Characterization of Geometric Isomers of Norbornene End-Capped Imides

Philip R. Young

NASA Langley Research Center,
Hampton, VA 23665

A. C. Chang

Kentron Technical Center,
Hampton, VA 23666

Received July 19, 1982

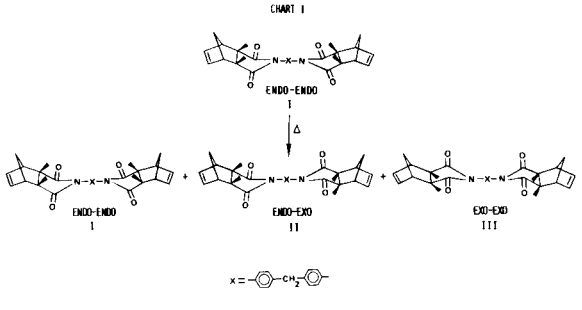
Three geometric isomers from the thermal isomerization of methylene-4,4'-bis(*endo-N*-phenylbicyclo-[2.2.1]hept-2-ene-5,6-dicarboximide) (I) were chromatographically separated and isolated. Nmr spectroscopy was used to assign *endo-endo* (I), *endo-exo* (II), and *exo-exo* (III) configurations to each compound. The three isomers, which serve as model compounds for norbornene end-capped polyimides, were then characterized by several chromatographic, spectroscopic, and thermal techniques. Upon heating, each isomer was found to establish an equilibrium mixture of all three isomers. The possibility that the compounds react by different mechanisms in air and in nitrogen is proposed.

J. Heterocyclic Chem., **20**, 177 (1983).

Introduction.

Norbornene end-capped imide oligomers display considerable promise for use in various aerospace adhesive and composite applications (1). These materials were developed (2-4) in an effort to retain the superior thermal performance of linear condensation polyimides without paying the inherent penalties of evolution of volatiles during cure and generally poor processability associated with that class of polymers. The mechanism by which these end-capped oligomers cure has been the subject of several recent investigations (5-9). Those investigations, primarily concerning *N*-phenylnadimide (IV) and bis-nadimide mixtures, have established an *endo-exo* isomerism of the norbornene group prior to addition-type chain extension through the reactive double bonds. However, several key intermediates have never been reported. This article addresses these compounds; specifically, the *endo-endo* (I), *endo-exo* (II) and *exo-exo* (III) geometric isomers from the thermal isomerization of (I) (See Chart 1).

CHART I



This effort to increase the fundamental understanding of norbornene end-capped oligomers involved the reaction of compound I under mild thermal conditions which rendered the product mostly soluble. The thermal isomerization product was chromatographically prepped and isomers (I) (starting compound), (II) and (III) were recovered. Each isomer was then characterized by a variety of chromatographic, spectroscopic, and thermal techniques. The results of this study are intended to provide insight into the thermal cure of norbornene terminated polyimide systems.

Results and Discussion.

Chromatography and Spectroscopy.

The existence of *endo-exo* isomerism in norbornene containing compounds is well known (5-9). How this isomerism relates to the cure mechanism of norbornene end-capped polyimides is still in question. Previous work in this laboratory showed that when compound I was heated in air to 285°, slightly above its fusion endotherm, 35% of the product remained soluble (10). Figure 1 gives the analytical hplc chromatogram obtained on this soluble

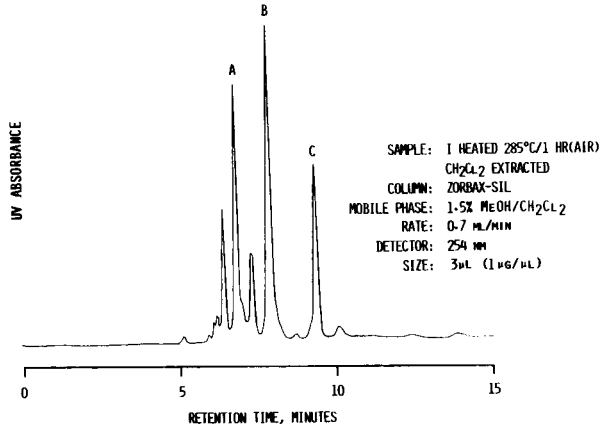
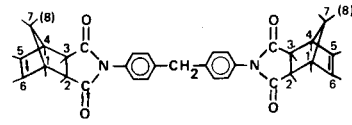


Figure 1. Analytical chromatogram of starting compound I heated to 285° in air for 1 hour.

