Macromolecules

Volume 27, Number 10 May 9, 1994

Reactivity of Disubstituted Benzocyclobutenes. Model Compounds of Cross-Linkable High-Performance Polymers

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Received November 24, 1993; Revised Manuscript Received February 7, 1994•

ABSTRACT: We have previously reported on the synthesis of a new 2,5-disubstituted benzocyclobutene monomer which is capable of undergoing thermally activated cross-linking. This monomer, a derivative of terephthalic acid, can be incorporated into the backbone of many high-performance polymers, processed into films or fibers, and then cross-linked to yield networks. To determine the operating window for polymerization and processing, we report here a study on small-molecule compounds derived from this monomer, many of which have well-known polymeric counterparts. When electron-withdrawing groups are present on the benzocyclobutene ring, stability toward strong protonic acids is shown to be excellent. This is in contrast to the case of the parent hydrocarbon and derivatives substituted with electron-donating groups and is consistent with acid degradation resulting from electrophilic aromatic substitution chemistry. Thermal analysis of the model compounds by differential scanning calorimetry reveals that exothermic reaction maxima are typically around 350 °C, which is ~100 °C higher than the maxima for 3-substituted benzocyclobutene derivatives. When the thermal reaction is performed in the presence of dienophiles, reaction temperatures are lowered by as much as 100 °C. Possible explanations for the thermal reactivity are discussed. No significant correlation to the electronic structure of the cyclobutaarene ring is observed nor is there any significant relationship between reactivity and melting transition. The apparent greater thermal stability for 2,5-disubstituted benzocyclobutenes is most consistent with the encumbered steric environment around the cyclobutaarene ring.

Introduction

The use of cross-linked polymers as engineering materials has been extensive due to their rigidity, strength, mechanical and thermal stability, and chemical resistance. Typically, these materials are synthesized using step-growth methods where polymer growth and cross-linking arise from the same chemical reaction.[1] These materials are usually processed as low molecular weight prepolymers because of the intractability of the final cross-linked material. The prepolymers are then cured to drive the polymerization reaction to higher conversions, initiating network formation. Chemically, this scheme has the problems that complete conversion is rarely achieved and defects due to unreacted chain ends and intramolecular cyclization are common. Although cross-linked polymers are mechanically and thermally very stable, the physical form of these materials can be hard to manipulate, ultimately limiting the versatility of these materials. For example, the preparation of a cross-linked network in the form of an oriented polymer fiber would be complicated using conventional methods.

In general, ordered polymer networks in any form are difficult to prepare by conventional methods. These difficulties might be avoided through the design of a system that would combine the processing advantages of high molecular weight thermoplastic materials with the enhanced stability of networks. Synthetically this could be realized by incorporating monomers having latent reactivity into a primary polymer.[2] This method would offer the following advantages. First, chain-growth and cross-linking reactions would be independent of one another, providing full control over the chemical structure of the primary polymer. Second, the cross-linking agent would be incorporated as a comonomer into the backbone of high molecular weight polymers; thus, the degree of cross-linking would be directly related to monomer composition. Finally, the early stages of polymer processing would be decoupled from network formation. In other words, the cross-linking agent would remain dormant during initial processing but could subsequently be triggered to chemi-

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• Abstract published in *Advance ACS Abstracts*, April 1, 1994.

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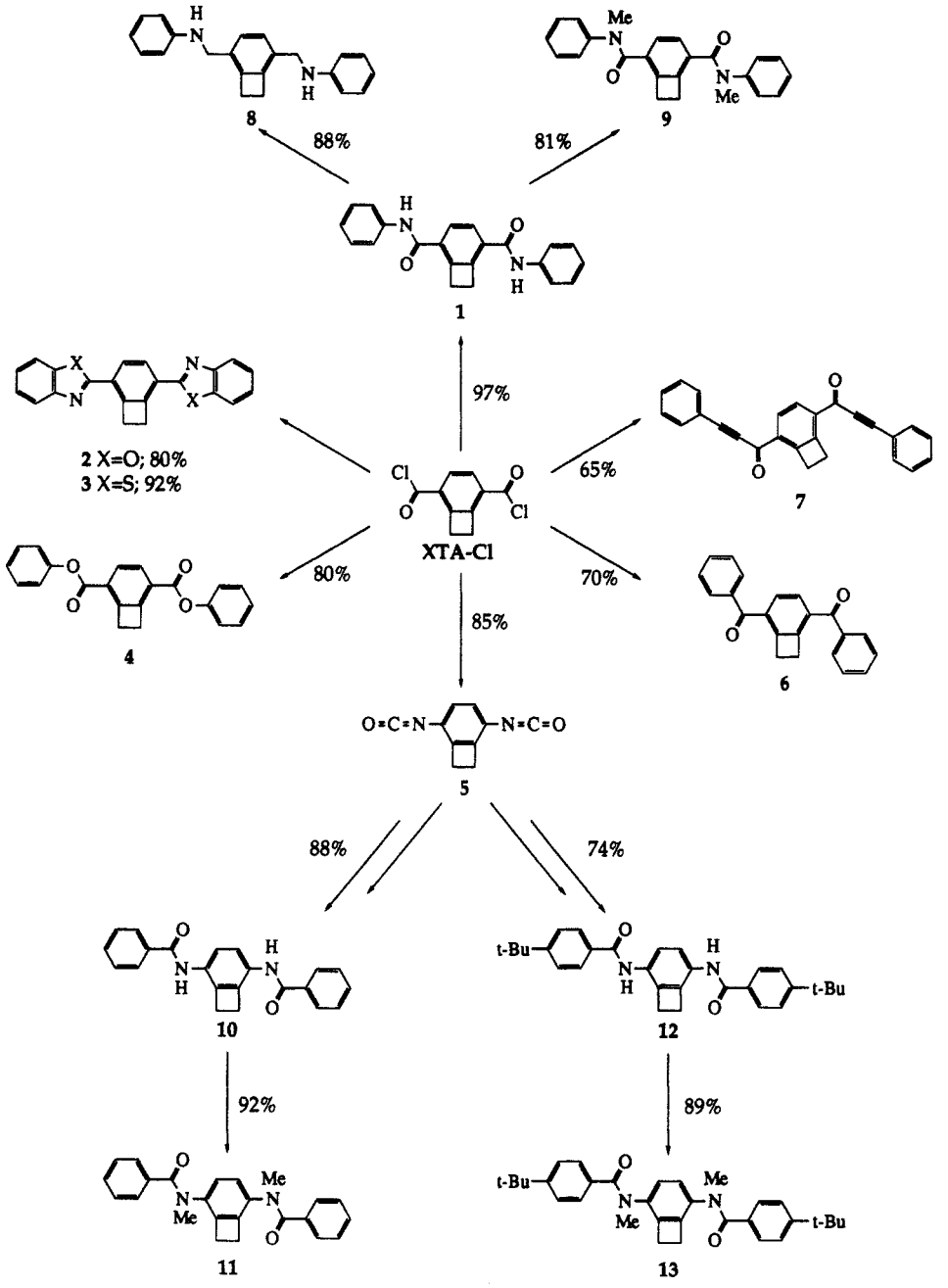
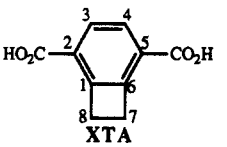


Figure 1. Disubstituted model compounds synthesized from **XTA-Cl**.

cally lock in the desired physical form.

