons in the cis, cis, cis configured 9c and 11 differ substantially from that of the trans, cis, trans 12; nevertheless, these protons always appear as broad ca. 1.5 Hz triplets. The observed splitting is the algebraic average of four values.\textsuperscript{12} The first two are the relatively small positive vicinal coupling constants ($^3J_{3,4}$ and $^3J_{5,6}$ = ca. 3.5 Hz, see Table 2), while the other two are the relatively large negative values (ca. −1 Hz) expected for the allylic coupling constants. The latter result from the fact that the allylic protons are largely perpendicular to the planes of the double bonds.\textsuperscript{12}

In summary, then, the values of proton-proton coupling constants for 9c, 11 and 12, while not unexpected, are too similar to be diagnostic of their respective configuration. We, therefore, turned to the vicinal carbon-proton interactions, examining the presence or absence of the relevant peaks in the two-dimensional HMBC spectrum. Because of symmetry, geminal C-H interactions also contribute cross-peaks, making a more quantitative analysis difficult. Nevertheless, Table 3 clearly indicates that the CH long-range coupling patterns fall into two groups: 9c and 11, on one hand, and 12, on the other. This validates our assertion that the
different groups are of different conformations: 9c and 11 share a *cis, cis, cis* configuration, while 12 has a *trans, cis, trans* one.

We close with the question of mechanism. We have suggested that enolization mediates this thermally initiated *cis-trans* isomerization. Indeed, when a sample of 11, containing 5% 12, was added to a dioxane solution containing conc. HCl (30% by volume) and stirred for 4 days, the 11:12 ratio decreased from 20:1 to 5:1. The 11:12 ratio similarly decreased when crude 11 was chromatographed on silica. It is likely that the steric crowding in 11 becomes particularly problematic at elevated temperatures (316 °C), where the rapidly vibrating phenyl groups knock into the carbonyl systems situated on the same face of the ring. It is the release of the steric blocking which is the driving force of the isomerization.

**Acknowledgment.** We thank the Ethel and David Resnick Chair in Active Chemistry at Bar Ilan and the High Operating Temperature Propulsion Components (HOT_PC) Program at NASA Glenn for their kind and generous support.
Scheme 1: Preparation and Thermolysis of MDA Tetrahydrophthalic Bisimides 5

1 + 2 → 3 → MDA → 4 (monoimide)

3 → 5 (bisimide) → 6 (crosslinking)

5 → 7 (aromatization)
Scheme 2: Preparation and Thermolysis of MDA 3,6-Diphenyltetrahydrophthalic Bisimides 11 and 12

8  +  O       6.55 ppm
       p-xylene  138 °C

Cis,Cis,Cis
Anhydride 9c

3.74 ppm

Cis,Cis,Cis
Monoimide 10

6.50 ppm

MDA
204 °C

9c  316 °C

Cis,Cis,Cis
Bisimide 11

3.59 ppm

6.49 ppm

6.01 ppm

316 °C

Cis,Cis,Cis
Bisimide 11

Trans,Cis,Trans
Bisimide 12

13

138 °C  p-xylene

Cess hundeed?
Table 1: NMR Chemical Shifts for Anhydride 9c and Bisimides 11 and 12.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H</th>
<th>$^{13}$C</th>
<th></th>
<th>$^1$H</th>
<th>$^{13}$C</th>
<th></th>
<th>$^1$H</th>
<th>$^{13}$C</th>
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<tr>
<td>1,2</td>
<td>3.74</td>
<td>47.47</td>
<td>3.59</td>
<td>46.38</td>
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<td>3.18</td>
<td>45.98</td>
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<tr>
<td>3,6</td>
<td>3.84</td>
<td>41.19</td>
<td>3.87</td>
<td>41.57</td>
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<td>3.76</td>
<td>39.76</td>
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</tr>
<tr>
<td>4,5</td>
<td>6.55</td>
<td>132.06</td>
<td>6.49</td>
<td>131.25</td>
<td></td>
<td>6.01</td>
<td>129.87</td>
<td></td>
</tr>
<tr>
<td>7,8</td>
<td>-</td>
<td>169.69</td>
<td>-</td>
<td>174.89</td>
<td>-</td>
<td>-</td>
<td>176.79</td>
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<tr>
<td>$\text{I}^a$</td>
<td>-</td>
<td>137.87</td>
<td>-</td>
<td>139.10</td>
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<td>-</td>
<td>143.46</td>
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<td>$\text{o}^a$</td>
<td>7.38</td>
<td>128.63</td>
<td>7.37</td>
<td>128.29</td>
<td>7.32</td>
<td>128.01</td>
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<td>$\text{m}^a$</td>
<td>7.43</td>
<td>128.72</td>
<td>7.37</td>
<td>128.87</td>
<td>7.35</td>
<td>128.82</td>
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<tr>
<td>$\text{p}^a$</td>
<td>7.36</td>
<td>127.67</td>
<td>7.30</td>
<td>127.10</td>
<td>7.27</td>
<td>127.11</td>
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<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>129.58</td>
<td>-</td>
<td>-</td>
<td>130.00</td>
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<tr>
<td>10</td>
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<td>-</td>
<td>6.86</td>
<td>126.02</td>
<td>7.24</td>
<td>126.17</td>
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<tr>
<td>11</td>
<td>-</td>
<td>-</td>
<td>7.04</td>
<td>129.36</td>
<td>7.24</td>
<td>129.63</td>
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<tr>
<td>12</td>
<td>-</td>
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<td>140.48</td>
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<tr>
<td>13</td>
<td>-</td>
<td>-</td>
<td>3.84</td>
<td>40.84</td>
<td>4.00</td>
<td>41.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. $i$, $o$, $m$, $p$ refer to the phenyl group.
Table 2: Calculated Dihedral Angles and Experimental $^{3}J_{HH}$ Values.