Table I

^{13}C and ^{1}H Chemical Shifts for Geometric Isomers



	$C_{2,3}$	$C_{1,4}$	$C_{5,6}$	C_7
N-Phenylnadimide IV (a)				
endo	45.5	45.8	134.6	52.2
exo	47.8	45.8	138.0	42.9
Prepped Fraction				
6 (*exo-exo* III)	47.9	45.8	138.0	43.0
9 (*endo-exo* II)	45.5	45.8	134.6	52.2
	47.9	45.8	138.0	43.0
13 (*endo-endo* I)	45.5	45.8	134.6	52.2

	$H_{2,3}$	$H_{1,4}$	$H_{5,6}$	$H_{7,8}$	
N-Phenylnadimide IV (a)					
endo	3.51	3.45	6.27	1.79,	1.62
exo	2.87	3.42	6.36	1.61,	1.50
Prepped Fraction					
6 (*exo-exo* III)	2.84	3.40	6.35	1.55,	1.50
9 (*endo-exo* II)	3.49	3.42	6.25	1.71,	1.62
	2.83	3.42	6.35	1.55	1.50
13 (*endo-endo* I)	3.50	3.43	6.25	1.70,	1.62

(a) From Reference (5).

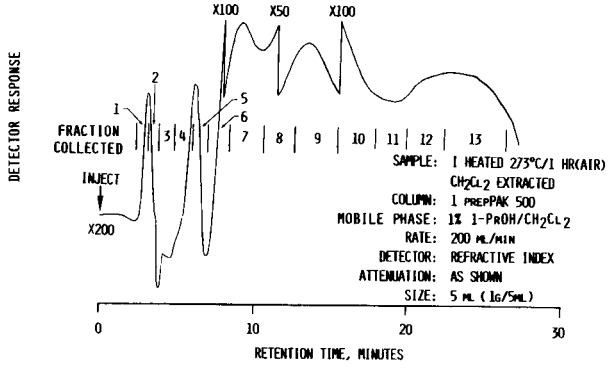


Figure 2. Preparative chromatogram of heated starting compound I.

portion. Three major peaks, initially assumed to be associated with *endo-exo* isomerism, are apparent in the chromatogram. Peak C, the only peak observed before heating, is starting material (I). The isolation and characterization of these major peaks was the prime objective of the present research.

To obtain sufficient sample for further study, 1.00 g of starting material was heated for one hour in air at 273°, a slightly lower temperature than previously employed (10). This time, approximately 87% of the residue remained soluble. The soluble portion was injected onto a

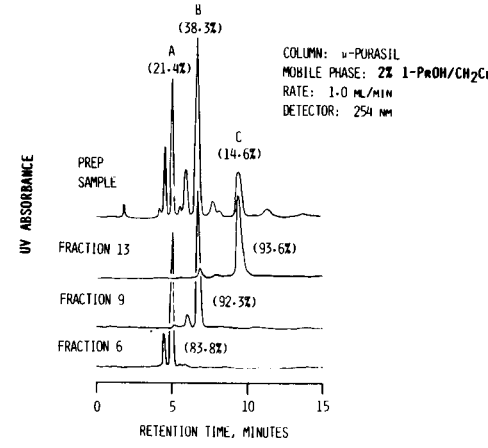
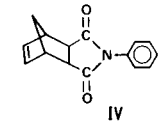


Figure 3. Analytical chromatograms of prepped fractions.

preparative chromatographic column and, as shown in Figure 2, 13 fractions were collected. A sample of each collected fraction was re-injected under analytical conditions to establish identity and purity. As summarized in Figure 3, fractions 6, 9, and 13 contained the particular peaks of interest. Chromatographic peaks A, B, and C, representing 21.4, 38.3, and 14.6%, respectively, of the total peak area for the crude sample, were recovered in 83.8, 92.3, and 93.6% purity. Thus, the preparative technique was quite efficient in purifying the components in the crude sample. The three recovered products were then characterized without further purification.