This approach to ordered polymer networks can be compared to methods based on the catenation of self-organized small molecules. For example, ordered networks have recently been prepared from liquid crystalline diacrylate and divinyl ether monomers.[3] Typically, these monomers are aligned using an external electric or magnetic field and then photochemically polymerized, yielding highly anisotropic networks. Ordered elastomers have been reported independently by Zentel[4] and Finkelmann,[5] where side-chain and main-chain liquid crystalline polymers were cross-linked to physically fix the order of the mesogenic units. Their anisotropy is demonstrated in interesting optical, electronic, and mechanical properties. For example, when chiral smectic C* mesogens were used, networks demonstrating piezoelectric properties were obtained.[4a,5a,c]

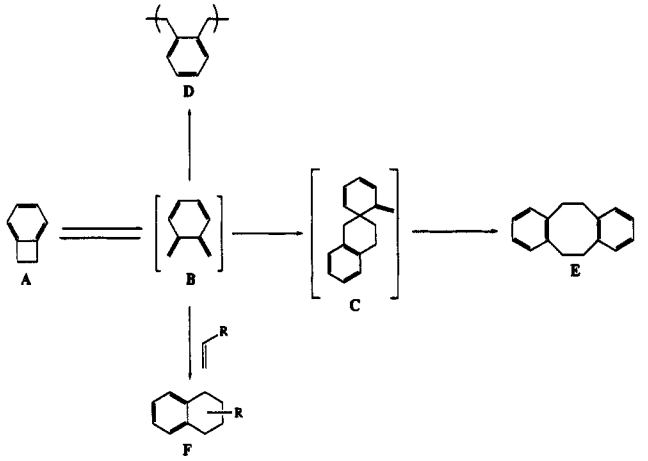
Our interest in oriented, high-strength aromatic fibers that could be cross-linked led to the design and synthesis of the new monomer **XTA**.[6] The diacid chloride derivative of this monomer (**XTA-Cl**) is shown in Figure 1. Since



this comonomer will be incorporated into the polymer backbone, it must be stable to polymerization and processing conditions common to these materials.[7] The challenge in designing a suitable monomer is that it must maintain sufficient chemical potential to undergo thermal or photochemical cross-linking and yet survive polymerization and processing conditions. This paper presents results from a model compound study on the reactivity of this monomer and several of its derivatives.

The design of **XTA** was based on the thermally reactive benzocyclobutene hydrocarbon whose melt and solution thermal chemistry has been well studied.[8] It has been shown that upon thermolysis the cyclobutaarene ring (**A**) is in equilibrium with the very reactive *o*-quinodimethane species[9] (**B**) (Scheme 1). This intermediate can undergo

Scheme 1. Solution and Melt Chemistry of Benzocyclobutene



self-polymerization to give poly(*o*-xylylene) (**D**) or dimerize to yield a bisbenzocyclooctadiene derivative (**E**). Alternatively, **B** can undergo [4 + 2] cycloaddition chemistry to yield **F** when heated in the presence of a dienophile.

Benzocyclobutenes have been used extensively as end-capping groups for oligomers and polymers of aromatic imides,[10] carbonates,[11] and quinolines[12] to produce networks with varying cross-link density. Also, benzocyclobutene chemistry has been used in Diels–Alder polymerizations to synthesize thermoplastic materials. Monomers in this case contain dienophiles such as aromatic alkenes,[13] maleimide groups,[14] or aromatic alkynes,[15] along with the cyclobutaarene ring. However, the incorporation of this thermally reactive group into the main chain of polymeric materials as a latent cross-linking functionality has not been extensively studied.[16,17] The advantages of introducing such a moiety into the backbone of polymeric materials are twofold. First, its small lateral dimension should preserve the high aspect ratio needed for spinning oriented fibers from liquid crystalline polymers. Second, its high reactivity should facilitate cross-linking of solid polymer materials such as melt-extruded parts or polymer fibers.

Results and Discussion

Model Compound Synthesis. Various 2,5-disubstituted benzocyclobutenes were synthesized to investigate their reactivity and potential as polymeric structural units (Figures 1 and 2). Many of these compounds were chosen because they serve as model compounds of high-performance polymers (e.g., **1**, **2**, **3**, **4**, **6**, and **10**). Their preparation served to test the possibilities of **XTA-Cl** in various polycondensation reactions. Other compounds shown in Figures 1 and 2 were synthesized to provide a broader representation of functionalities to establish structure/reactivity correlations.

Model compounds prepared in this study were derived from two key intermediates (**XTA-Cl**, Figure 1; **BCB-Br$_2$**, Figure 2). In general, the synthesis of these derivatives involved simple condensation reactions, and no further explanation is needed. The isolated yields of many of the compounds shown in Figure 1 suggest that **XTA-Cl** could be used in the synthesis of polyaramids, poly(bisbenzoxazole)s, poly(bisbenzthiazole)s, and polyarylates. Somewhat surprisingly, **XTA-Cl** was found to survive the high temperatures, strong acid, and extended reaction times required to synthesize bisoxazole **2** and bisthiazole **3**. Interestingly, **2** and **3** could be resubjected to these reaction conditions for 24 h with no noticeable degradation. This observation provided the first indication of the unusual stability of 2,5-disubstituted benzocyclobutenes, which is intriguing in light of the reported sensitivity of the benzocyclobutene hydrocarbon to Lewis and Brønsted acids.[18] For example, cyclobutaarene ring opening with substitution at the bridgehead carbon is a common side reaction in electrophilic aromatic substitution reactions on the parent hydrocarbon.

Acid Stability. To investigate the apparent acid stability in greater detail, a ^{1}H NMR experiment was performed on amide derivatives **1** and **10**. These compounds were chosen because of their relevance to the spinning of aramid fibers, which generally takes place from concentrated sulfuric acid at elevated temperature. Structures **1** and **10** differ only in the mode of attachment of the amide linkage to the cyclobutaarene unit. The two model compounds were separately dissolved in D_2SO_4 and heated to 90 °C, and their ^{1}H NMR spectra were monitored over a 24-h period (Figure 3). For amide **1**, the singlet resonance at δ 7.50 corresponds to the protons (H_a) on the benzocyclobutene aromatic ring. This resonance is virtually unchanged over the course of the experiment. In the aliphatic region, the cyclobutene methylene singlet (δ 3.31) also remains constant. After 6 h, a small doublet at δ 7.14 is observed, which might be indicative of cyclobutaarene ring opening or could result from substitution on the anilide ring. These possibilities were not examined further. What is of significance is that adequate stability for spin dope preparation and fiber spinning is exhibited.

This behavior is in marked contrast to that of the bisbenzanilide derivative **10**. After only 2 h, the intensity of the benzocyclobutene aromatic proton singlet at δ 6.90 (H_b) is reduced considerably, and dramatic changes in the remainder of the aromatic region are observed. We considered the possibility that the decrease in intensity of the H_b resonance resulted from proton–deuterium exchange. In an independent experiment, **10** was heated in H_2SO_4 for 24 h at 90 °C, and a ^{1}H NMR spectrum was then recorded in D_2SO_4. The spectrum was identical to that obtained in the previous experiment. Finally, the cyclobutaarene methylene singlet at δ 3.28 lost intensity and two triplets developed at δ 4.10 and 2.65. These observations are consistent with opening of the cyclobutene ring in **10**, yielding a β-ethyl sulfonate ester.

The electronic structures of **1** and **10** may explain the observed reactivity differences. The electron-donating amide nitrogens in **10** increase the electron density on the benzocyclobutene group, activating it toward electrophilic aromatic substitution. In contrast, the electron-withdrawing amide carbonyl groups in **1** deactivate the benzocyclobutene ring. These results along with the synthesis of **2** and **3** suggest that **XTA-Cl** could be used in the synthesis of high-performance polymers requiring strong acids and high temperatures. Additionally, it should be possible to process materials from strong acid solutions without cyclobutaarene ring opening.

Thermal Characterization. Differential scanning calorimetry (DSC) was used to characterize melting transitions and exothermic reactions for many of the model compounds shown in Figures 1 and 2. The results are summarized in Table 1, and sample DSC traces are provided in Figure 4 for **1** and **3**. In general, the melting points were reversible provided that the sample remained sufficiently below the reaction exotherm. The exothermic transition was irreversible as shown by subsequent cooling and heating cycles. In all cases, the reaction took place in the melt. The most unusual feature seen in Table 1 is the high temperature at which the reaction exotherm is

