chloride could interact with the catalyst and the interaction might reduce the catalytic activity, lithium chloride should be used at an amount low enough to prevent precipitation except for aramid **3bd**.

All the aramids obtained had inherent viscosities in the range 0.2–0.8 $dL \cdot g^{-1}$. Since some of the aramids had poor solubility in the reaction media, they were obtained in relatively low viscosity values. It is noteworthy that the tetraphenylthiophene-containing aramids had better solubility in organic solvents, and thereby the inherent viscosities of the resulting aramids were 0.5–0.8 $dL \cdot g^{-1}$. These viscosity values were almost equal to those of the aramids prepared from 2,5-bis(4-chloroformylphenyl)-3,4-diphenylthiophene and aromatic diamines through low-temperature solution polycondensation.[11]

Thus, we have developed a novel and facile method for the synthesis of aramids from aromatic dibromides, aromatic diamines, and carbon monoxide through palladium-catalyzed polycondensation. Aramids are conventionally prepared by the polycondensation of aromatic diacids or acid chlorides with aromatic diamines. Generally, most of aromatic diacids and their acid chlorides are obtained with difficulty through many steps of reactions, whereas some of aromatic dibromides are synthesized simply by the bromination of aromatic compounds. (Exceptional examples are isophthaloyl and terephthaloyl chlorides which are commercially available.) Therefore, the present method had advantages over the conventional diacid chloride–diamine route due to ready availability of aromatic dibromides and is applicable to the synthesis of various types of aramids.

Registry No. (**1a**)(**2a**)(CO) (copolymer), 114492-48-7; (**1a**)(**2b**)(CO) (copolymer), 114492-49-8; (**1a**)(**2c**)(CO) (copolymer), 114492-50-1; (**1a**)(**2d**)(CO) (copolymer), 114492-47-6; (**1b**)(**2a**)(CO) (copolymer), 114492-51-2; (**1b**)(**2b**)(CO) (copolymer), 114492-52-3; (**1b**)(**2c**)(CO) (copolymer), 114492-53-4; (**1b**)(**2d**)(CO) (copolymer), 114492-54-5; (**1c**)(**2a**)(CO) (copolymer), 114492-55-6; (**1c**)(**2b**)(CO) (copolymer), 114504-80-2; (**1c**)(**2c**)(CO) (copolymer), 114492-56-7; (**1c**)(**2d**)(CO) (copolymer), 114492-57-8; (**1d**)(**2a**)(CO) (copolymer), 114492-58-9; (**1d**)(**2b**)(CO) (copolymer), 114492-59-0; (**1d**)(**2c**)(CO) (copolymer), 114492-60-3; (**1d**)(**2d**)(CO) (copolymer), 114492-61-4; (**1e**)(**2a**)(CO) (copolymer), 114492-62-5; (**1e**)(**2b**)(CO) (copolymer), 114492-63-6; (**1e**)(**2c**)(CO) (copolymer), 114492-64-7; (**1e**)(**2d**)(CO) (copolymer), 114532-24-0; $PdCl_2(PPh_3)_2$, 13965-03-2; PPh_3, 603-35-0; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2$, 7647-10-1; $Pd(OAc)_2$, 3375-31-3; $PdCl_2(PhCN)_2$, 14220-64-5.

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Synthesis and Characterization of 1,2-Cyclobutenedicarboxamides: Thermally Generated Polymers and Diels–Alder Adducts

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ABSTRACT: A series of model diamides were synthesized from mono- and disubstituted amines with the diacid chloride of cyclobutene-1,2-dicarboxylic acid. Yields ranged from 30 to 70%. Melting points of the purified diamides ranged from less than 23 °C for *N*-alkyl and *N,N*-dialkyl species to 204 °C for the *N*-phenyl model. Relative rates of thermolysis (by DSC) with maxima from 208–224 °C at 10 °C/min were dependent on the number and type of substituents and on intramolecular hydrogen bonding. Thermolysis products were Diels–Alder dimers for N-monosubstituted materials and for bulky tetrasubstituted models and spontaneously formed polymers for two tetrasubstituted models with at least one methyl group on each nitrogen. Thermal imidization of cycloadducts was possible in some cases with concomitant oxidation to tetrasubstituted aromatic diimides.

