Benzonorbornadiene End Caps for PMR Resins

Michael J. Panigot,† John F. Waters,†,‡ Uday Varde,† James K. Sutter,‡ and Chaim N. Sukenik*,†

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and Polymer Science Branch, NASA Lewis Research Center, Cleveland, Ohio 44135

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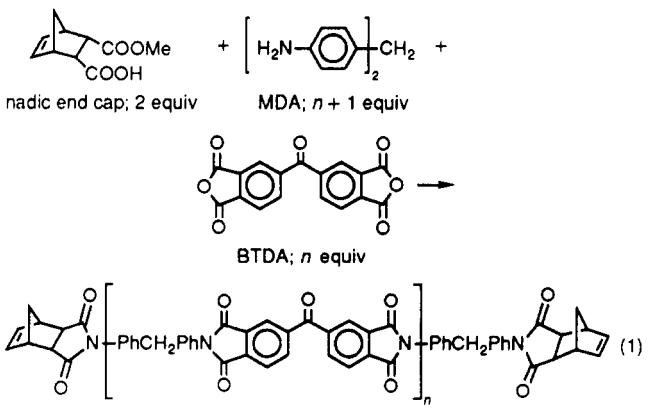
ABSTRACT: Several ortho-disubstituted benzonorbornadiene derivatives are described. These molecules contain acid, ester, or anhydride functionality permitting their use as end caps in PMR (polymerization of monomer reactants) polyimide systems. The replacement of the currently used norbornenyl end caps with benzonorbornadienyl end caps affords resins of increased aromatic content. It also allows evaluation of some mechanistic aspects of PMR cross-linking. Initial testing of *N*-phenylimide model compounds and of actual resin formulations using the benzonorbornadienyl end cap reveals that they undergo efficient thermal cross-linking to give oligomers with physical properties and thermal stability comparable to commercial norbornene-end-capped PMR systems.

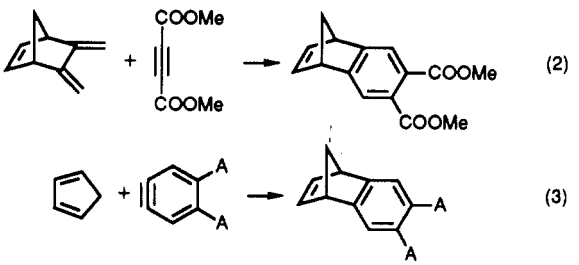
PMR-15 (polymerization of monomer reactants), developed jointly by NASA and TRW,[1] is a commercially important polyimide-based composite with good high-temperature properties. Imidization of the indicated monomers (eq 1) is followed by a higher temperature curing.



The molecular weight of the resin is controlled by end-capping molecules which are also responsible for cross-linking the cured composite. Despite its commercial success, lowering the cross-linking temperature and/or improving the thermal stability of the PMR resin are still important research and development goals.[1b] Since the cross-linking of these polyimide oligomers occurs through their end caps and since it has been demonstrated that the nadic end cap contributes the most to the thermal decomposition of PMR resins,[1c] we have approached the study and improvement of PMR-15 by modifying its norbornenyl end cap. Modification involving the substitution of both the bridgehead and vinyl positions of the norbornenyl ring has been reported elsewhere.[2] We herein address the use of benzonorbornadienyl end caps.

Benzonorbornadienyl incorporation should have a number of ramifications: (1) replacing the substituted succinic acid derivative of the nadic end cap with a phthalic acid derived unit should give the end cap imide-forming reactivity more comparable to that of the BTDA units (eq 1) providing a more predictable distribution of oligomer molecular weight; (2) the retro-Diels–Alder (RDA) reaction that is readily available to the norbornenyl end cap[3] would be strongly disfavored; (3) benzonorbornadienes raise the possibility of photochemical reactivity in terms of possible photopolymerization and in terms of end-cap rearrangement via the di-π-methane reaction[4] that is unavailable to norbornenes; (4) if the cross-linking of such imide oligomers could still be achieved by chemistry other than RDA reactions, the resulting resins should have increased aromatic content. To the extent that RDA chemistry has been implicated in the thermal polymerization of PMR-15,[5] preventing such reactions might impair the cross-linking of such systems. However, if the thermal cross-linking of the polyimide oligomers still occurred, then preventing RDA reaction and increasing aromatic content might contribute to better high-temperature resin stability.[6]

