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

Aryeh A. Frimer,[†,*] *Pessia Gilinsky-Sharon,*[†] *Hugo E. Gottlieb,*[†] *Mary Ann B. Meador*[‡] *and*
J. Christopher Johnston[‡]

Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel and NASA Glenn Research Center, Cleveland, Ohio 44135

---

[*] Ethel and David Resnick Chair in Active Oxygen Chemistry. To whom correspondence should be addressed.

[†] Bar-Ilan University

[‡] NASA Glenn

Abstract

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

#5 means what?

Scheme 1

what does this mean?

We noted[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[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 $CDCl_3$ 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.[6]

***Cis, Cis, Cis* Methylenedianiline 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'-(methylenedi-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. R_f 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 (DCI, CH_4) calcd ($C_{53}H_{42}N_2O_4$, 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 $CHCl_3$ (10 mL) and water (10 mL), and solid K_2CO_3 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

HOW DOES ONE KNOW TO DO THIS?

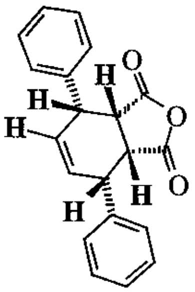
by a few percent of impurities, but these could not be identified. The **11**:**12** ratio similarly decreased when crude **11** was chromatographed on silica.

Results and Discussion

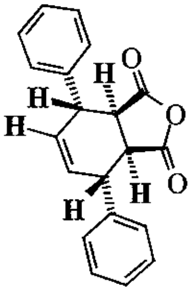
We prepared the *cis, cis, cis* isomer[7,8] **11** *via* a Diels-Alder reaction between diphenylbutadiene **8** and MDA bismaleimide **13** in refluxing p-xylene. The vinyl (H-4 and H-5) and bridgehead (H-1 and H-2) hydrogens in the bisimide **11** formed indeed resonate, as observed for the *cis, cis, 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 $^3J_{HH}$ 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).



Cis,Cis,Cis
Anhydride 9c



Trans,Cis,Trans
Anhydride 9t

(1)

Gaussian 03 *ab initio* calculations[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[10] is only 5.3 kcal/mol). Relevant dihedral angles from the *ab initio* calculations are provided in Table 2. Very similar geometries were then obtained with molecular mechanics calculations[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 ($^3J_{HH}$) 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 *pseudo*-AA'XX' system.[12]

The aforementioned similarity in the observed splittings for the different configurations can be understood as follows. For **9c**, **9t** and **11**, the values of the vicinal coupling constants between the bridgehead hydrogens H-1 and H-2 ($^{3}J_{1,2}$) are in excellent agreement with the calculated dihedral angle of *ca.* 40° (Table 2 and note e).[13] Interestingly, the individual vicinal coupling constants ($^{3}J_{1,6}$ and $^{3}J_{2,3}$) 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 **9t**). 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 ($^{5}J_{3,6}$ and the averages of $^{4}J_{1,3}$ and $^{4}J_{2,6}$) 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.[12] The first two are the relatively small positive vicinal coupling constants ($^{3}J_{3,4}$ and $^{3}J_{5,6}$ = *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.[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.

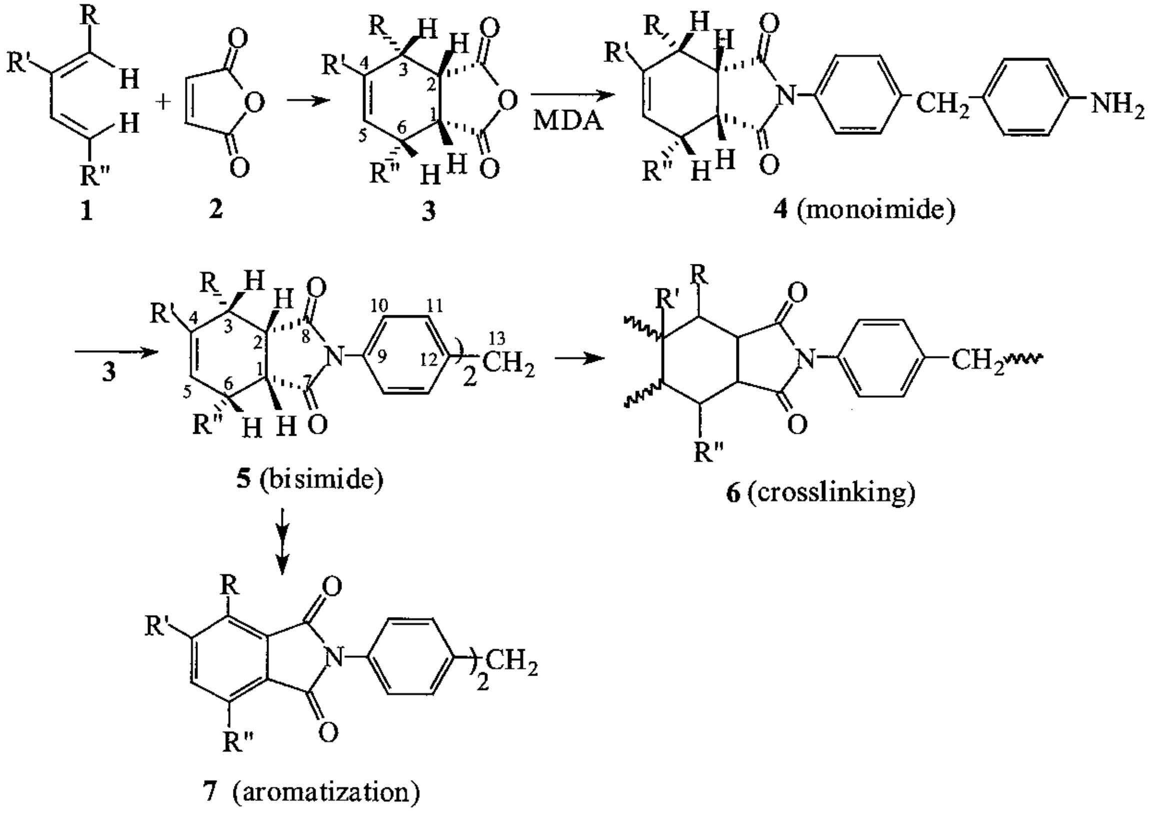
superscript 2.