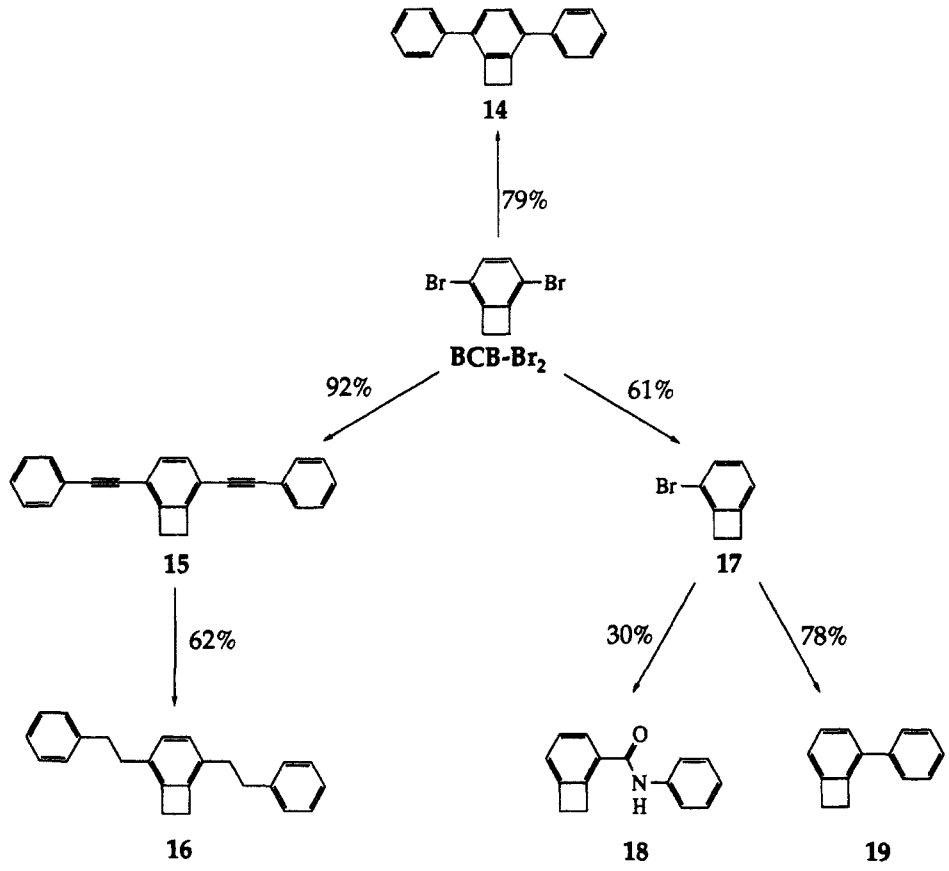


Figure 2. Model compounds synthesized from **BCB-Br$_2$**.

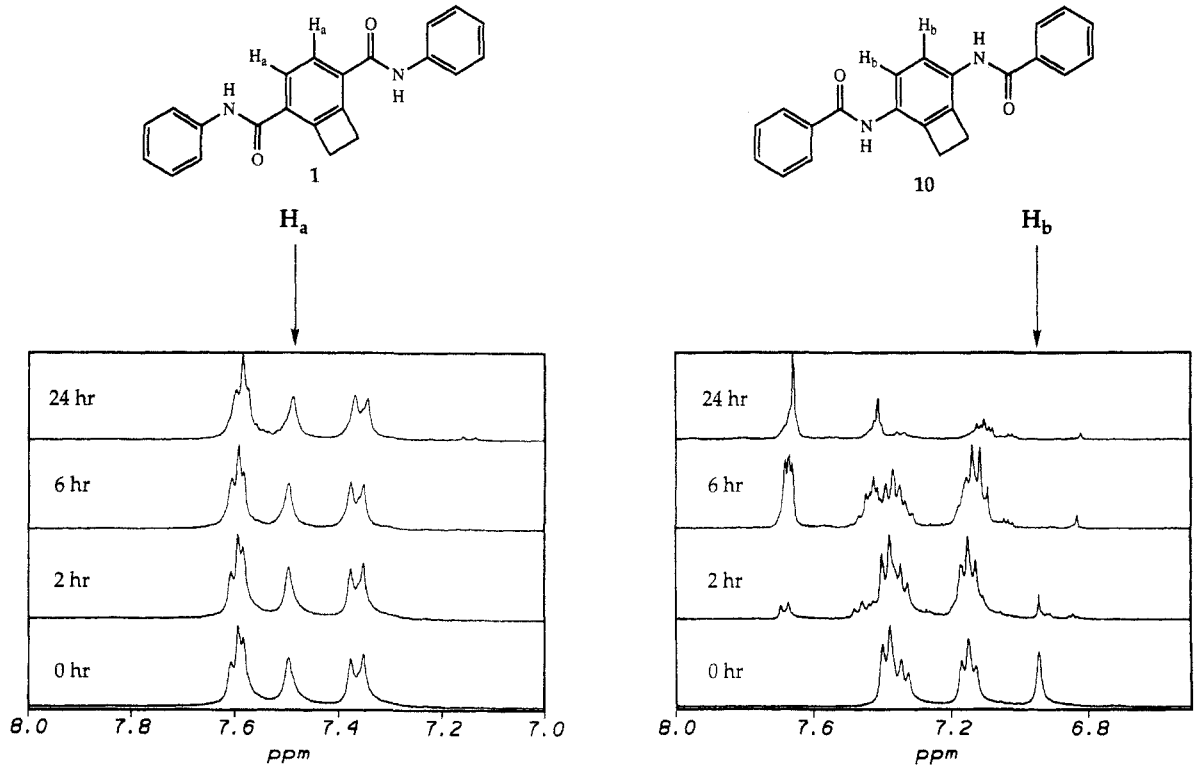


Figure 3. ^{1}H NMR spectra (360 MHz) of (a) model compound 1 and (b) model compound 10 in D_2SO_4. The spectra were recorded after the solutions had been heated at 90 °C for the indicated times. The proton resonance on the cyclobutaarene ring of 1 (H_a, δ 7.50) remains unchanged during the time of the experiment, demonstrating the stability of 1 to strong acids. In contrast, the proton resonance on the cyclobutaarene ring of 10 (H_b, δ 6.90) disappears in <6 h.

observed. For most of the 2,5-disubstituted derivatives of benzocyclobutene, the temperature of maximum heat release was observed to be around 350 °C, which is ~100 °C greater than that of the 3-monosubstituted derivatives reported by Kirchhoff,[8a,b] Hahn,[13] and Arnold.[10a,14,15]

Interestingly, when the model compounds contained a dienophile (7 and 15), the reaction temperatures appeared to drop significantly and were within the temperature range reported for 3-monosubstituted derivatives. To investigate this effect further, mixtures of 1, 2, and 3 with various

Table 1. Summary of DSC[a] Data for Disubstituted Benzocyclobutene Model Compounds

model compd	T_{melt}[b] (°C)	T_{rxn}[c] (°C)	ΔH_{rxn} (kcal/mol)	model compd	T_{melt}[b] (°C)	T_{rxn}[c] (°C)	ΔH_{rxn} (kcal/mol)
1	313	364	-20.5	9	191	330	-12.4
2	293	370	-18.1	10	341	345	-10.7
3	221	392	-16.9	12	276	306	-9.6
4	171	395	-13.4	13	144	368	-10.0
6	68	347	-24.2	14	183	393	-17.3
7	161	289	-61.6	15	129	264	-49.6
8	96	320	-11.1	16	62	350	-27.6

[a] Scan rate of 20 °C/min. [b] Melting point as measured by the onset of the melting endotherm. [c] Temperature of maximum heat release.

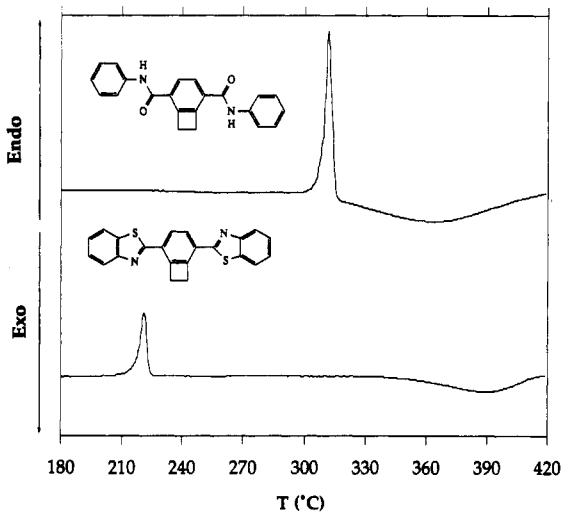
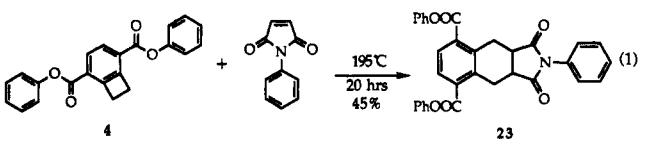
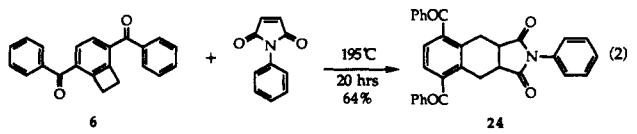