To allow proper consideration of these issues, an efficient synthesis of suitably substituted benzonorbornadienes had to be developed. Two complementary options are the cycloaddition reactions shown below. Reaction of the indicated bicyclotriene with dimethyl acetylenedicarboxylate (eq 2) has been reported.[7] Alternatively, the reaction of cyclopentadiene with substituted benzynes (eq 3; A = acid or its equivalent) has strong analogy.[8]



We report herein an efficient synthesis of the benzonorbornadienyl end cap and its use in PMR resin formulations and (as an *N*-phenylimide) in model studies. The photochemistry of these compounds is described in a separate paper presently in preparation.[9]

Results

A. Syntheses of Monomers and Model Compounds. The diester synthesis shown in eq 2 was adequate for the production of small samples of the desired end-capping material,[10] but it is a low-yield process that is not amenable to scale-up. On the other hand, dibromobenzyne generation and its addition to cyclopentadiene (modeled after Hart et al.[11]), followed by cyanation of the dibromoben-

* Author to whom correspondence should be addressed.
† Case Western Reserve University.
‡ NASA Lewis Research Center.

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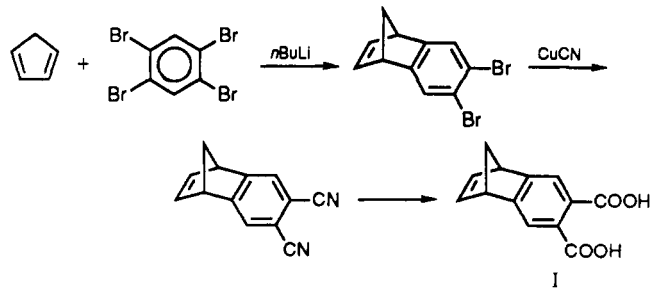
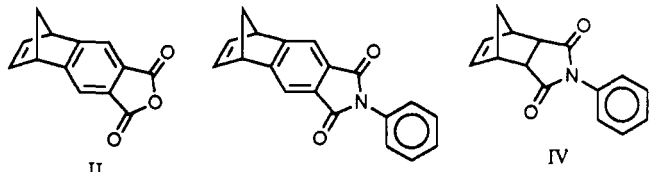
Scheme I



I

zonorbornadiene and hydrolysis of the dinitrile to diacid I, proved to be more practical (Scheme I). Alternative implementations of this scheme (different substituents and/or different benzyne precursors) were less successful.[12]

Compound I served as the starting material for the two substituted benzonorbornadienes needed for this study. It was converted to anhydride II which can be used directly

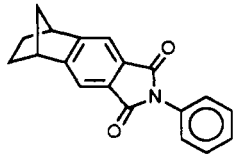


II III IV

or after methanolysis to its half-acid half-ester as a PMR end cap. Also, I, its diester, or anhydride, could be used to make *N*-phenylimide III for use as a model compound with which to study the thermal chemistry of the end cap and compare it to the corresponding nadic *N*-phenylimide IV.[2,13]

B. Thermal Chemistry and Testing of Model Compounds. Thermal cross-linking of benzonorbornadiene units was studied by comparing the behavior of III and IV by a combination of DSC, NMR, and SEC measurements. DSC experiments on the two isomers of IV[13] (endo and exo ring junctions) each show sharp endotherms at their respective melting points and a strong, higher temperature exotherm whose onset coincides with the high-temperature cure of the PMR resin. Similarly, the DSC of III shows the onset of endothermic activity at 147.4 °C (peak at 161.9 °C) and a strong exotherm starting at 308.4 °C which peaks at 351.5 °C.