Introduction

2,3-Disubstituted cyclobutenes and their thermally generated butadiene derivatives undergo a rich variety of reactions. The cyclobutenes can behave as dienophiles in cycloaddition reactions with appropriate dienes and thermally ring-open to the corresponding substituted butadienes.[1,2] The resulting dienes in turn have been found to spontaneously dimerize and polymerize[3,4] and to react with dienophiles in typical [4 + 2] cycloadditions.[4] We are currently exploring these compounds for synthesis of polybutadienes and for curing of thermosetting polymers and composites. The latter application involves the incorporation of a relatively nonreactive functionality into tough composite matrix polymers for potential use as one-pot, thermally activated curing systems. The former provides a synthetic pathway to a unique family of 2,3-disubstituted poly-1,4-butadienes which may be converted to the head-to-head polyacrylamides not readily available by other synthetic routes.

We previously described our initial results on the thermal reactions of several model diamides and polyamides.[5] Of three derivatives with two or four nitrogen substitutents (**1–3**), only compound **2** spontaneously polymerized while the others cyclodimerized. In an effort to further understand the factors controlling the spontaneous reactions of the butadienes generated by thermal

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Table I
1,2-Cyclobutenedicarboxamide Yields, Melting Points, and ^{13}C NMR Characteristics

cmpd	yield, %	T_m, °C	chem shift, ppm C-1	C-2	C-3	alkyl and aryl carbons
1	55	185–187	163.5	144.2	29.3	126–130
2	63	150–152	163.9	143.5	29.3	37.4, 37.0, 126–131
3[a]	68	202–204	159.9	144.7	25.5	137.5, 128.3, 123.9, 120.0
4[a]	46	72–73	169.3	142.2		46.8
5	34	56–57	165.0	146.2	24.7	41.4, 34, 31.3, 31.1, 29.0
6[a]	45	oil	166	148.5	25	49, 43, 30.1, 25, 23.8, 18.4
7	77	oil	163.5	139.5	28.4	36.3, 33.8 (N–CH_3)
8	40	155–160	161.1	143.7	32.6	
9	32	159–162	164.8	136.5		

[a] In DMSO-d_6 rather than $CDCl_3$.

Table II
Thermal Analysis Results by DSC

cmpd	R	R′	T_m, °C	T_{max}, °C	ΔH_t, kcal/mol
1	phenyl	phenyl	186.2	224.2	13.6
2	methyl	phenyl	151.8	220.6	20.5
3	H	phenyl	202.5	211[a]	
4	H	*n*-dodecyl	72.0	208.3	11.4
5	H	*n*-heptyl	56.4	208.2	23.2
6	H	isopentyl	*b*	208.2	17.4
7	methyl	methyl	*b*	214.5	24.6
8	H	cyclohexyl	156.0	208.2	14.7
9	cyclohexyl	cyclohexyl	183.6	228.4	21.4

[a] Peak obscured by melt endotherm. [b] Viscous oils at room temperature.

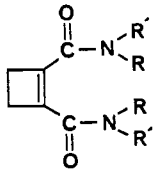
ring-opening, we have synthesized a number of additional derivatives, **4–9** (Figure 1), and examined their properties and behavior. We report here the general synthesis of these compounds, their thermal reaction energetics, and their expected and unexpected reaction products.

Results and Discussion

Substituted Cyclobutene Synthesis. Amide formation traditionally involves thermal dehydration of amine–carboxylic acid mixtures, although this method requires temperatures which, in our case, cause thermolysis of the cyclobutene group. Alternative procedures utilize high-energy intermediates such as acid chlorides, anhydrides, or mixed anhydrides or in situ generated active esters of the carboxylic acid group.[6,7] The previously reported diacid chloride of 1,2-cyclobutenedicarboxylic acid was found to provide a facile route to the desired compounds. The general synthesis described previously[5] was extended to the derivatives **4–9**. Isolated yields, melting points, and ^{13}C NMR spectral properties of these compounds are given in Table I.

Many of the crude compounds contained residual amines which would inhibit radical polymerization. Purification in some cases required chromatography and/or recrystallization. Final purity was established with GC to be greater than 99% in all cases.