Figure 4. Representative DSC traces obtained at 20 °C/min of the diamide **1** and bisbenzthiazole **3**. In these traces an irreversible reaction is observed in the melt at ca. 350 and 390 °C, respectively.

dienophiles were analyzed by DSC (Table 2). The dienophiles by themselves were thermally stable at the temperatures indicated in Table 2. By comparing reaction temperatures of the mixtures and pure model compounds, one can conclude that dienophiles lower the exotherm by as much as 100 °C. One explanation of these results (and the behavior of **7** and **15**) would be that the cyclobutaarene ring reversibly opens above ~250 °C but further reaction is inhibited in the absence of a dienophile. When dienophiles are present, [4 + 2] cycloaddition chemistry presumably occurs. To explore the possibility of cycloaddition reactions, **4** and **6** were heated to 195 °C in the presence of *N*-phenylmaleimide without solvent for 6 h (eqs 1 and 2). After purification, **23** and **24** were obtained



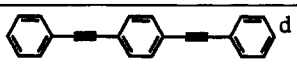
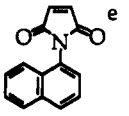
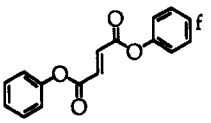
4 23



6 24

in 45% and 64% yield, respectively. The low yield and the presence of benzocyclobutene starting material (**4** and **6**) are believed to be the result of *N*-phenylmaleimide homopolymerization and sublimation. No dimerization products were observed in this reaction. The isolation of

Table 2. Maximum Heat Release Temperatures (°C) for Mixtures of Dienophiles and XTA Model Compounds 1-3

dienophile	1[a]	2[b]	3[c]
 d	348	366	355
20			
 e	297	282	292
21			
 f	294	284	291
22			

[a-f] XTA model compounds showed reaction exotherms in the absence of a dienophile at (a) 346, (b) 370, and (c) 392 °C. Dienophiles were stable to (d) 370, (e) 310, and (f) 350 °C.

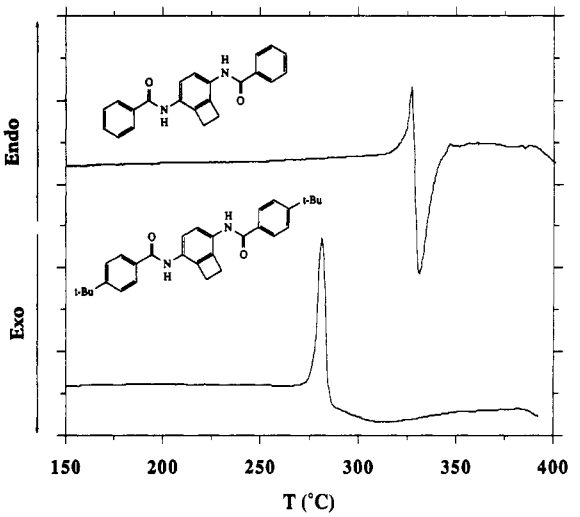


Figure 5. Representative DSC traces obtained at 20 °C/min of bisbenzanilide **10** and *tert*-butyl-substituted bisamide **12**. In the case of **10** the reaction occurs simultaneously with melting, indicating a strong dependence of the reaction on the crystal transition.

23 and **24** is clear evidence that these model compounds are following the expected [4 + 2] chemistry of *o*-quinodimethanes (**A** → **F**, Scheme 1).

The chemistry of 2,5-disubstituted benzocyclobutene in the absence of a dienophile is not yet fully understood. Size exclusion chromatography (SEC) was used to explore the possibility of homopolymerization (Scheme 1, **D**) vs dimerization (Scheme 1, **E**). Compounds **4** and **6** were heated separately in the melt (30 s, 400 °C) and the products were analyzed using SEC. The major species in both cases were consistent with dimer and trimer. Some starting material also remained. Further characterization of the product mixture was not pursued.

From data in Tables 1 and 2 it is apparent that 2,5-disubstitution hinders benzocyclobutene thermal chemistry. As noted above, exotherms only occurred after the compounds first melted. From this observation, it was initially thought that a crystal-to-liquid transition may be inhibiting the benzocyclobutene reaction at least in some cases. Evidence for this can be seen in the DSC traces for **10** and **12** (Figure 5). In the DSC trace for **10**, a sharp reaction exotherm immediately follows the melting

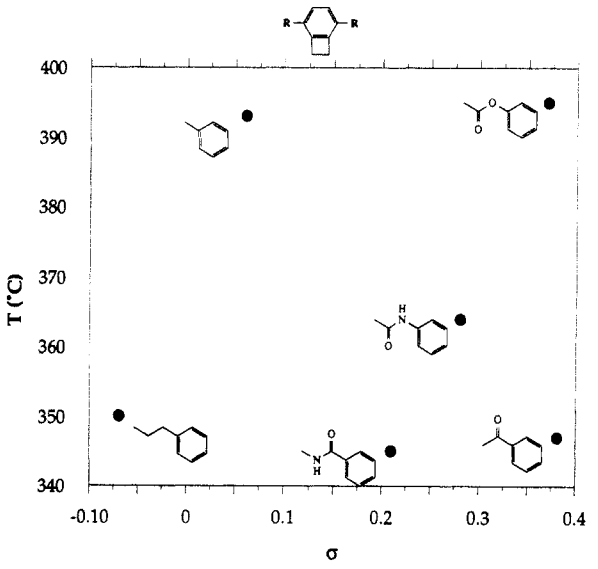
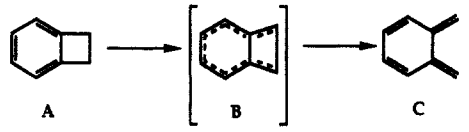


Figure 6. Plot of Hammett parameters versus temperature of maximum heat flow for disubstituted model compounds. The chemical structures of the substituents are shown alongside the data points.

transition. In the analogous *tert*-butyl compound **12** (which melts at a lower temperature), this effect is still observed but to a lesser degree. Moreover, the majority of the compounds melt well below the exothermic reaction (**3**, **4**, **6**, **8**, **9**, **12–14**, and **16**). We conclude that solid-state inhibition of benzocyclobutene chemistry is, in general, not responsible for the high reaction temperatures, but may be in isolated cases.

Electronic factors were also considered as a possible explanation for the high reaction temperatures of the 2,5-disubstituted derivatives. On the basis of *ab initio* calculations, Kirchhoff et al.[8a] have shown that substituting electron acceptors on the arene ring and donors on the cyclobutene ring lowers the energy of the transition state (**B**) (eq 3). Their explanation is that the HOMO and



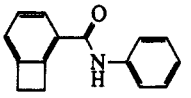
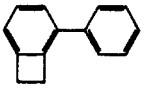
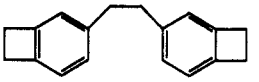
(3)

LUMO of **B** are stabilized by this substitution, making it more accessible. Using ^{13}C NMR data, Kametani has found a correlation between the sp^2 character of the C-1 to C-8 bond and the ring-opening reaction temperature.[19] Double-bond character was greatest and reaction temperatures lowest when electron-donating groups were substituted on the cyclobutene ring. On the basis of this literature, it is possible that electronic factors are responsible for the high reaction temperatures.

According to the above arguments, **1–6** and **9**, being substituted with electron-withdrawing functional groups, should favor ring opening relative to **8**, **10–14**, and **16**. However, the differences in reaction temperatures for these compounds are not significant enough to suggest a strong correlation between functional groups and reaction temperatures. To further support this statement, a plot of Hammett parameters[20] versus reaction temperatures was made and is shown in Figure 6.[21] The scattered nature of this plot further suggests that there is no significant correlation between electronic structure and reaction temperature.

An alternative explanation for the high reaction temperatures of the 2,5-disubstituted derivatives could be based on steric factors. It is well known that steric interactions can dramatically affect the rates of [4 + 2] cycloaddition reactions. This has been documented, for example, through kinetic studies between maleic anhydride and various 1,4-substituted dienes.[22] Rates are decreased by bulky substituents that either impede the diene/dienophile approach or reduce the stability of the required s-cis conformation of the diene. Evidence that steric effects may be playing a role in the present case can be seen by comparing the reaction temperatures of **1** and **18** and **14** and **19** (Tables 1 and 3). These comparisons reveal a 70 and 90 °C temperature difference, respectively, which may be due to the lower steric encumbrance in the monosubstituted compounds (**18** and **19**) compared to the 2,5-disubstituted derivatives (**1** and **14**). Benzocyclobutene dimers are believed to proceed through the spiro intermediate **C** shown in Scheme 1. The fact that lower reaction temperatures can be observed when dienophiles are present suggests that the nature of the unfavorable steric interactions involves the approach of the second *o*-quinodimethane. In other words, the steric effects do not impede ring opening. Molecular models of spiro intermediates support this explanation.