Samples of III and IV which had been heated (as neat solids) to 250 °C showed a steady disappearance of vinyl protons in their solution NMR spectra. The comparison of aromatic to nonaromatic material in cured samples was done by ^{13}C NMR, and it showed a steady increase in the relative amount of aromatic carbons as the heating of the samples of III proceeded. In the heating of IV, no corresponding increase in the relative aromatic content was observed. Also, as part of the effort to characterize the mixture of materials formed by heating III, as much as 10% of the dihydro compound V was isolated. *None* of the corresponding hydrogenated analogues of IV was found in any of its thermolysis experiments.



V

Table I
Extent of Polymerization of III and IV[a]

entry	temp, °C	time, h	% oligomer III	% oligomer IV
1	195	96	75	32
2	250	1	41 (41)[b]	7 (14)[b] (2)[c]
3		2	56 (52)[b]	12 (24)[b] (2)[c]
4		4	69 (71)[b]	74 (71)[b] (11)[c]
5		24	83	93
6		120, 144	98	
7	285	1	79	10
8		2	88	32
9		3	92	72
10		4	94	79
11		15	98	95
12		24	99	97
13	330	1	98	96

[a] Reactions done in glass tubes sealed under 50-mm vacuum (unless otherwise indicated): temperature, ±5 °C, time, ±2 min. [b] Reactions done under ambient pressure of argon. [c] Sealed under 1.5 × 10^{-3} mm vacuum.

The extent of thermal oligomerization of III at various times and temperatures, as well as a profile of oligomer size and distribution, was determined by size-exclusion chromatography (SEC). Table I reports the progress of oligomer formation from heating neat samples (sealed tube, reduced pressure or inert atmosphere) of III and of IV. SEC analysis was facilitated by the solubility in THF of these model end caps and their thermal products. Table II reports the characterization of these oligomers. These data highlight the similarity of III and IV with regard to the size and polydispersity of the oligomers formed. However, two differences in oligomerization kinetics should be noted. First, entries 2–4 (Table I) indicate that while polymerization of the benzonorbornadienyl unit in III is pressure independent, this is not true for the norbornenyl imide. Second, there is a discontinuity in the rate of oligomer formation from IV that is not seen with III. Comparing entries 3 to 4 and 8 to 9 (Table I) suggests an induction period for the cross-linking of IV that is not seen for III.

C. Formulation and Testing of Molding Powder and Resin Disks. Thermal analyses and analyses of the thermooxidative stability of the cross-linked, benzonorbornadiene-end-capped polyimides were performed on molding powders and resin disks. The molding powders were prepared from II, BTDA, and MDA by chemistry analogous to that shown in eq 1 ($n = 2$) and were held at 260 °C (500 °F) for 1 h after imidization was complete. The resin disks were prepared by heating molding powders under pressure in a die.

DSC analysis (40 °C/min) of molding powders using II as the end cap showed the onset of exothermic activity at 375 °C, consistent with the behavior of the corresponding model compound (III). Rheological testing data were used to assess the viscosity of the heated molding powders as a function of temperature. These tests showed that the commercial PMR-15 system (Hysol brand) melts at 225 °C and polymerizes at 300 °C. Molding powders using II as the end cap both melted and polymerized at approximately 50 °C higher temperature.

Resin disks were tested in the following ways. Thermogravimetric analysis (TGA, 10 °C/min) provided some information about the thermal stability of the modified polyimides. These data indicated that weight loss began at 494 °C, compared to 460 °C for PMR-15.[1c] Thermomechanical analysis (TMA) of the benzonorbornadienyl resin disks showed a glass transition temperature (T_g) of 222 °C, while that of a commercial PMR-15 disk is 275 °C.

The thermooxidative stability of the resin disks was tested with an isothermal weight loss experiment for 1000