We close with the question of mechanism. We have suggested[6] 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.

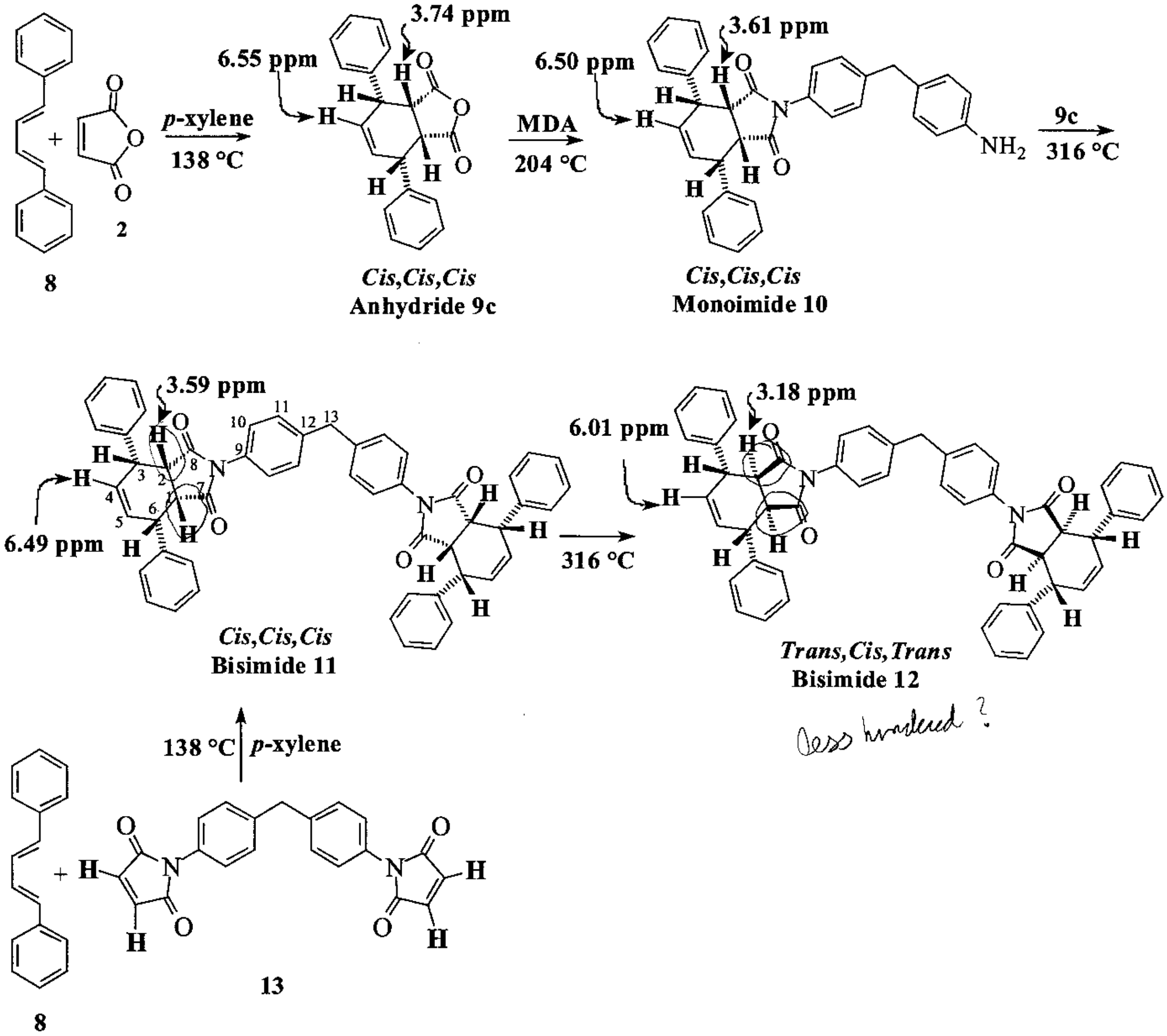
2

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



Scheme 2: Preparation and Thermolysis of MDA 3,6-Diphenyltetrahydrophthalic Bisimides 11 and 12



less hindered ?

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

	9c		**11**		**12**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1,2	3.74	47.47	3.59	46.38	3.18	45.98
3,6	3.84	41.19	3.87	41.57	3.76	39.76
4,5	6.55	132.06	6.49	131.25	6.01	129.87
7,8	–	169.69	–	174.89	–	176.79
i [a]	–	137.87	–	139.10	–	143.46
o [a]	7.38	128.63	7.37	128.29	7.32	128.01
m [a]	7.43	128.72	7.37	128.87	7.35	128.82
p [a]	7.36	127.67	7.30	127.10	7.27	127.11
9	–	–	–	129.58	–	130.00
10	–	–	6.86	126.02	7.24	126.17
11	–	–	7.04	129.36	7.24	129.63
12	–	–	–	140.48	–	140.69
13	–	–	3.84	40.84	4.00	41.04

a. *i, o, m, p* refer to the phenyl group.

Table 2: Calculated Dihedral Angles and Experimental $^3J_{HH}$ Values.

	***Cis, Cis, Cis* 9c**					***Trans, Cis, Trans* 9t**				
	dihedral angle[a]		$^3J_{HH}$	av. $^3J_{HH}$		dihedral angle[a]		$^3J_{HH}$	av. $^3J_{HH}$	
H – H	ai[b]	mm[c]	mm[c]	mm[c]	NMR	ai[b]	mm[c]	mm[c]	mm[c]	NMR[d]
1 – 2	42	39	6.9		7.3[e]	38	39	7.0		5.9
1 – 6	22	28	8.5	7.0	6.5[e]	154	159	11.3	5.9	5.7
2 – 3	43	40	6.5			100	94	0.5		
3 – 4	80	72	3.0	3.7		64	58	3.8	3.3	
5 – 6	56	49	4.3			81	80	2.7		
4 – 5	2	2				1	1			

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**, $^3J_{1,2} = 6.3$, $^3J_{1,6} = 6.8$ Hz.

Table 3: $^3J_{CH}$ Interactions from HMBC Spectra[a,b]

C – H	9c and 11	12
1 – 5	–	++
5 – 1	++	–
4 – 6	–	+
6 – 4	++	++
i – 1	–	+
i – 4	++	+