Thermal Analysis by DSC. DSC was used to investigate the onset and breadth of the various thermally induced transitions and reactions and to determine the enthalpy of the individual or combined processes. Figure 2 gives several typical DSC traces showing multiple exotherms during the heating of compounds that either polymerize exclusively or only cyclodimerize. Table II lists the values for the melting points determined by DSC, the



Cmpd	R	R′
1	phenyl	phenyl
2	methyl	phenyl
3	H	phenyl
4	H	n-dodecyl
5	H	n-heptyl
6	H	i-pentyl
7	methyl	methyl
8	H	cyclohexyl
9	cyclohexyl	cyclohexyl

Figure 1. Structure of cyclobutene 1,2-disubstituted amides 1–9 and their corresponding substituents.

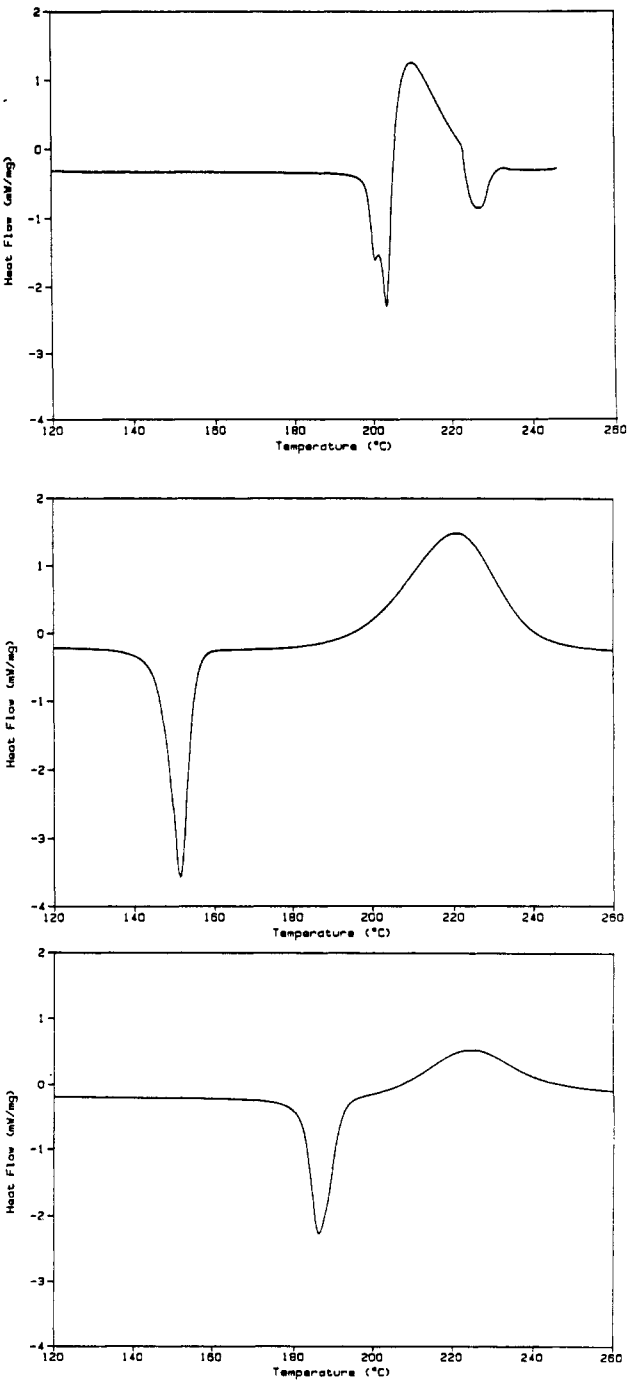


Figure 2. DSC traces of compounds 1–3 (bottom to top) showing melt endotherms and thermolysis exotherms.