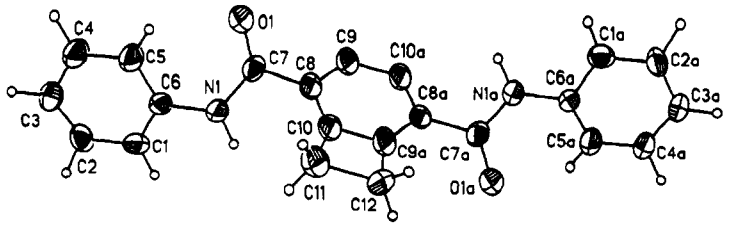
Table 3. Summary of DSC Data for Monosubstituted Benzocyclobutene Model Compounds

model compd	no.	T_{melt} (°C)	T_{rxn} (°C)	ΔH_{rxn} (kcal/mol)
	18	124	298	−17.1
	19	67	303	−19.9
	25[a]	82–86	260	−26.6

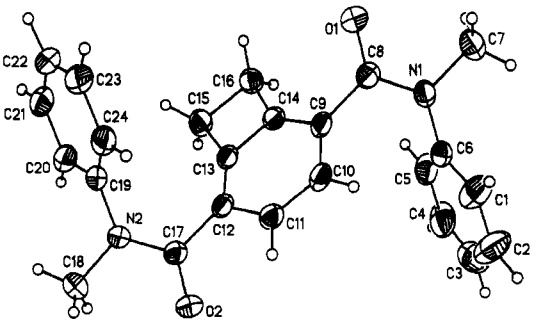
[a] Reference 8a.

Compounds **16** and **25**[8a] provide further support that the role of steric factors is influencing the reactivity of the *o*-quinodimethane species (see Table 3). These compounds are electronically similar in that they are substituted with phenylethyl groups and both melt below 100 °C. The only difference in these compounds is that **25** is substituted in the 3 position and **16** in the 2 and 5 positions, making the steric demand of the ortho substituents in **16** a possible reason for the 90 °C reaction temperature difference. Finally, the role of sterics is illustrated by **12** and **13**. As discussed above, the *tert*-butyl groups in **12** were used to decrease the melting point of **10**, which also lowered the reaction temperature. From these results it was expected that N-methylating the amide functionality in **12** would further reduce the melting point and thus reduce the reaction temperature. Even though the melting point for **13** is over 100 °C less than that of **12**, the reaction temperature was found to be ~60 °C higher. This again points to steric hindrance.

Structure. The small-molecule compounds studied here offered the opportunity to examine their chemical and solid-state structure by single-crystal X-ray diffraction. For amide derivatives **1**, **9**, and **11**, it was of interest to correlate the effect of substituents to the cyclobutaarene structure and to determine how chemical modifications altered solid-state conformations and packing. This information might be relevant to reactivity as well as the formation of ordered fluid phases like those commonly observed in concentrated solutions of aramids. The



1



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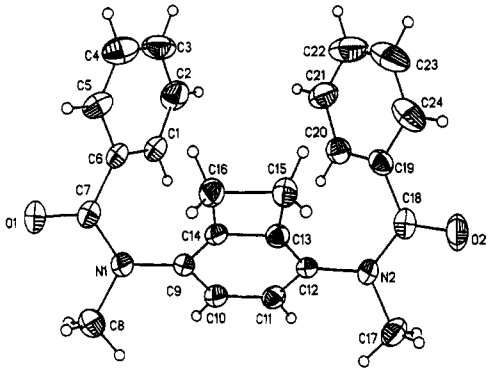
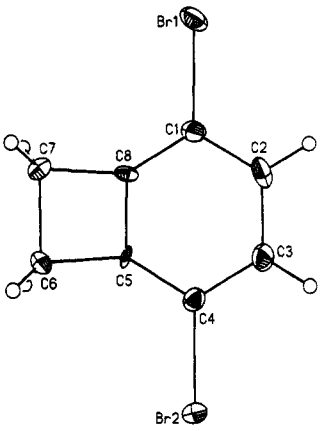


11



BCB-Br_2

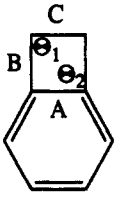
Figure 7. ORTEP drawings of XTA diamide 1, XTA *N,N'*-dimethyl diamide **9**, BCB *N,N'*-dimethyl bisbenzamide 11, and **BCB-Br_2**. Structure 1 has trans amide bonds and is transoid in geometry with respect to the carbonyl oxygens. The cyclobutaarene ring minimally increases the monomer's lateral dimensionality, all of which are favorable for lyotropic liquid crystallinity.

original design of **XTA** was made with the intention of preserving the high aspect ratio characteristic of terephthalic acid derivatives.

Crystal structures of four benzocyclobutene derivatives are shown in Figure 7 in addition to relevant valence angles and bond lengths shown in Table 4. Accurate determination of geometry parameters for the cyclobutene ring in 1 could not be made because of the disorder encountered in the cyclobutene ring orientation. In the remaining compounds, there is no significant difference in benzocyclobutene valence angles and bond lengths, suggesting that arene substituents have little electronic effect on the structure and in turn the reactivity of the cyclobutene unit. Intermolecular hydrogen bonding was observed in 1 between H1N and O1. N-Methylation can be seen to significantly change amide bond geometry. This chemical modification causes the trans amide bond in 1 to change to the cis conformation in **9**. Geometry changes of this type upon N-methylation have been reported for other amides.[23]

The ability of benzocyclobutene model compounds to form ordered liquid phases in concentrated solutions was investigated using cross-polarized light microscopy. Concentrated samples of 1 in H_2SO_4 and **2** and **3** in poly(phosphoric acid) were attempted at 20, 35, and 50% w/w. We were unsuccessful at preparing homogeneous samples at 50% w/w, limiting the study to the 20 and 35% w/w solutions. Samples were thermally cycled in an inert atmosphere from 24 °C to their clearing temperatures and recooled to 24 °C. Birefringent fluid phases were not observed in any of the solutions. However, data on poly(*p*-phenylene terephthalamide-*co*-XTA) and poly(bisbenzthiazole-*co*-XTA) polymers indicate that the cyclobutaarene ring does not disrupt liquid crystallinity in the macromolecular systems.[16c]

Table 4. Summary of Important Valence Angles and Bond Lengths for Some 2,5-Disubstituted Benzocyclobutene Model Compounds



compd	bond A (Å)	bond B (Å)	bond C (Å)	valence angle θ_1	valence angle θ_2
1	1.40(8)	1.31(1)	1.65(1)	85.0(6)	95.0(6)
9	1.38(4)	1.52(3)	1.57(4)	86.1(2)	94.2(2)
11	1.38(8)	1.51(7)	1.58(9)	86.6(4)	94.1(4)
BCB-Br_2	1.40(1)	1.51(2)	1.58(1)	85.8(8)	94.1(9)

Conclusions

We have presented results from a model compound study investigating the thermal and acid stability of the new cross-linking monomer **XTA-Cl**. Through the synthesis of these model compounds it has been shown that this cross-linkable monomer can tolerate conditions used in the synthesis of high-performance polymers such as polyaramids, poly(bisbenzthiazole)s, poly(bisbenzoxazole)s, and polyarylates. ^{1}H NMR experiments performed in D_2SO_4 on model compounds 1 and **10** indicate that the cyclobutaarene ring in **XTA-Cl** derivatives is stable to strong acids and high temperatures. This unusual stability to strong acids was attributed to the electron-