Table II
Oligomer Characterization for III and IV[a]

entry	temp (°C)/time (h)	M_n (N) III	M_n (N) IV	M_w III	M_w IV	PDI III	PDI IV
1	195/96	2310 (8.1)	1330 (5.6)	2800	1650	1.21	1.24
2	250/1	2040 (7.1)	1340 (5.6)	3320	1340	1.63	1.24
3	250/2	1970 (6.9)	1420 (5.6)	2280	1920	1.20	1.24
4	250/4	1880 (6.5)	1540 (6.4)	2280	1920	1.21	1.25
5	250/24	2190 (7.6)	1530 (6.3)	2590	1990	1.18	1.30
6	250/120	2110 (7.4)		2470		1.17	
7	250/144	1880 (6.5)		2170		1.15	
8	285/1	2080 (7.2)	1390 (5.8)	2460	1770	1.18	1.28
9	285/4	1730 (6.0)	1400 (5.9)	2230	1750	1.29	1.25
10	285/15	1760 (6.1)	1530 (6.4)	2180	1820	1.24	1.19
11	285/24	1790 (6.2)	1500 (6.3)	2230	2000	1.24	1.33
12	330/1	1720 (6.0)	1790 (7.5)	2100	2150	1.22	1.20
13	330/2	1630 (5.7)	1280 (6.1)	2000	1450	1.23	1.13

[a] Temperatures are ±5 °C; times are ±2 min. Samples were heated in glass tubes sealed under 50-mm vacuum.

Table III
Weight Loss for Resin Disks Aged at 600 °F (316 °C)

polyimide	weight loss, % postcure	250 h	500 h	750 h	1000 h
nadic/BTDA/MDA	1.0 ± 0.2	4.4 ± 0.2	6.6 ± 0.1	10.7 ± 0.5	14.8 ± 0.3
Hysol brand resin	0.8 ± 0.2	3.8 ± 0.2	5.8 ± 0.3	9.0 ± 0.5	12.5 ± 0.5
II/BTDA/MDA	1.8 ± 0.1	3.2 ± 0.3	5.4 ± 0.2	9.3 ± 0.6	12.9 ± 0.6

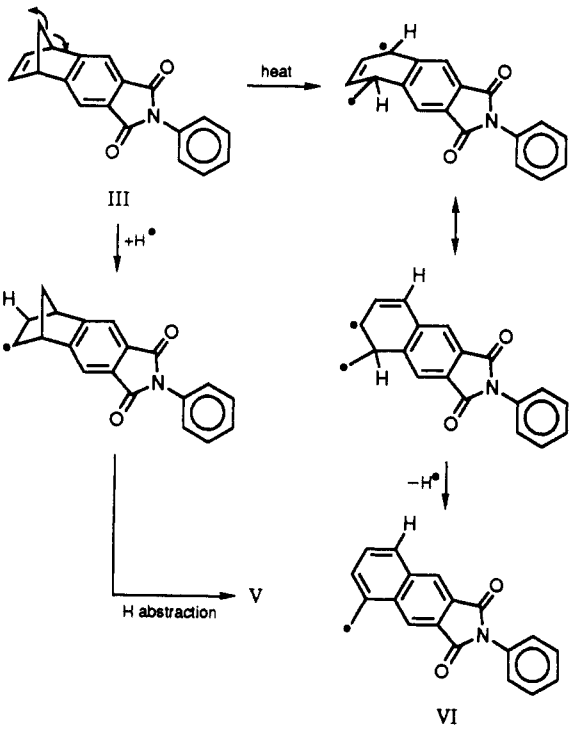
h at 316 °C (600 °F). Similar size resin samples were weighed and placed in open vials which were then heated in a thermostated oven, and samples were removed and reweighed at 250-h intervals. Since the melting and polymerization temperatures of the nadic end cap and of II are different, resins with these different end caps may have different optimal curing conditions. However, since PMR-15 is cross-linked at 600 °F for 2 h at 1000 psi following an atmospheric pressure staging at 260 °C, these conditions were also used for the system end capped with II (Table III). These data (each reflecting an average of at least three independent determinations) clearly show that resins end capped with II can achieve thermal stability comparable to that of a PMR-15 polyimide.

Discussion

Despite the lack of RDA chemistry, benzonorbornadienyl end caps cross-link to give oligomers whose size and properties are comparable to commercial nadic systems. The lack of pressure dependence in the oligomerization of III probably reflects this absence of RDA reaction. The increased aromatic content of cross-linked III and the recovery of V from these samples are both consistent with a cure mechanism involving initial cleavage to a diradical (Scheme II). The formation of radical VI is one possible fate of such a diradical. This loss of a hydrogen atom would contribute to the aromatic content of the resins and provide a basis for the hydrogenation of III to V. The initial diradical could also isomerize (H shift) to methylnaphthalene derivatives, affording a further increase in the aromatic content.