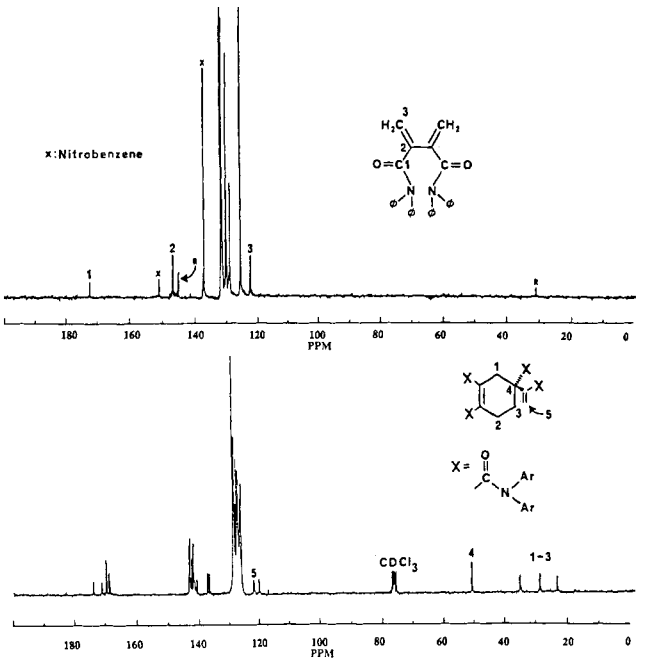


Figure 3. ^{13}C NMR of the thermolysis products of compound **1**: Upper trace shows formation of the substituted butadiene in nitrobenzene solution (R indicates residual cyclobutene resonances) while the lower trace shows the cyclodimer formed after prolonged heating.

exotherm maxima (T_{max}), and enthalpies for the peaks. For a given scan rate, the position of the maximum of a specific peak is an indication of the relative reaction rate.[8] Interestingly, for the cyclobutene ring-opening process, T_{max} varies less than 20 °C for the series of derivatives **1–9**.

Cyclobutenes substituted in the 3-position, on the other hand, show a wide range of thermolysis rates depending strongly on the type of substituent.[9] It may be that the nitrogen substituents on **1–9** are too far removed from the strained ring to much affect the ring-opening energetics which are controlled mostly by the presence of the two adjacent carboxamide moieties. Within the 20 °C range observed, however, there does seem to be some correlation between the ability of the amide groups to intramolecularly hydrogen bond and whether the substituents are alkyl or aryl. The rate of reaction decreases in the order *N*-alkyl > *N*-aryl > *N*,*N*-dialkyl > *N*-alkyl-*N*-aryl > *N*,*N*-diaryl. Hydrogen bonding increases the rate while aryl substituents decrease it.

The experimental heats of reaction (ΔH_t) vary widely but do not appear to relate to the number or type of substituents. This is probably the result of the DSC exotherms being combinations of two or more reactions: ring-opening followed by either or both polymerization and cycloaddition such that

$$\Delta H_t = \Delta H_r + (\Delta H_p + \Delta H_c)$$

Indeed, compounds **4–6** show two overlapping exotherms, clearly demonstrating the consecutive nature of the reactions. These three compounds undergo almost exclusive Diels–Alder addition while compounds **2** and **7** give only polymeric products. The DSC scans of the last two compounds show only one exothermic peak, however.

The appearance of a single peak is not exclusive to polymer formation, however, since compound **1** shows only one peak yet undergoes only cycloaddition with itself to give the cyclodimer (Figure 3, lower trace). The rate of the addition reaction is so much slower than ring-opening that only the latter is detected by DSC at these scan rates. In fact, NMR analysis of this compound clearly shows the

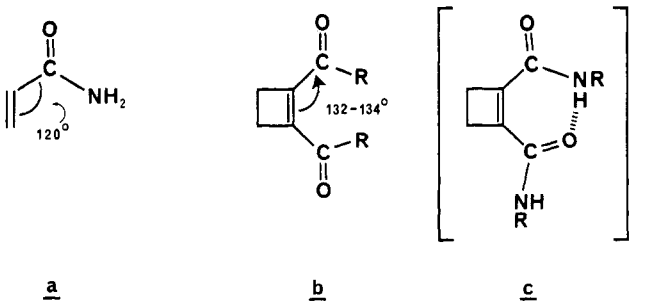


Figure 4. Relative angles of sp^2 hybridized carbons in alkenes: (a) normal angle of 120° in acrylamide; (b) extended angle found in substituted cyclobutenes; (c) hypothetical intramolecular hydrogen bonding facilitated by the extended angle.