Table 5. Crystallographic Data for 2,5-Disubstituted Benzocyclobutene Derivatives

parameter	1	9	11	BCB-Br_2
mol formula	$C_{22}H_{18}N_2O_2$	$C_{24}H_{22}N_2O_2$	$C_{24}H_{22}N_2O_2$	$C_8H_6Br_2$
mol wt	342.40	370.455	370.455	261.94
cryst dimens (mm)	0.22 × 0.10 × 0.12	0.22 × 0.28 × 0.40	0.20 × 0.22 × 0.48	0.20 × 0.22 × 0.30
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*Pcab*	$P2_1$	$Pc2_1n$	$P2_1/c$
Z (molecules/unit cell)	4	2	4	4
a (Å)	9.580(1)	7.855(1)	8.248(1)	10.699(4)
b (Å)	9.697(7)	9.664(3)	9.195(2)	4.063(1)
c (Å)	18.709(9)	13.212(4)	26.637(8)	18.553(6)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	98.49	90.00	100.96
γ (deg)	90.00	90.00	90.00	90.00
V (Å^{-3})	1738(2)	991.9(4)	2020.3(8)	791.8(4)
d(calcd) (g cm^{-3})	1.30	1.24	1.21	2.19
diffractometer	Siemens $R3m/v$	Syntex $P2_1$	Syntex $P2_1$	Siemens $R3m/v$
radiation, λ (Å)	Mo Kα; 0.7107	Mo Kα; 0.7107	Mo Kα; 0.7107	Mo Kα; 0.7107
no. of unique refls	1136	3927	1905	1828
no. of refls considered obsd	883	3722	1450	937
scan mode; Θ_{max} (deg)	$\theta/2\theta$; 45	$\theta/2\theta$; 52	$\theta/2\theta$; 50	$\theta/2\theta$; 55
solved by	SHRLXTL PLUS	SHRLXTL PLUS	SHRLXTL PLUS	SHRLXTL PLUS
refined by	full-matrix least squares	full-matrix least squares	full-matrix least squares	full-matrix least squares
final R value	0.0809	0.0506	0.0535	0.0617
ω	2.39	1.12	1.29	2.13
final R_w value	0.0866	0.0675	0.0525	0.0753
temp (°C)	−100	24	24	−100
cryst solvent	DMF/H_2O	THF/Et_2O	THF/Et_2O	hexane
H atoms	Riding model, d_{C-H} = 0.96 Å	THF/Et_2O Riding model, d_{C-H} = 0.96 Å	THF/Et_2O Riding model, d_{C-H} = 0.96 Å	hexane Riding model, d_{C-H} = 0.96 Å
$(\Delta/\sigma)_{max}$	<0.001	0.001	0.001	<0.001
μ, (cm^{-1}) S	0.79	0.73	0.73	100.58
highest map residual (e/Å^3)	+0.30/−0.35	+0.37/−0.29	+0.18/−0.17	+1.66/−1.61

withdrawing nature of the amide carbonyl functionality in 1, which deactivates the cyclobutaarene ring toward electrophilic aromatic substitution. Differential scanning calorimetry was used to determine the thermal reactivity of these model compounds. Reaction temperatures around 350 °C were typically encountered, which is ~100 °C greater than those for previously reported benzocyclobutene compounds. Only in the presence of dienophiles are the reaction temperatures comparable to those reported for 3-monosubstituted derivatives. Analysis of the DSC traces for these compounds shows that the thermal chemistry of **XTA-Cl** model compounds is not significantly influenced by electronic effects or crystal-to-liquid transition temperature. The most important reason for the higher reaction exotherms appears to be the greater steric encumbrance of the 2,5-disubstituted cyclobutaarene ring. Cross-polarized optical microscopy was used to investigate the lyotropic liquid crystallinity in **1–3**. Liquid crystallinity was not observed in these compounds.

Experimental Section

Instrumentation. Synthetic manipulations involving air- and/or moisture-sensitive compounds were carried out on a Schlenk line or in a nitrogen-filled Vacuum Atmospheres drybox. DSC analyses were performed using a Perkin-Elmer 7 apparatus at a rate of 20 °C/min. NMR spectra were recorded on a Bruker AM-300 (300-MHz ^{1}H; 75-MHz ^{13}C) and AM-360 (360-MHz ^{1}H; 90-MHz ^{13}C) spectrometers and referenced to the residual proton solvent resonance. ^{1}H NMR data are presented with the following convention: chemical shift (ppm), multiplicity, and integrated intensity. Multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet) and broad signals are indicated by br. Carbon NMR shifts are given in ppm and referenced to the solvent ^{13}C signal. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a Finnigan 4021 mass spectrometer and a VG 70-S mass spectrometer, respectively.

X-ray Diffraction. Crystallographic data for the 2,5-disubstituted benzocyclobutene derivatives are reported in Table 5. Complete tables of final atomic positional parameters with equivalent isotropic and anisotropic thermal parameters for all non-hydrogen atoms, bond lengths, and bond angles have been deposited and are available from the Cambridge Crystallographic Data Center. Crystals of **1** were grown by vapor phase transfer of water into a solution of **1** in dimethylformamide. Crystals of **BCB-Br_2** were grown from hexane. Crystals of **7** and **11** were grown from tetrahydrofuran and ethyl ether/methylene chloride (8:1), respectively.

Materials. 1,2-Dichloroethane and methylene chloride were vacuum transferred off calcium hydride. Tetrahydrofuran and ethyl ether were vacuum transferred from sodium benzophenone ketyl. Sodium hydride was washed with pentane to remove mineral oil, filtered under vacuum, dried, and stored in a nitrogen-filled drybox. Compounds **1** and **2** were prepared by the previously reported procedure.[2] Other reagents were purchased from Aldrich Chemical Co. and used as received. Phenyltrimethyltin,[24] (bis(triphenylarsine)palladium dichloride,[25] and bis(dibenzylideneacetone)palladium (Pd[(dba)$_2$])[26] were all prepared as described in the literature. The synthesis of **20** has previously been reported,[27] as has **21**.[28]

2,5-Bis(benzthiazol-2-yl)-7,8-dihydrocyclobutabenzene (3). A 100-mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer was charged with *o*-aminothiophenol (1.65 g, 13.2 mmol), 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl dichloride (**XTA-Cl**) (510 mg, 2.2 mmol), and 85% poly(phosphoric acid) (PPA, 50 mL). The suspension was rapidly stirred, and the flask was evacuated and backfilled with nitrogen three times at 24 °C and then heated to 100 °C over a period of 3 h, evacuating periodically to remove HCl. The solution was then heated to 150 °C, evacuated periodically, and stirred for 20 h. The resulting yellow-orange solution was partitioned in ice water (100 mL), brought to neutral pH using aqueous NaOH, and filtered to collect the solid. The solid was recrystallized from DMSO to provide **3** as a yellow powder (0.73 g, yield 92%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 8.19 (s, 2H), 8.11 (d, 2H), 7.91 (d, 2H), 7.58 (t, 2H), 7.49 (t, 2H), 3.60 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 163.7, 153.1, 145.2, 134.8, 128.9, 126.9, 125.8, 125.4, 123.1, 122.5, 30.6; HRMS (EI, 70 eV) calcd for $C_{22}H_{14}N_2S_2$, 370.0598; found, 370.0580. Anal. Calcd for $C_{22}H_{14}N_2S_2$: C, 69.33; H, 4.07; N, 8.09; S, 18.51. Found: C, 69.25; H, 4.09; N, 8.11; S, 18.41.

2,5-Diphenyl 7,8-Dihydrocyclobutabenzenedicarboxylate (4). A 100-mL Schlenk flask was charged with **XTA-Cl** (1.02 g,

4.5 mmol), phenol (820 mg, 9.0 mmol), and dry methylene chloride (20 mL), evacuated, and cooled to 0 °C. While this mixture was stirred rapidly, a solution of triethylamine (2.5 mL) and methylene chloride (10 mL) was added dropwise, forming a yellow precipitate. The mixture was warmed to room temperature, washed with water (3 × 20 mL), dried over molecular sieves, filtered, and concentrated to yield a white solid. The solid was recrystallized from hexane and methylene chloride (3:1) to give **4** as fluffy white crystals (1.24 g, yield 80%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.43 (t, 4H), 7.21 (m, 6H), 3.56 (s, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 163.5, 151.0, 149.6, 129.5, 128.7, 128.2, 126.0, 121.5, 31.5; HRMS (EI, eV) calcd for $C_{22}H_{16}O_4$, 344.1049; found, 344.1048. Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.49; H, 4.66.