The practical use of end caps such as II depends on the performance advantage they offer in terms of thermal and mechanical properties and in terms of ease of processing. The DSC measurements of the model end cap III and of the benzonorbornadienyl containing molding powder show that thermal cross-linking of the end cap occurs and the SEC measurements indicate that heating III yields oligomers ($n = 6$–7) comparable to those formed from heating the nadic model IV. The TGA and TOS data also suggest

Scheme II



that a performance comparable to that achieved with nadic end caps should be available with our benzannulated analogue. Further testing of both the mechanical properties and the thermal stability of such new resins and composites is still needed.

In terms of resin processing, these materials should offer the advantage of cure temperatures that are comparable to those of current PMR technology without the need for the high-pressure processing characteristic of the nadic end cap. Moreover, the imidization of a benzannulated end cap leads to phthalimides analogous to those from BTDA. Thus, while further work is needed to optimize the processing conditions for this new end cap, imidization of such resins is likely to be more uniform, with less triester formation or residual anhydride, than current nadic systems.

Experimental Section

General Procedures. NMR spectra are reported in δ units and were recorded on a Varian XL-200 spectrometer in $CDCl_3$ solvent (unless otherwise noted). ^1H NMR spectra (200 MHz) in $CDCl_3$ are referenced to $CHCl_3$ at 7.24 ppm. ^{13}C NMR spectra (50 MHz) are referenced to the solvent triplet centered at 77.0

ppm. Infrared spectra were run on a Mattson Cygnus 25 FTIR equipped with a water-cooled source and a TGS detector (4-cm^{-1} resolution). High-resolution mass spectra (EI) were run on a Kratos MS 25RFA spectrometer. UV–visible spectra were run in CH_3CN in quartz cuvettes with a path length of 1 cm on a Cary 2300 UV–visible spectrophotometer connected to a DS-15 work station. HPLC used a Waters 590 pump equipped with a Rheodyne 7125 injector and a Waters 401 differential refractometer or an ISCO V4 UV–visible detector. TLC was done on aluminum-backed 0.2-mm 60F254 silica gel plates from EM Science using phosphomolybdic acid or UV light for visualization. Column chromatography was done with silica gel (Aldrich, 230–400 mesh).

General Procedure for *N*-Phenylimide Polymerization Studies. Samples of III and IV (3–5 mg) were sealed (after three freeze/thaw cycles) under a 50- or 0.0015-mm vacuum, or under argon at ambient pressure, in untreated thick-walled (1.5-mm) Pyrex glass tubes. The tubes were then immersed in a sand bath maintained at constant temperature. Tubes were withdrawn, cooled, opened, and assayed by NMR and SEC. SEC was run at 1 mL/min in THF using an IBM LC/9533 pump, IBM Ultrastyragel columns A and C, and a UV–vis detector. Number-average and weight-average molecular weights and the polydispersity index were determined using the Chromatochart program (Interactive Microwave) on an Apple IIe personal computer. Molecular weights were calculated from calibration curves which were obtained using polystyrene standards. From these same experiments, the extent of polymerization was determined using a cut and weigh technique. An average of three copies of the GPC trace was used, and the extent of polymerization was determined by the weight of the GPC trace for polymeric material divided by the total weight of the GPC trace for monomer and polymer.

General Procedures for Thermal Studies. Differential scanning calorimetry was run on either a Du Pont Model 910 or a Perkin-Elmer 7 Series differential scanning calorimeter under air pressure at a rate of 10 °C/min (unless otherwise specified) from 20 to 500 °C. The data were processed using the Omnitherm ATVantage II thermal analysis program on an IBM personal computer. Thermogravimetric analysis and thermomechanical analysis were run on a Perkin-Elmer 7 Series thermal analysis system and were run at a rate of 10 °C/min from 20 to 700 °C. Molding powders were prepared by combining the calculated amounts of $n + 1$ equiv of diamine, n equiv of dianhydride, and 2 equiv of end cap in 30 mL of acetic acid and heating to reflux overnight and then adding 5 mL of acetic anhydride and refluxing for an additional 3 h to ensure complete imidization. The molding powder is isolated by filtration and dried in a vacuum oven at 100 °C. Staging of the molding powder at 260 °C for 1 h, open to the air, assured complete removal of volatiles. Resin disks were prepared by placing the molding powder in a die, heating the die to between 288 and 399 °C under 1000 psi pressure for 2 h, and then cutting for use in the various thermal analyses. For the thermooxidative stability studies, samples with a surface area of 40–60 cm^2 were used.