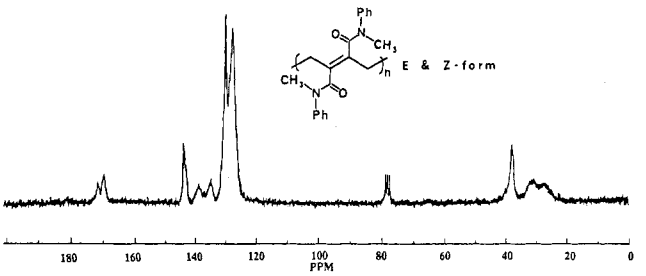


Figure 5. ^{13}C NMR (in $CDCl_3$) of the polymer from **2**.

appearance of the butadiene species (Figure 3, upper trace) before gradual disappearance with formation of the cyclodimer.

The polymerizability of the butadiene compounds, as well as the imidization process described later in the text, may be directly related to the occurrence of intramolecular hydrogen bonding in both the cyclobutene and the butadiene. Although the seven-membered cyclic structure required for the hydrogen bond in the former may at first appear strained, the large angle of the sp^2 hybridized carbons[10] of the ring may actually favor this structure (Figure 4). X-ray analysis has confirmed the existence of strong intramolecular hydrogen bonding in cyclobutene-1,2-dicarboxylic acid[11] which has been suggested as the reason for the opposite endo:exo ratio for its cycloaddition adducts compared to non-hydrogen-bonding analogue. The dimethyl ester, which is not capable of intramolecular hydrogen bonding, gives only polymer on thermolysis.[12,13]

The polydiene from **2** was a brittle transparent solid. DSC showed a transition (T_g) at 122.5 °C. The polymer had an intrinsic viscosity of 0.36 dL/g in hexafluoroisopropyl alcohol and is soluble in methylene chloride, acetone, and dimethylformamide. GPC analysis showed a broad molecular weight distribution typical of free radical addition polymers with an M_n of 189 000 (based on polystyrene standards). The polydiene from **7** was a brown, viscous oil which was soluble both in common organic solvents and in water. This polymer, however, precipitated in THF making GPC analysis impractical for our systems.

Figure 5 shows ^{13}C NMR of the polydiene from thermolysis of **2**. The vinyl and methylene resonances of the polymer backbone are typically broad while the pendent methyl and phenyl groups on the nitrogen are much sharper. The absence of resonances in the region 110–120 ppm indicates little, if any, 1,2-addition in the polymers. Although the polymerization appears to be exclusively by 1,4-addition, the presence of two distinct resonances each for the carbonyl, vinyl, and methylene indicate that the stereochemistry about the double bond is a mixture of *E* and *Z* isomers. No attempt was made to assign the reso-

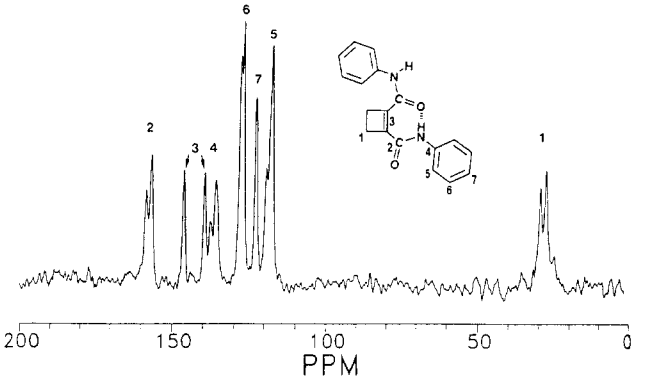


Figure 6. ^{13}C CP-MAS NMR of **3** showing peak assignments and chemical-shift differences in the cyclobutene vinyl resonance.

nances to a particular geometrical isomer.

Figure 6 shows the solid-state ^{13}C NMR of **3** along with the proposed intramolecularly hydrogen-bonded structure. The difference in chemical shift seen for the vinyl carbons is consistent with different shielding and deshielding environments that would be experienced by the nuclei in such a structure. This demonstrates a unique solid-state interaction which we believe affects the ultimate reactivity of the model compounds and polyamides in the melt and even in solution.

Diels–Alder Cycloaddition Reactions. Various 2,3-disubstituted butadienes have been found to be excellent dienes in cycloaddition reactions despite the fact that they contain electron-withdrawing substituents. For example, the dinitrile reacts with a variety of dienophiles when used as a previously generated species[2,3] or when formed in situ by thermolysis of the cyclobutene.[4] The 1,3-butadiene-2,3-dicarboxylic acid has also been reported to undergo Diels–Alder dimerization in solution.[4] The cycloaddition chemistry of the dicarboxamide derivatives offers potential application in composite matrix-forming reactions. Model systems were studied to evaluate such reactions with compounds **1–9**.