Figure 4 shows ^{13}C nmr spectra of prepped fractions 6, 9, and 13. Table I summarizes chemical shift data. By comparing chemical shifts with previously reported data for *endo* and *exo* isomers of *N*-phenylnadimide (IV) (5), peak A, contained in fraction 6, was identified as due to the compound where both norbornene end groups are in



IV

the *exo* (III) configuration. Peak C represented the compound with both end groups in the *endo* (I) configuration. Peak B had features common to both configurations and is obviously due to the *endo-exo* (II) isomer. The ^{1}H-nmr chemical shifts for these three isomers are included in Table I. The observed values also agree with previously reported data (5). The nmr spectra provided the most convincing evidence as to the identity of the components in the three chromatographic peaks of interest.

Mass spectra of the three isomers, shown in Figure 5, were quite similar. The actual sample temperature during mass spectral analysis was approximately 100°, too low to cause the compounds to react or isomerize. Thus, the spec-

Table II

Imide IR Absorption for Geometric Isomers

Assignment (a)	C=O Asymmetric stretch	C=O Symmetric stretch	Frequency, cm^{-1} C-N-C Axial vibration	C-N-C Transverse vibration	C-N-C Out-of-plane vibration
Isomer					
endo-endo I	1772 (w)	1706 (s)	1380 (m)	1183 (m)	721 (w)
endo-exo II	1773 (w)	1705 (s)	1381 (m)	1184 (m)	721 (w)
exo-exo III	1774 (w)	1709 (s)	1376 (m)	1195, 1178 (sp) (m)	721 (w)
Other (b)					
endo-N-phenylnadimide IV	1769 (w)	1703 (s)	1377 (m)	1183 (m)	725 (w)
endo-endo I	1772 (w)	1708 (s)	1377 (m)	1180, 1168 (sp) (m)	721 (w)

(a) From reference (11). (b) Highly crystalline starting materials.

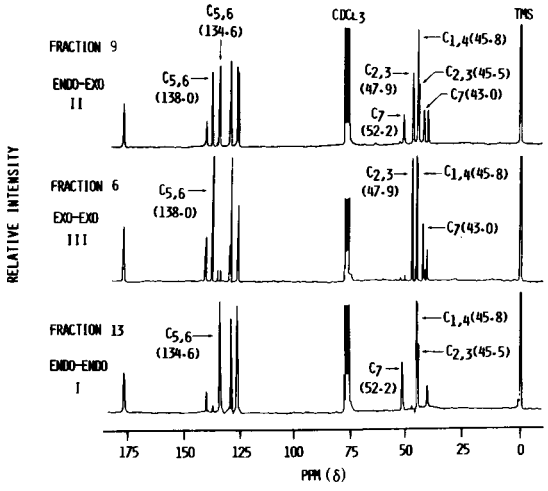


Figure 4. ^{13}C-Nmr spectra of prepped fractions.

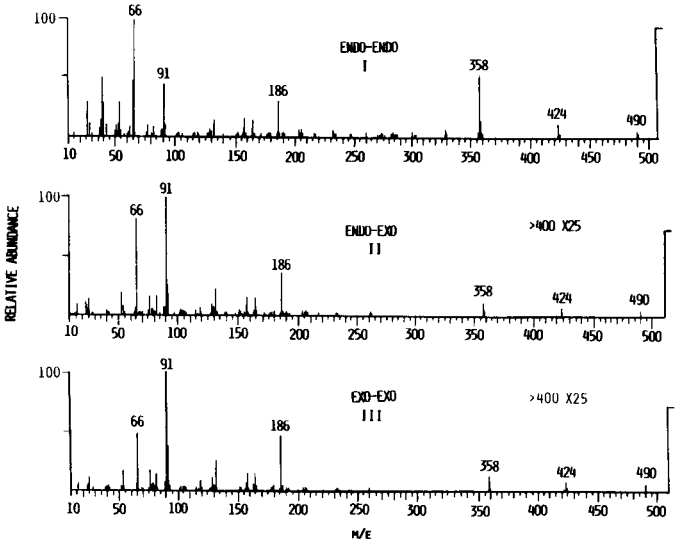


Figure 5. Mass spectra of isomers.

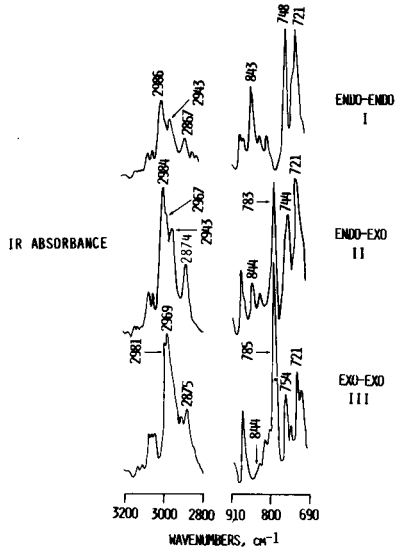


Figure 6. FTir spectra of geometric isomers.