2,5-Diisocyano-7,8-dihydrocyclobutabenzene (5). A 100-mL three-neck flask was equipped with a magnetic stirrer and was charged with **XTA-Cl** (2.0 g, 8.77 mmol), sodium azide (1.43 g, 21.92 mmol), methylene chloride (30 mL), and H_2O (30 mL). After the reaction mixture was allowed to stir for 8 h at room temperature, the aqueous layer was removed, the organic solvent was dried over $MgSO_4$, filtered, and concentrated, and the white solid was redissolved in dry benzene (50 mL). *Caution!* Shock sensitive. The solution was refluxed for 12 h, the solvent was removed, and the resultant white solid was sublimed (50 °C, 20 mTorr), yielding **5** as a white solid (1.39 g, yield 85%): ^{1}H NMR (360 MHz, THF-d_8) δ 6.90 (s, 2H), 3.16 (s, 4H); ^{13}C NMR (90 MHz, THF-d_8) δ 141.3, 126.4, 125.0, 27.9; HRMS (EI, eV) calcd for $C_{10}H_6N_2O_2$: 186.0429; found, 186.0430. Anal. Calcd for $C_{10}H_6N_2O_2$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.63; H, 3.36; N, 15.11.

2,5-Dibenzoyl-7,8-dihydrocyclobutabenzene (6). A 10-mL Schlenk flask was charged with **XTA-Cl** (50 mg, 2.19 mmol), phenyltrimethylstannane (1.15 g, 4.79 mmol), bis(triphenylarsine)palladium dichloride (18 mg, 0.02 mmol), and methylene chloride (3 mL) in a nitrogen-filled drybox. The solution was stirred at 24 °C for 36 h and then at 50 °C for 12 h, diluted with methylene chloride (5 mL), and washed with water (3 × 10 mL). The extracts were dried over $MgSO_4$, and the solvent was removed. Flash column chromatography (3:1 hexane/diethyl ether) provided **6** as a white solid (470 mg, yield 70%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 4H), 7.67 (s, 2H), 7.57 (t, 2H), 7.48 (t, 4H), 3.17 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 147.3, 137.9, 135.2, 132.7, 129.5, 128.4, 128.1, 31.0; HRMS (EI, 70 eV) calcd for $C_{22}H_{16}O_2$, 312.1150; found, 312.1141. Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.60; H, 5.04.

2,5-Bis[(phenylethynyl)carbonyl]-7,8-dihydrocyclobutabenzene (7). A 50-mL Schlenk flask was charged with **XTA-Cl** (1.0 g, 4.38 mmol), phenylacetylene (1.9 g, 18.6 mmol), copper iodide (21 mg, 0.11 mmol), triphenylphosphine (92 mg, 0.35 mmol), triethylamine (20 mL), and $Pd[(dba)_2]$ (63 mg, 11 mmol). The suspension was stirred rapidly and evacuated, and stirring was continued at room temperature for 20 h. The suspension was filtered, and the filtrate was diluted with methylene chloride (20 mL), washed with water (3 × 30 mL), dried over molecular sieves, and concentrated. Purification by flash column chromatography on silica gel eluted with hexane, methylene chloride, and tetrahydrofuran (6:2:1) gave a yellow solid. Recrystallization from diethyl ether/tetrahydrofuran (3:1) yielded **7** as yellow crystals (1.00 g, yield 65%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.64 (d, 4H), 7.40 (m, 6H), 3.67 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 149.1, 134.8, 133.0, 130.9, 128.7, 127.4, 120.1, 93.4, 88.6, 32.1; HRMS (EI, 70 eV) calcd for $C_{26}H_{16}O_2$: 360.1150; found, 360.1154. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47. Found: C, 86.88; H, 4.57.

***N,N'*-Diphenyl-7,8-dihydrocyclobutabenzene-2,5-dimethanamine (8).** A 20-mL round-bottom flask was charged with lithium aluminum hydride (33 mg, 0.87 mmol) and tetrahydrofuran (5 mL) in a nitrogen-filled drybox. The suspension was removed from the drybox, and a slurry of **1** (100 mg, 0.29 mmol) in tetrahydrofuran (5 mL) was added under a nitrogen atmosphere. The mixture was stirred at 70 °C for 3 h, cooled to room temperature, quenched with water (10 mL) and then 1 N HCl (10 mL), neutralized, and extracted with diethyl ether (3 × 10 mL). The solvent was removed to yield **8** (80 mg, yield 88%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.06 (s, 2H), 7.02 (t, 4H), 6.54 (d, 4H), 6.48 (s, 2H), 6.02 (t, 2H), 4.13 (d, 4H), 3.03 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 148.8, 143.2, 132.9, 128.8, 125.7, 115.6, 112.0, 43.1, 28.5; HRMS (EI, 70 eV) calcd for $C_{22}H_{22}N_2$, 314.1783; found, 314.1780. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.51; H, 6.86; N, 8.89.

***N,N'*-Diphenyl-*N,N'*-dimethyl-7,8-dihydrocyclobutabenzene-2,5-dicarboxamide (9).** A 50-mL three-necked flask equipped with a nitrogen inlet and a magnetic stir bar was charged with **1** (250 mg, 0.74 mmol) and sodium hydride (37 mg, 1.55 mmol). A solution of iodomethane (0.12 mL, 1.84 mmol) in tetrahydrofuran (20 mL) was added, and the suspension was stirred overnight. The resulting yellow suspension was quenched with ice water (50 mL), extracted with diethyl ether (3 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed, yielding a white solid. The solid was recrystallized from tetrahydrofuran and washed with diethyl ether, providing **9** as white crystals (220 mg, yield 81%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.24 (t, 4H), 7.17 (m, 2H), 7.05 (d, 6H), 7.04 (s, 2H), 3.31 (s, 6H), 2.4 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 167.1, 143.5, 143.0, 132.0, 128.8, 126.5, 126.4, 126.3, 37.3, 29.0. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.52; H, 5.98; N, 7.56.

2,5-Dibenzamido-7,8-dihydrocyclobutabenzene (10). A dry, 100-mL round-bottom flask was charged with dry tetrahydrofuran (20 mL), water (0.3 mL), and 12 N HCl (3.2 mL). To this mixture a solution of **5** (1.50 g, 8.06 mmol) in dry tetrahydrofuran (4 mL) was added dropwise, causing a white solid to precipitate from solution. The white solid was filtered, washed with tetrahydrofuran (3 × 10 mL), and vacuum-dried to yield 1,2-dihydrocyclobutabenzene-3,6-diamine dihydrochloride as a white solid in adequate purity to continue (1.63 g, 98%): ^{1}H NMR (360 MHz, D_2O) δ 7.12 (s, 2H), 3.16 (s, 4H). A 50-mL Schlenk flask charged with 1,2-dihydrocyclobutabenzene-3,6-diamine dihydrochloride (750 mg, 3.64 mmol) and dry methylene chloride (20 mL) was evacuated and cooled to 0 °C. To this rapidly stirring suspension was added benzoyl chloride (0.93 mL, 8.00 mmol), and the mixture was cooled. A solution of triethylamine (2 mL) and methylene chloride (5 mL) was added and allowed to stir for 3 h. The white suspension was filtered and the solid was washed with methylene chloride (3 × 15 mL) to yield **10** as a white solid (1.13 g, yield 90%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 10.21 (br s, 2H), 7.94 (d, 4H), 7.54 (m, 6H), 7.25 (s, 2H), 3.15 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 164.5, 137.3, 134.6, 131.5, 129.5, 128.4, 127.8, 119.8, 30.3; HRMS (EI, eV) calcd for $C_{22}H_{18}N_2O_2$, 342.1368; found, 342.1358.

***N,N'*-Dimethyl-2,5-dibenzamido-7,8-dihydrocyclobutabenzene (11).** Compound **11** was prepared from **10** (110 mg, 0.32 mmol) and sodium hydride (19 mg, 0.80 mmol) using the procedure for **9**. The reaction mixture was quenched with ice water (50 mL), extracted with ether (3 × 20 mL), dried over $MgSO_4$, and concentrated. The crude product was recrystallized from diethyl ether and methylene chloride (8:1), yielding **11** as white crystals (110 mg, yield 92%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.34 (t, 2H), 7.22 (m, 8H), 6.89 (s, 2H), 3.26 (s, 6H), 2.56 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 169.2, 140.5, 136.7, 135.4, 129.9, 128.1, 127.7, 125.0, 36.7, 27.9; HRMS (EI, eV) calcd for $C_{24}H_{22}N_2O_2$, 370.1681; found, 370.1683. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.30; H, 7.78; N, 5.82.