The butadiene derived from **1** was chosen first as an extreme example involving intermolecular steric interactions of the four *N*-phenyl groups. This diene forms readily by thermolysis in bulk and in *N*-methylpyrrolidone but does not polymerize. It can be isolated and is stable at room temperature. NMR analysis of a nitrobenzene solution of this diene confirms gradual dimerization at 185 °C leading to high yields of the cyclodimer shown in Figure 3.

Cyclobutene **1** was also reacted with *N*-phenylmaleimide in nitrobenzene at 185 °C. NMR monitoring indicated high conversion to the cycloadduct **10** (Figure 7, eq 1) with no evidence of unreacted starting material or byproducts.

The cycloaddition of *N*-phenylmaleimide was also carried out with **3** under the same conditions over a 24-h period. Gold platelets precipitated from the homogeneous solution in 11% yield. Microanalysis of these crystals, however, was inconsistent with the expected cycloadduct structure **11**. Solution NMR was not possible since the crystals were insoluble even in concentrated sulfuric acid. IR and solid-state ^{13}C NMR analysis confirmed aromatization of the cyclohexene ring and disappearance of the amide hydrogens. The reaction process was finally deduced to involve loss of one of the amide nitrogen groups via imide formation, which converts **11** to **12** (Figure 7). Structure **12** is consistent with the data and with a previously reported melting point for this compound of 452–453 °C[14] versus our value of 452.5 °C (determined by DSC).

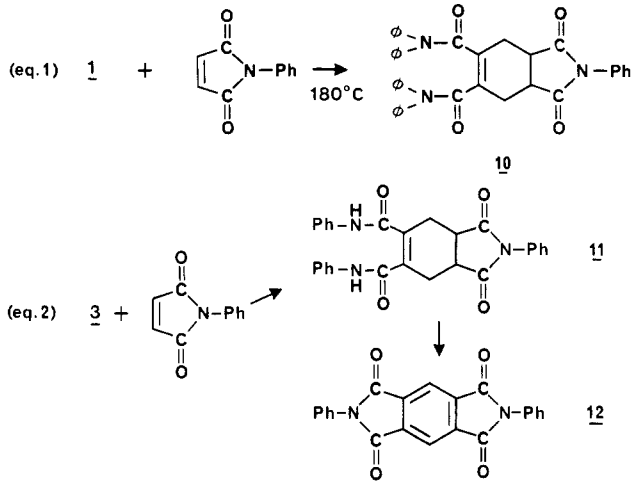


Figure 7. Diels–Alder reactions of in situ generated dienes with *N*-phenylmaleimide: (eq 1) reaction of **1** to give adduct **10**; (eq 2) reaction of **3** to give **11** followed by imidization and aromatization to give the diimide **12**.

The remaining soluble fraction from the above reaction was precipitated from nitrobenzene to give a solid that readily dissolved in DMF and DMSO. Heating this solid in air led to gradual formation of an insoluble material that appeared to consist mainly of **12**. Conversion of the initial cycloadduct to the 1,2,4,5-benzenetetracarboxylic diimide provides a novel synthesis of this material and opens up a new synthetic approach to rigid rod polyimides involving soluble intermediate polymers undergoing thermal cyclization and aromatization.

Experimental Section

General Procedure for Preparation of Model Cyclobutene Amides. Preparation and purification of cyclobutene-1,2-dicarboxylic acid chloride is described elsewhere.[4] In a typical reaction, the amine was dissolved in 75 mL of dry chloroform or methylene chloride in a 125-mL Erlenmeyer flask with an equimolar amount of triethylamine added as a scavenger for the HCl produced. One equivalent of the acid chloride was added dropwise via pipette to the stirred solution. A generous amount of heat was liberated and the addition was moderated to prevent the solvent from boiling. The pipette was rinsed with the stirred solution to remove any remaining acid chloride and the solution allowed to stir for 20–30 min. The homogeneous solution was taken up in an extraction funnel and washed twice with 10-mL portions of aqueous 1 M NaOH, 1 M HCl, and deionized water. The organic layer was dried over anhydrous $MgSO_4$. The drying agent was filtered and washed with methylene chloride and the combined solvent layers evaporated from the product.