Chemicals. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (Aldrich), DDQ (Sigma), dimethyl acetylenedicarboxylate (Aldrich), 1,2,4,5-tetrabromobenzene (Aldrich), and copper cyanide (Aldrich) were used as received. DMF (Fisher) was vacuum distilled from molecular sieves. Hexane for flash chromatography was distilled prior to use. Aniline (Fisher) was vacuum distilled from CaH_2. Dry THF and ether were distilled from sodium. HPLC-grade hexane was used as received for preparative HPLC. Bis(4-aminophenyl)methane (Eastman) was recrystallized from benzene prior to use.

6,7-Bis(carbomethoxy)benzonorbornadiene was synthesized by combining 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (1 g, 8.47 mmol),[14] dimethyl acetylenedicarboxylate (2.4 g, 16.94 mmol), and 40 mg of hydroquinone in a thick-walled (1.5-mm) Pyrex glass tube which was heated in an oil bath at 80 °C for 3 days (*Caution!* In other experiments, heating to higher temperatures resulted in rupture of the glass tube). The resulting product was dissolved in 15 mL of benzene and added dropwise to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (18.93 g, 8.47 mmol) cooled in an ice bath. The reaction mixture was stirred in an ice bath (2 h) and then at room temperature overnight. The precipitate was filtered and washed with 100 mL of benzene. The combined organic layers were concentrated and passed through a column (15 × 5 cm) of alumina with benzene (800 mL) as eluant. The eluant was concentrated and further purified by flash chromatography (silica gel, 20% ethyl acetate in heptane, R_f 0.2): ^1H NMR δ 7.5 (s, 2 H), 6.75 (t, 2 H, J = 1.9 Hz), 3.93 (t, 2 H, J = 1.8 Hz), 3.86 (s, 6 H), 2.34, 2.23 (ABq, 2 H, J = 7.55 Hz) [lit.[7] ^1H NMR δ 7.43, 6.66, 3.86, 3.76, 2.31, 2.18].

6,7-Dibromobenzonorbornadiene. To a three-neck 5-L flask fitted with a mechanical stirrer, 250-mL addition funnel, N_2 inlet, and septum were added 1,2,4,5-tetrabromobenzene (50 g, 0.127 mol) and 2.25 L of dry toluene. The mixture was cooled to −78 °C and 87 mL of a 1.6 M solution of n-butyllithium in hexane (140 mmol) was added over a period of 45 min. After an additional 25 min, 14.7 g (222 mmol) of freshly cracked cyclopentadiene was added. The mixture was kept at −78 °C for 1.5 h and then allowed to come to room temperature overnight. The reaction was quenched by the addition of CH_3OH (10 mL). The toluene solution was washed with 500 mL of water, and the aqueous layer was extracted with 2 × 200 mL of ether. The combined organic extracts were dried over $MgSO_4$, concentrated to a yellow oil, and chromatographed (hexane) to yield 22.1 g (58%) of waxy white solid: R_f 0.38 (hexane); IR (CCl_4) 3073, 2992, 2977, 2940, 2865, 1448, 1434, 1355, 1303, 1226, 1082, 913, 878, 607 cm^{-1}; ^1H NMR δ 7.43 (s, 2 H), 6.74 (br s, 2 H), 3.83 (br s, 2 H), 2.28, 2.20 (ABq, 2 H, J_{AB} = 7.4 Hz); ^{13}C NMR δ 153.1, 142.6, 126.6, 119.3, 69.5, 49.9. A small sample was recrystallized from CH_3OH, mp 61–63 °C. High-resolution mass. Calcd for $C_{11}H_8Br_2$: 297.8992. Found: 297.8951.