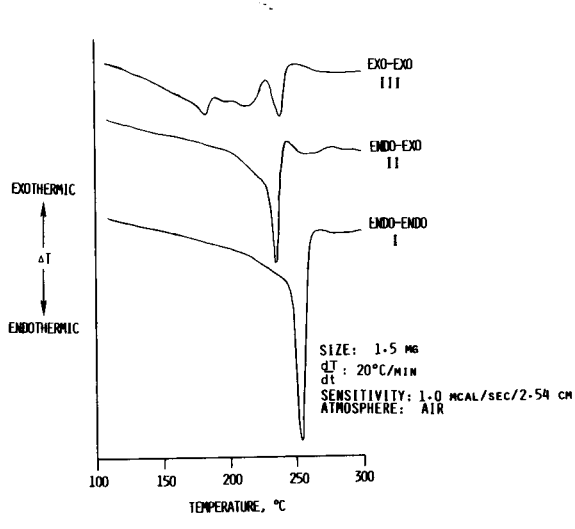
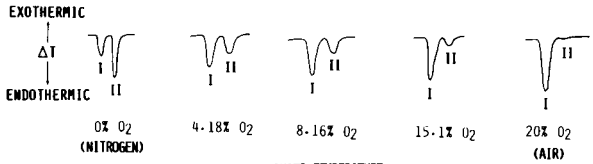


Figure 7. Dsc thermograms of geometric isomers.



% OXYGEN	ΔH (CAL/G) PEAK I	PEAK II	TOTAL
0	9.4	17.6	27.0
4.18	15.5	6.1	21.6
8.16	16.6	4.4	21.0
15.1	20.5	0.6	21.1
20	22.7	—	22.7

Figure 8. Dsc calorimetry for *endo-endo* isomer I.

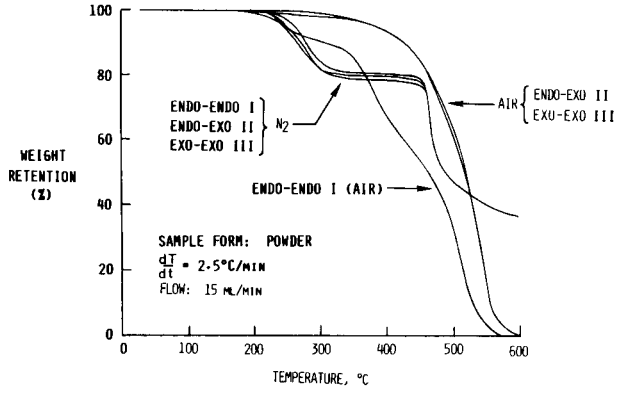


Figure 9. Tga thermograms of geometric isomers in air and in nitrogen.

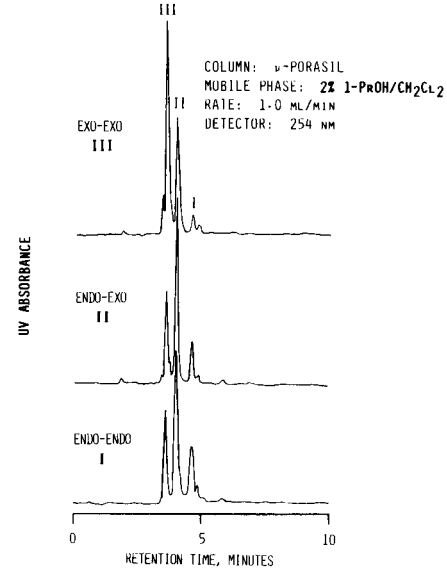


Figure 10. Hplc of geometric isomers heated to 260° in air.