<table>
<thead>
<tr>
<th></th>
<th>Cis, Cis, Cis 9c</th>
<th>Trans, Cis, Trans 9t</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>dihedral angle$^a$</td>
<td>$^{3}J_{HH}$</td>
</tr>
<tr>
<td></td>
<td>mm$^c$</td>
<td>mm$^c$</td>
</tr>
<tr>
<td>H - H</td>
<td>ai$^b$</td>
<td>mm$^c$</td>
</tr>
<tr>
<td>1 - 2</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>1 - 6</td>
<td>22</td>
<td>28</td>
</tr>
<tr>
<td>2 - 3</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td>3 - 4</td>
<td>80</td>
<td>72</td>
</tr>
<tr>
<td>5 - 6</td>
<td>56</td>
<td>49</td>
</tr>
<tr>
<td>4 - 5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

a. Absolute values.

b. *Ab initio*.

c. Molecular mechanics.

d. Since trans, cis, trans anhydride 9t was never obtained experimentally, we have compared its calculated data with the experimental NMR data for the analogous bisimide trans, cis, trans 12$^6$.

e. For 11, $^{3}J_{1,2} = 6.3$, $^{3}J_{1,6} = 6.8$ Hz.
Table 3: $^3J_{CH}$ Interactions from HMBC Spectra$^{a,b}$

<table>
<thead>
<tr>
<th>C – H</th>
<th>9c and 11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 5</td>
<td>–</td>
<td>++</td>
</tr>
<tr>
<td>5 – 1</td>
<td>++</td>
<td>–</td>
</tr>
<tr>
<td>4 – 6</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>6 – 4</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>$i$ – 1</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>$i$ – 4</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

a. May include $^2J_{CH}$ interactions, see text; $i$ refers to ipso carbon of the phenyl group.

b. Relative size of the $^3J_{CH}$ interaction observed: – none; + weak; ++ strong. The HMBC spectrum was optimized for a 10 Hz $J_{CH}$. 
References and Notes


6. Meador, M. A. B.; Frimer, A. A.; Johnston, J. C. Macromolecules, 2004, 37, 1289-1296. We note that the FTIR data reported in this paper for compound 12f is in error and should read as follows: IR (KBr) 1778 and 1710 (imide C=O), 1602, 1514 (Ar) cm⁻¹. There are also some minor differences in the NMR chemical shifts and assignments reported herein (see Table 1).


10. (a) Anet, F. A. L.; Haq, M. Z. J. Am. Chem. Soc. 1965, 87, 3147-3150. (b) Jensen, F. R.; Bushweller, C. H. J. Am. Chem. Soc. 1969, 91, 5774-5782. (c) Substitution as observed in bisimide 11 is highly unlikely to triple this barrier to ca. 15 kcal/mol - the barrier at which at which extensive experience teaches us that two sets of peaks would normally be seen.

11. PCMODEL version 7.50.00, Serena Software, Bloomington, Indiana, USA. PCMODEL uses the MMX force field of J.J. Gajewski and K.E. Gilbert which is derived from the MM2 force field of N.L. Allinger. We note, however, that while molecular mechanics does generate the two asymmetric conformers, it actually indicates that the lowest energy structures (by 0.7 and 1.8 kcal.mol\(^{-1}\) for 9e and 9t, respectively) are different, symmetrical ones. We have used, however, the \textit{ab initio} calculations\(^9\) because of their greater degree of exactness and reliability. What’s more, we believe that the experimental results show (\textit{vide infra}, note 13) that the asymmetric conformations predominate in solution.


13. This is in line with the asymmetrical conformation predicted by \textit{ab initio} calculations. In the symmetrical conformations predicted by molecular mechanics (\textit{vide supra}, note 11), the equivalent dihedral angle would be closer to 0\(^\circ\) and the predicted coupling constants 11.8 Hz.