Purification of the crude product was accomplished by dissolving in a minimal amount of boiling methanol or methanol/water mixture and allowing recrystallization at room temperature. Compounds **1** and **3** were additionally purified by column chromatography (silica gel with a mobile phase of 1:1 chloroform/methanol). Compounds **6** and **7** were viscous oils and failed to crystallize. They were purified by column chromatography and dried in vacuo at 70 °C.

Polymers derived from the thermolysis of **2** and **7** were purified by dissolving them in methylene chloride and precipitating in *n*-hexane.

Dimethylamine was purchased from Alfa Chemical as a solution in ether. Other amines were purchased from Aldrich Chemical Co. and were used as received. Triethylamine was distilled from NaOH and stored over 4A molecular sieves. All solvents were of reagent grade purity or better and used without further purification.

^{13}C NMR high-resolution and solid-state spectra were acquired on a Bruker MSL 200 spectrometer at a frequency of 50.32 MHz. NMR chemical shifts are reported in ppm from TMS (0 ppm). FT-IR spectra were recorded on a Nicolet 5DX FT-IR spectrometer and data station. Microanalyses was performed by

Desert Microanalysis, Tucson, AZ. Thermal analyses were performed on a Du Pont 910 differential scanning calorimeter equipped with a Du Pont 9000 controller and data station. GPC of polymers was performed by using a Waters 6000A solvent pump, UV detector (250 nm), and Styragel columns (THF solvent).

***N,N,N',N'*-Tetraphenylcyclobutene-1,2-dicarboxamide (1)**: prepared in 55% yield from diphenylamine, mp 185–187 °C; IR (KBr, cm^{-1}) 3057, 2938, 1659, 1641, 1619, 1593, 1493, 1350, 762, 696. Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 79.83; H, 5.44; N, 6.10.

***N,N'*-Diphenyl-*N,N'*-dimethylcyclobutene-1,2-dicarboxamide (2)**: prepared in 63% yield from *N*-methylaniline, mp 150–152 °C; IR (KBr, cm^{-1}) 3044, 2970, 2919, 1657, 1643, 1632, 1614, 1590, 1372, 1110, 702. Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.76. Found: C, 74.67; H, 6.33; N, 8.73.

***N,N'*-Diphenylcyclobutene-1,2-dicarboxamide (3)**: prepared in 68% yield from aniline, mp 202–204 °C; IR (KBr, cm^{-1}) 3294, 3027, 2937, 1664, 1620, 1595, 1537, 751, 689. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.51; N, 9.59. Found: C, 73.85; H, 5.69; N, 9.61.

***N,N'*-Di-*n*-dodecylcyclobutene-1,2-dicarboxamide (4)**: prepared from *n*-dodecylamine in 46% yield, mp 72–73 °C; IR (neat, cm^{-1}) 3289, 2961, 2921, 2852, 1659, 1616, 1582, 1538, 667. Anal. Calcd for $C_{30}H_{56}N_2O_2$: C, 75.57; H, 11.84; H, 5.88. Found: C, 75.53; H, 12.17, N, 5.97.

***N,N'*-Di-*n*-heptylcyclobutene-1,2-dicarboxamide (5)**: prepared from *n*-heptylamine in 34% yield, mp 56–57 °C; IR (neat, cm^{-1}) 3240, 3036, 2924, 2853, 1658, 1604, 1537, 1241, 695. Anal. Calcd for $C_{20}H_{36}N_2O_2$: C, 71.38; H, 10.78; N, 8.33. Found: C, 71.25; H, 11.16; N, 8.21.

***N,N'*-Diisopentylcyclobutene-1,2-dicarboxamide (6)**: prepared from 1-methyl butylamine in 45% yield as a viscous oil. Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06; N, 9.99. Found: C, 67.03; H, 9.94; N, 9.38.

***N,N,N',N'*-Tetramethylcyclobutene-1,2-dicarboxamide (7)**: prepared from a solution of dimethylamine in ether in 77% yield as a viscous oil. IR (neat, cm^{-1}) 2926, 1712, 1620, 1504, 1404, 1195, 875.