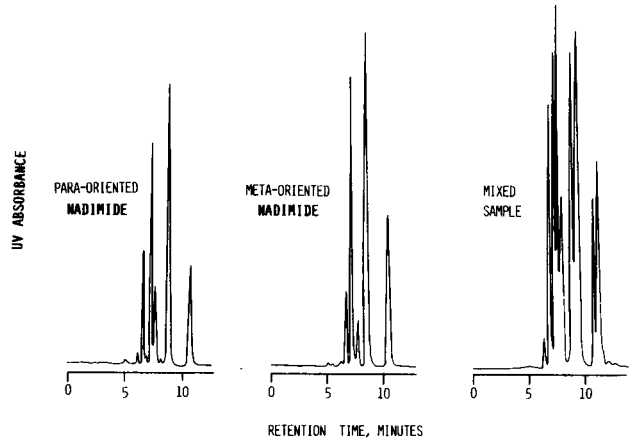


Figure 11. Hplc of *meta-* and *para*-oriented compounds heated to 285° in nitrogen. Conditions: same as in Figure 1.

tra obtained are undoubtedly for unique isomeric configurations. Peaks at m/e 424 and 358 correspond to the loss of one and two molecules of cyclopentadiene (m/e 66) from the molecular ion peak at m/e 490. The m/e 186 peak resulted from fragmentation at the methylene group connecting the aromatic rings. The m/e 91 peak is possibly due to tropylium ion.

Infrared spectra were understandably similar. Table II lists the five bands associated with imide ring vibrations (11). This absorption, based on the imide portion of the molecule, could not be used to distinguish between the three isomers. However, a possible correlation can be made by comparing the aliphatic C-H stretching and skeletal vibration regions of the spectrum between 3000-2800 cm^{-1} and 900-700 cm^{-1}, respectively. These regions are shown in Figure 6. Careful FTir inspection revealed that the *exo-exo* isomer had a band at 2969 cm^{-1} which was absent in the spectrum of the *endo-endo* isomer. This band (2969 cm^{-1}) appeared as a shoulder in the *endo-exo* isomer spectrum. The *exo-exo* isomer also had a unique band at 785 cm^{-1} while the *endo-endo* isomer exhibited a unique band at 843 cm^{-1}. These two bands are of intermediate intensity in the *endo-exo* isomer spectrum. Correlations in this region are particularly apparent if peak heights are made relative to the 721 cm^{-1} imide band. These observations, probably associated with the norbornene portion of the molecule, are not expected to be useful in determining isomerism in cured systems where ir absorption tends to be broader and less well defined.

Thermal Analysis.

Figure 7 shows differential scanning calorimetry (dsc) thermograms of the three prepped samples run in air. The compounds appeared to soften and then undergo fusion. Since these compounds were only about 90% pure, the

thermal transitions are not well defined. However, a purified *endo-endo* sample was extensively studied both in air and in nitrogen. In air, the melt endotherm peaked sharply at 256°. In nitrogen, a small endotherm at 256° followed by a larger endotherm at 265° was observed. The intensity of the two endotherms appeared to be a function of the amount of oxygen in the sample atmosphere. To illustrate, figure 8 shows five dsc thermograms where the oxygen content in the sample atmosphere varied from 0% (pure nitrogen) to 20% (air). Calorimetric data is also included in the figure. Peak I in air and peak II in nitrogen corresppond with visual melting. Peak I increased in intensity period between "melting" and "peak" while peak II decreased as the oxygen content increased. The heat content associated with the two endotherms remained fairly constant. No explanation is offered for this behavior. Similar studies were not made on the *endo-exo* and *exo-exo* isomers.

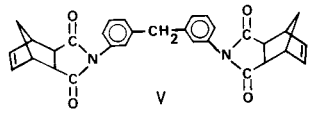
Thermal gravimetric analyses (tga) confirmed the differences in thermal behavior in air and nitrogen. Figure 9 gives weight loss curves for the three isomers in both atmospheres. These curves suggest that two different cure mechanisms are occurring. The nitrogen-cured samples lost the equivalent of 1.5 moles of cyclopentadiene at 300°. With the exception of the *endo-endo* isomer, the air-cured samples did not exhibit significant weight loss until decomposition commenced around 450°. Isothermal weight loss measurements on samples heated at 330° for one hour in air and in nitrogen showed the same effect. In air, the *endo-endo* isomer lost 4.4% of its original weight; in nitrogen, it lost 34.5%.

If different mechanisms indeed occur, the ultimate structure of model compounds cured in the two atmospheres should probably be different. The portions remaining soluble during cure are essentially the same as established by hplc. All attempts to determine a difference in molecular structure of insoluble portions by FTir were unsuccessful. The reverse Diels-Alder mechanisms initially proposed by Burns *et al.* (2) may dominate in nitrogen while a more direct chain extension without the loss of cyclopentadiene may dominate in air. The latter behavior can be explained by mechanisms proposed by Gaylord and Martan (6) or by Wong *et al.* (7-9). The apparently different reaction mechanisms in air and in nitrogen may have implications in the cure of polymeric systems. The environment in which these materials are cured may be reflected in their performance.