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

1. Meador, M. A. B.; Lowell, C. E.; Cavano, P. J.; Herrera-Fierro, P. *High Perform. Polym.* **1996**, *8*, 363-379.

2. Meador, M. A. B.; Johnston, J. C.; Cavano, P. J.; Frimer, A. A.; *Macromolecules*, **1997**, *30*, 3215-3223.

3. Meador, M. A. B.; Johnston, J. C.; Cavano, P. J.; Frimer, A. A.; Gilinsky-Sharon, P. *Macromolecules* **1999**, *32*, 5532-5538.

4. Meador, M. A. B.; Johnston, J. C.; Hardy-Green, D.; Frimer, A. A.; Gilinsky-Sharon, P.; Gottlieb, H.E. *Chemistry of Materials*, **2001**, *13*, 2649-2655.

5. Meador, M.A.B.; Frimer, A.A. U.S. Patent Number 6,303,744, October 16, 2001.

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).

7. Ballistreri, F. P.; Maccarone, E.; Perrini, G.; Tomaselli, G. A.; Torre, M. *J. Chem. Soc., Perkin Trans. II*, **1982**, 273-277 and references cited therein.

8. March, J. "Advanced Organic Chemistry - Reactions, Mechanisms and Structure", Fourth Edition; Wiley: New York, 1992; p. 843 and 852.

9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.;

Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Fox, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh PA, 2003.

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 **9c** and **9t**, respectively) are different, symmetrical ones. We have used, however, the *ab initio* calculations[9] because of their greater degree of exactness and reliability. What's more, we believe that the experimental results show (*vide infra*, note 13) that the asymmetric conformations predominate in solution.

12. Gunther, H. "NMR Spectroscopy", Second Edition, Wiley: Chichester, 1995, p. 181-187.

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