6,7-Dicyanobenzonorbornadiene. To a solution of 6,7-dibromobenzonorbornadiene (15.5 g, 51.6 mmol) in dry DMF (155 mL) was added CuCN (11.5 g, 129 mmol). The mixture was heated at reflux for 16 h, allowed to cool, and poured into concentrated aqueous NH_4OH (200 mL). Water (600 mL) was added, and the entire aqueous solution was extracted with ether (2 × 400 mL). The combined ether extracts were washed (3 × 500 mL) with 1:3 NH_4OH/water until the blue in the aqueous layer disappeared. The organic layer was dried over $MgSO_4$, and solvent was removed. Flash chromatography (1:3 EtOAc/hexane) of the greenish residue yielded 3.4 g (34%) of a white crystalline solid: mp 111–113 °C; ^1H NMR δ 7.55 (s, 2 H), 6.81 (t, 2 H, J = 1.8 Hz) 4.02 (t, 2 H, J = 1.8 Hz), 2.42, 2.29 (ABq, 2 H, J_{AB} = 7.87 Hz); ^{13}C NMR δ 158.9, 142.6, 125.3, 116.1, 112.2, 70.0, 50.3; R_f (20% EtOAc/hexane) 0.2; IR (CCl_4) 2997, 2992, 2980, 2234, 1461, 1303, 1227, 901 cm^{-1}. High-resolution mass. Calcd for $C_{13}H_8N_2$: 192.0688. Found: 192.0696.

Benzonorbornadiene-6,7-dicarboxylic Acid (I). 6,7-Dicyanobenzonorbornadiene (332 mg, 1.73 mmol) was suspended in 4 mL of 6 N aqueous KOH, refluxed for 8 h, cooled to room temperature, acidified to pH 1 with 20% HCl, and continuously extracted with CH_2Cl_2 for 8 h. The CH_2Cl_2 layer was dried ($MgSO_4$) and solvent removed to give a nearly quantitative yield of a white powder: mp 170 °C (lit.[7] mp 178 °C); ^1H NMR (acetone-d_6) δ 7.44 (s, 2 H), 6.69 (br s, 2 H), 3.86 (br s, 2 H), 2.19, 2.06 (ABq, 2 H, J_{AB} = 7.7 Hz); IR (KBr) 1670 cm^{-1}; UV λ_{max} 219 nm, log ϵ 3.98. High-resolution mass. Calcd for $C_{13}H_{10}O_4$: 230.0579. Found 230.0579.

Benzonorbornadiene-6,7-dicarboxylic Anhydride (II). Benzonorbornadiene-6,7-dicarboxylic acid (3.8 g, 16.5 mmol) was heated in acetic anhydride (75 mL) at reflux for 2 h. The mixture was allowed to cool, and acetic anhydride was removed under vacuum. The crude brown solid was filtered through silica gel ($CHCl_3$) to yield 2.874 g (82%) of a white crystalline solid, mp 120–121 °C. A small sample was further purified by sublimation [90 °C (0.1 mmHg)]: ^1H NMR δ 2.35, 2.49 (ABq, 2 H, J_{AB} = 7.8 Hz); 4.08 (t, 2 H, J = 1.9 Hz); 6.82 (t, 2 H, J = 1.9 Hz); 7.70 (s, 2 H); ^{13}C NMR δ 50.50, 70.07, 117.51, 129.24, 142.68, 162.65, 163.26; IR (CCl_4) 3000, 2980, 2940, 1850, 1780, 1450, 1390, 1285, 1165, 1090, 1075, 1000, 895 cm^{-1}; UV λ 299 nm, log ϵ 3.39; λ_{max} 234 nm, log ϵ 4.33. High-resolution mass. Calcd for $C_{13}H_8O_3$: 212.0473. Found: 212.0468.