Thermal Isomerism.

Samples of the *exo-exo* and *endo-exo* isomers were each heated to 260° in air and chromatographically analyzed to determine whether their individual molecular structure was retained at this temperature. Figure 10 gives chromatograms for these two samples as well as that obtained for the prepped *endo-endo* isomer also heated to 260°. Chromatograms before heating are given in Figure 3. The chromatographs in Figure 10 clearly establish that each compound isomerized to a mixture of all three compounds when heated. A more comprehensive study probably would have shown that the same equilibrium mixture of isomers is established regardless of the geometric configuration of the initial isomer.

Some novel observations were made while studying compound V, obtained by using 3,3'-methylenedianiline as



V

the aromatic diamine. The kinetically favored *endo-endo* configuration is undoubtedly obtained when the compound is synthesized. Under thermal conditions, this material exhibited the same isomerism as the para-oriented compound. Figure 11 compares the chromatograms of the two isomers heated to 285° in nitrogen. The amounts of the various isomerization products were essentially the same. Figure 11 also shows the chromatogram obtained on an artificial mixture of the two samples. *Endo-endo, endo-exo,* and *exo-exo* geometrical isomers in this mixed sample were separated based on the positional orientation of the amine nitrogens in the methylenedianiline portion of the molecule.

Summary.

In summary, three geometric isomers associated with the thermal isomerism of (I) were chromatographically separated and isolated. Nmr spectroscopy was used to assign *endo-endo, endo-exo,* and *exo-exo* configurations to each isomer. Fundamental characterization information was then obtained using ms, FTir, dsc, tga, and hplc techniques. Each compound appeared to thermally isomerize to an equilibrium mixture of all three compounds prior to cure. A meta-oriented model compound was shown by hplc to behave in the same manner as the more extensively studied para-oriented model. Finally, the possibility that these compounds react by different mechanisms depending on the sample atmosphere was proposed.

EXPERIMENTAL

General.

Analytical separations were obtained on a Waters Associates ALC/GPC-244 hplc equipped with a Model 6000A Solvent Delivery System, Model 720 System Controller, and Model 730 Data Module. Analyses were performed at 254 nm on either Waters μ-Porasil (3.9 mm id × 30 cm) or DuPont Zorbax-Sil (4.6 mm id × 25 cm) columns. Preparative separations were performed on a Waters PrepLC/System 500 using a PrepPak-500/Silica column. The mobile phase for all separation was prepared from chromatographic grade methylene chloride,

methanol, and 1-propanol. Carbon-13 nmr spectra were run on a Varian Model XL-100-15 FT-NMR spectrometer (12). Proton nmr spectra were recorded on a Varian EM-360A spectrometer. Chemical shifts are expressed in parts per million (δ values) relative to an internal TMS standard. All experiments were performed at 30° with deuterated chloroform as the solvent.

Mass spectral data were collected on a Finnigan Model 3300 Quadrapole Mass Spectrometer equipped with a Model 6000 Data System. Samples were introduced into the ion source by a programmable temperature solid inlet probe. A 70 eV fragmtation spectrum was obtained by continuously scanning the 10-1000 amu range while the sample was heated at 3°/minute from the ion source temperature (100°) to a temperature where sufficient sample had vaporized to obtain a usable spectrum.

The ir spectra of potassium bromide pellets were recorded on a Nicolet 3600A FTIR system. All ir absorption values are expressed in wave numbers (cm^{-1}) and intensitities are indicated by the symbols s (strong), m (medium), w (weak) and sp (split). Thermal analyses were performed on a DuPont Model 990 Thermal Analyzer in combination with a standard dsc cell. Each sample was weighed and hermetically sealed in DuPont supplied cups. Premixed gases provided the appropriate sample atmosphere. Three determinations were made in the time base mode for each sample and transition areas were measured with a planimeter by drawing a line from the point where the thermogram departed from the baseline to where it returned. Peak area was calibrated using indium as the standard.

Weight loss as a function of temperature was determined on a Perkin-Elmer TGS-2 Thermogravimetric System. Approximately 2.0 mg samples were programmed at 2.5°/minute in 15 ml/minute flowing air and nitrogen.