***N,N'*-Dicyclohexylcyclobutene-1,2-dicarboxamide (8)**: prepared from cyclohexylamine in 40% yield as a white, crystalline, solid, mp 155–160 °C after recrystallization from methanol. IR (KBr, cm^{-1}) 3276 (br), 3045, 2927, 2854, 1657, 1619, 1562, 1535, 1449, 1350, 1245, 1168, 893, 700.

***N,N,N',N'*-Tetracyclohexylcyclobutene-1,2-dicarboxamide (9)**: prepared from dicyclohexylamine in 32% yield as a white, crystalline solid, mp 159–162 °C after recrystallization from methanol. IR (KBr, cm^{-1}) 2934, 2853, 1713, 1626, 1546, 1439, 1366, 1313, 1227, 1182, 1126, 896, 750.

1,2-Bis[(diphenylamino)carbonyl]-*N*-phenylcyclohexene-4,5-dicarboximide (10): 0.0578 g of **1** (0.118 mmol) and 0.247 g of *N*-phenylmaleimide (0.142 mmol) were dissolved in 1 mL of nitrobenzene in a screw-cap vial. The vial was heated in an oil bath at 185–190 °C for 6 h. The nitrobenzene was evaporated under vacuum yielding 0.063 g of crude product. The product was purified by liquid chromatography (1:1 MeOH/$CHCl_3$ on silica gel) and the solvent evaporated to give 0.037 g (51%) of **10**: mp 145–148 °C; IR (KBr, cm^{-1}) 3060, 2931, 1710, 1650, 1490, 1381, 1176, 759, 695; ^{13}C NMR (nitrobenzene) 177.5, 168.8, 143, 40.2 (d), 27.9 (t).

1,2-Bis[(phenylamino)carbonyl]-*N*-phenylcyclohexene-4,5-dicarboximide (11): 0.0814 g of **3** (0.28 mmol) and 0.05 g of *N*-phenylmaleimide (0.29 mmol) were dissolved in 1 mL of nitrobenzene in a screw-cap vial. The vial was heated in an oil bath at 180–190 °C for 24 h. During this time, a small amount of precipitate formed. The crude mixture was dissolved in 50 mL of hot methanol and insoluble precipitate filtered from the solution. The methanol and residual nitrobenzene were evaported to give 0.067 g (52%) crude **11**: mp 138–142 °C; IR (KBr, cm^{-1}) 3360, 3057, 2931, 1722, 1500, 1384, 1129, 742, 658; ^{13}C NMR (DMSO-d_6) 170.7, 168.9, 51.8, 28.9, 22.1, 21.5. This material was readily soluble in DMSO, DMF, and methanol. On heating, the product became insoluble in these solvents, perhaps due to aromatization of the cycloadduct. The NMR spectrum indicates a mixture of the cycloadduct and other unidentified compounds.

***N,N'*-Diphenyl-1,2,4,5-benzenetetracarboximide (12)**. The precipitate from purification of **11** was washed with a 4:1 methanol/DMF solution and dried at 120 °C for 24 h to yield 0.015 g (11.7%) of **12** as gold colored plates: mp 452.5 °C (lit. 452–53 °C[9]); IR (KBr, cm^{-1}) 3060, 1722, 1502, 1129, 742, 720 (lit.[15] 1720, 1132, 752, 730). Anal. Calcd for $C_{22}H_{12}N_2O_4$: C, 71.73; H, 3.29; N, 7.61. Found: C, 71.53; H, 3.09; N, 7.45.

Registry No. 1, 106681-09-8; 1 (cyclodimer), 114693-09-3; **2**, 106680-87-9; **2** (homopolymer), 106680-88-0; **3**, 106680-85-7; **4**, 114693-01-5; **5**, 114693-02-6; **6**, 114693-03-7; **7**, 114693-04-8; **7** (homopolymer), 114693-10-6; **8**, 114693-05-9; **9**, 114693-06-0; **10**, 114693-07-1; **11**, 114693-08-2; **12**, 6626-68-2; cyclo-1,2-dicarboxylic acid chloride, 52477-78-8; diphenylamine, 122-39-4; *N*-methylaniline, 100-61-8; aniline, 62-53-3; dodecylamine, 124-22-1; heptylamine, 111-68-2; 1-methylbutylamine, 625-30-9; dimethylamine, 124-40-3; cyclohexylamine, 108-91-8; dicyclohexylamine, 101-83-7; *N*-phenylmaleimide, 941-69-5.

References and Notes

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