***N*-Phenyl-6,7-benzonorbornadienecarboximide (III).** Aniline (10 mL, 10.22 g, 110 mmol) and benzonorbornadiene-6,7-dicarboxylic acid (2 g, 8.7 mmol) were heated at 130 °C for 17 h, cooled, diluted with ether (75 mL), and washed with 2 × 100 mL of 5% HCl. The crude imide was dissolved in CH_2Cl_2, treated with decolorizing carbon, and filtered, and the solvent

removed to yield the desired *N*-phenylimide (2.29 g, 92%): ^{1}H NMR δ 7.62 (s, 2 H), 7.44–7.22 (m, 5 H), 6.74 (t, J = 5 Hz, 2 H), 3.97 (m, 2 H), 2.38 (d, J = 3 Hz, 1 H), 2.24 (d, J = 3 Hz, 1 H); ^{13}C NMR δ 164.71, 160.05, 143.14, 132.16, 129.41, 128.63, 127.84, 127.06, 116.47, 70.20, 49.80; mp 149–150 °C; IR (KBr) cm^{-1}; UV λ_{max} = 240 nm, log ϵ = 4.60. High-resolution mass. Calcd for $C_{19}H_{13}NO_2$: 287.0744. Found: 287.0750.

2,3-Dihydro-*N*-phenylbenzonorbornadiene-6,7-dicarboximide (V) was synthesized by dissolving III (50 mg) in EtOH (200 mL) and adding Pd/C (5 mg). Low-pressure hydrogenation was complete within 24 h. The reaction mixture was centrifuged to separate the catalyst which was rinsed with fresh EtOH (50 mL). The combined solutions were concentrated, and the product was purified by preparative TLC (25% ethyl acetate in hexane, R_f 0.25). Since only a small amount of purified material was needed, no attempt was made to maximize, or even determine, the yield of this reaction: ^{1}H NMR δ 7.54 (s, 2 H), 7.48–7.08 (m, 5 H), 3.46 (s, 2 H), 1.64 (d, J = 3 Hz, 1 H), 1.45 (d, J = 3 Hz, 1 H), 1.42 (d, d, J = 18 Hz, 4 Hz, 1 H); ^{13}C NMR δ 173.10, 160.99, 137.14, 135.42, 134.23, 132.99, 131.74, 121.20, 54.55, 49.19, 31.40; mp 150 °C. High-resolution mass. Calcd for $C_{19}H_{15}NO_2$: 289.0850. Found: 289.0856.

***N*-Phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (IV)** was synthesized by the method of Wong and Ritchey from *N*-phenylmaleimide and cyclopentadiene.[13] The endo isomer thus produced showed mp 140–141 °C (lit.[13] mp 140–141 °C): ^{1}H NMR δ 7.46–7.09 (m, 5 H), 6.24 (t, 2 H, J = 1.8 Hz), 3.4–3.5 (m, 4 H), 1.76, 1.59 (ABq, 2 H, J = 8.7 Hz). The exo isomer was obtained by heating the endo isomer (195 °C/15 h) to obtain an endo/exo mixture. Pure exo isomer was obtained by preparative HPLC (CH_2Cl_2 eluant): mp 198–199 °C (lit.[13] mp 198–199 °C); ^{1}H NMR δ 7.22–7.50 (m, 5 H), 6.33 (t, 2 H, J = 1.8 Hz), 3.39 (t, 2 H, J = 1.6 Hz), 2.83 (d, 2 H, J = 1.3 Hz), 1.66, 1.42 (ABq, 2 H, J = 9.9 Hz).

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References and Notes

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Registry No. I, 56306-44-6; II, 137495-56-8; III, 137467-22-2; III (homopolymer), 137467-23-3; IV, 26234-46-8; IV (homopolymer), 31533-50-3; V, 137495-55-7; (II)[(BTDA)(MDA)]$_n$ (homopolymer), 137515-58-3; 6,7-bis(carbomethoxy)benzonorbornadiene, 56306-25-3; 5,6-dimethylenebicyclo[2.2.1]hept-2-ene, 5628-77-3; dimethyl acetylenedicarboxylate, 762-42-5; 6,7-dibromobenzonorbornadiene, 137495-57-9; 1,2,4,5-tetrabromobenzene, 636-28-2; cyclopentadiene, 542-92-7; 6,7-dicyanobenzonorbornadiene, 137495-58-0.