Preparation of Model Compounds.

Model compounds were prepared under a grant with Mississippi University for Women, Dr. J. Richard Pratt, Principal Investigator (13). In general, imidized compounds were synthesized by reacting stoichiometric amounts of the recrystallized or distilled amine with sublimed *endo*-5-norbornene-2,3-dicarboxylic anhydride in refluxing glacial acetic acid for 3 hours. The product was precipitated into water, recovered, washed with water until neutral, and recrystallized from acetone.

Methylene-4,4'-bis(*endo-N*-phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide) (I).

Anal. Calcd. for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71; O, 13.05. Found: C, 76.03; H, 5.18; N, 5.39; O, 12.92.

Endo-N-phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (*N*-phenylnadimide) (IV).

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85; O, 13.37. Found: C, 75.13; H, 5.41; N, 5.63; O, 13.00.

Methylene-3,3'-bis(*endo-N*-phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide) (V).

Anal. Calcd. for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34. Found: C, 75.95; H, 5.33.

Thermal Reaction of Model Compound I.

Compound I, 1.000 g, in a covered ceramic crucible, was placed in a forced air oven at 273° for 1 hour. Upon cooling, a 1.8% weight loss was determined and the residue was extracted with boiling methylene chloride. Filtration yielded a 13.3% insoluble fraction which was apparently polymer. The soluble portion was obtained upon evaporation of the solvent.

Preparative Chromatography.

Preparative chromatographic conditions were established on the analytical chromatograph. The silica prep column was first deactivated by purging with 2000 ml of 10% 1-propanol in methylene chloride and then brought into equilibrium with the 1% 1-propanol in methylene chloride mobile phase. Approximately 0.85 g of the thermal reaction product in 5 ml of mobile phase was injected. The collection of 13 fractions was aided by monitoring the developing chromatogram. Solvent was removed from each fraction on a rotary evaporator and the residue reinjected under analytical chromatographic conditions to establish purity and peak identity. Fractions 6 and 7 were combined to give 76.5 mg (83.8% 1c purity) of what was determined to be the *exo-exo* isomer. Fraction 9 contained 114.5 mg (92.3% 1c purity) of *endo-exo* isomer, and fractions 12 and 13 were combined to yield 57.8 mg (93.6% 1c purity) of *endo-endo* isomer. These three samples were characterized without further treatment. Almost 50% of the injected sample was recovered in the 13 collected fractions.

Acknowledgements.

The authors gratefully acknowledge the technical assistance of Karen S. Whitley, K. Mason Proctor, and James F. Dezern in determining the thermal analyses and mass spectra. The efforts of John G. Dillard and Thomas E. Glass at Virginia Polytechnic Institute and State University in obtaining the ^{13}C-nmr spectra are also appreciated.

REFERENCES AND NOTES

(1) Graphite/Polyimide Composites, NASA CP-2079, 1979, and references therein.

(2) E. A. Burns, R. J. Jones, R. W. Vaughan, and W. P. Kendrick, NASA CR-72633, January 1970.

(3) T. T. Serafini, P. Delvigs, and G.R . Lightsey, *J. Appl. Polym. Sci.*, **16**, 905 (1972).

(4) T. L. St. Clair and R. A. Jewell, 8th Nat. SAMPE Tech. Conf., *Prepr.*, **8**, 82 (1976).

(5) A. C. Wong and W. M. Ritchey, *Spectroc. Letters*, **13** (7), 503 (1980).

(6) N. G. Gaylord and M. Martan, *Am. Chem. Soc., Div. Polym. Chem. Prepr.*, **22** (1), 11 (1981).

(7) A. C. Wong and W. M. Ritchey, *Macromolecules*, **14**, 825 (1981).

(8) A. C. Wong, A. N. Garroway, and W. M. Ritchey, *ibid.*, **14**, 832 (1981).

(9) A. C. Wong, Ph.D. Dissertation, Case Western Reserve Univ., Cleveland, Ohio, Univ. Microfilms Order No. 8118640, 1981.

(10) P. R. Young, NASA TM-83192, August 1981.

(11) R. A. Dine-Hart and W. W. Wright, *Makromol. Chem.*, **143**, 189 (1971).

(12) NASA Contract NAS1-15080, Task Order 20, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

(13) NASA Grant NSG-1539, Mississippi University for Women, Columbus, MS 39701.