2,5-Bis(4-*tert*-butylbenzamido)-7,8-dihydrocyclobutabenzene (12). Compound **12** was prepared from 1,2-dihydrocyclobutabenzene-3,6-diamine dihydrochloride (410 mg, 1.99 mmol) and *p*-*tert*-butylbenzoyl chloride (860 mg, 4.38 mmol) using the procedure for **10** (0.69 g, yield 76%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.88 (d, 4H), 7.52 (d, 4H), 7.24 (s, 2H), 3.14 (s, 4H), 1.31 (s, 18H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 164.4, 154.3, 137.2, 131.9, 129.4, 127.6, 125.1, 119.6, 34.6, 30.9, 30.2; HRMS (EI, 70 eV) calcd for $C_{30}H_{34}N_2O_2$, 454.2620; found, 454.2616.

***N,N'*-Dimethyl-2,5-bis(4-*tert*-butylbenzamido)-7,8-dihydrocyclobutabenzene (13).** Compound **13** was prepared from **12** (100 mg, 0.22 mmol) and sodium hydride (15 mg, 0.63 mmol) using the procedure for **9**. The reaction mixture was quenched with ice water (50 mL), extracted with ether (3 × 20 mL), dried over $MgSO_4$, and concentrated. The crude product was recrystallized from diethyl ether and methylene chloride (8:1), yielding **11** as white crystals (110 mg, yield 89%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.28 (d, 4H), 7.21 (d, 4H), 6.89 (s, 2H), 3.25 (s, 6H),

2.58 (s, 4H), 1.25 (s, 18H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 168.9, 152.7, 140.1, 136.6, 132.9, 128.2, 124.7, 124.3, 36.9, 34.5, 30.9, 28.1; HRMS (EI, 70 eV) calcd for $C_{32}H_{38}N_2O_2$, 370.1681; found, 370.1683. Anal. Calcd for $C_{32}H_{38}N_2O_2$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.30; H, 7.78; N, 5.82.

2,5-Diphenyl-7,8-dihydrocyclobutabenzene (14). A 10-mL Schlenk flask was charged with 3,6-dibromo-1,2-dihydrocyclobutabenzene[2] (257 mg, 0.98 mmol), phenylboronic acid (263 mg, 2.15 mmol), tetrakis(triphenylphosphine)palladium (22 mg, 0.019 mmol), potassium phosphate (1.37 g, 6.47 mmol), and 5 mL of *N*-methylpyrrolidine in a nitrogen-filled drybox. The orange solution was brought out of the drybox, and 3 mL of water was added. The solution was heated in a 90 °C oil bath for 24 h. The orange-brown solution was cooled, partitioned into 1 N HCl (10 mL), and extracted with methylene chloride (3 × 10 mL). The extractions were combined and dried over $MgSO_4$, and the solvent was removed. Recrystallization (methylene chloride) provided **14** as a white solid (199 mg, yield 79%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 4H), 7.57 (s, 2H), 7.44 (t, 4H), 7.32 (t, 2H), 3.47 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 138.0, 133.8, 128.8, 127.3, 126.9, 125.6, 30.6; HRMS (EI, 70 eV) calcd for $C_{20}H_{16}$, 256.1252; found, 256.1239. Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.67; H, 6.35.

2,5-Bis(phenylethynyl)-7,8-dihydrocyclobutabenzene (15). A 50-mL Schlenk flask was charged with 3,6-dibromo-1,2-dihydrocyclobutabenzene[2] (1.0 g, 3.81 mmol), phenylacetylene (820 mg, 8.03 mmol), triphenylphosphine (100 mg, 0.38 mmol), copper iodide (15 mg, 0.078 mmol), Pd[(dba)$_2$] (44 mg, 0.077 mmol), and triethylamine (20 mL). The suspension was stirred rapidly, evacuated, and placed in a 60 °C oil bath for 48 h. The suspension was filtered and the filtrate was diluted with methylene chloride (20 mL), washed with water (3 × 30 mL), dried over molecular sieves, and concentrated. Purification by flash column chromatography on silica gel eluted with hexane provided **15** as a white solid (1.07 g, yield 92%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.55 (m, 4H), 7.43 (m, 8H), 3.22 (s, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 147.1, 131.4, 130.1, 129.1, 128.8, 122.0, 117.2, 93.6, 85.8, 28.4; HRMS (EI, 70 eV) calcd for $C_{24}H_{16}$, 304.1252; found, 304.1240. Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.53; H, 5.31.

2,5-Bis(2-phenylethyl)-7,8-dihydrocyclobutabenzene (16). A 20-mL round-bottom flask was charged with 3,6-bis(phenylethynyl)-1,2-dihydrocyclobutabenzene (250 mg, 0.82 mmol) and toluene (10 mL). Tri-*n*-propylamine (1.25 mL, 6.57 mmol) and *p*-toluenesulfonhydrazide (1.22 g, 6.57 mmol) were added to the rapidly stirred solution, a reflux condenser was added to the flask, and the mixture was heated to reflux for 24 h. The red-orange solution was cooled to room temperature, washed with water (3 × 20 mL), and concentrated. Purification by flash column chromatography on silica gel eluted with hexane/tetrahydrofuran (8:1) yielded an off-white solid. Recrystallization from hexane/tetrahydrofuran (4:1) gave **16** (159 mg, yield 62%): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.25 (m, 4H), 7.18 (m, 6H), 6.88 (s, 2H), 2.90 (s, 4H), 2.82 (m, 4H), 2.49 (m, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 143.2, 141.6, 133.2, 128.3, 128.1, 126.9, 125.8, 35.7, 32.8, 27.7. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.77.

2-Bromo-7,8-dihydrocyclobutabenzene (17). A 100-mL three-neck flask was charged with 3,6-dibromo-1,2-dihydrocyclobutabenzene[2] (1.01 g, 3.86 mmol) and dry diethyl ether (38 mL). The solution was cooled to −78 °C, resulting in a white suspension. To this suspension was added *n*-butyllithium (1.48 equiv, 2.5 M solution in hexanes), yielding a yellow solution. The reaction mixture was quenched with water (30 mL) and allowed to warm to room temperature. The aqueous phase was extracted with diethyl ether (3 × 20 mL), dried over $MgSO_4$, and concentrated to yield a yellowish oil (110 mg, yield 61%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.27 (d, 1H), 7.06 (t, 1H), 6.98 (d, 1H), 3.12 (s, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 147.3, 146.0, 129.4, 128.8, 121.4, 115.6, 29.5, 28.5; HRMS (EI, 70 eV) calcd for C_8H_7Br, 118.9731; found, 181.9735.

***N*-Phenyl-7,8-dihydrocyclobutabenzene-2-carboxamide (18).** A 5-mL Schlenk flask was charged with **17** (106 mg, 0.580 mmol), aniline (0.06 mL, 0.657 mmol), 1,8-diazabicyclo[5.4.0]-undec-7-ene (0.2 mL, 1.34 mmol), triphenylphosphine (19.3 mg, 0.074 mmol), and bis(triphenylphosphine)palladium dichloride (22.1 mg, 0.032 mmol). The solution was stirred rapidly, evacuated, and backfilled with CO three times, placed in a 90 °C oil bath, and stirred for 48 h. The solution was partitioned into 1 N HCl (10 mL) and extracted with methylene chloride (3 × 10 mL). Purification by flash column chromatography on silica gel gave **18** as a white solid (40 mg, 30%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.82 (d, 1H), 7.67 (s, 1H), 7.62 (d, 2H), 7.34 (m, 3H), 7.19 (d, 1H), 7.12 (t, 1H), 3.48 (t, 2H), 3.31 (t, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 163.8, 145.7, 142.6, 137.5, 129.0, 128.8, 128.1, 126.3, 125.9, 124.4, 120.0, 30.1, 29.9; HRMS (EI, 70 eV) calcd for $C_{15}H_{13}NO$, 223.2770; found, 223.2768.

2-Phenyl-7,8-dihydrocyclobutabenzene (19). A 10-mL Schlenk flask was charged with **17** (108 mg, 0.590 mmol), phenylboranic acid (97 mg, 0.649 mmol), potassium phosphate (413 mg, 1.95 mmol), tetrakis(triphenylphosphine)palladium (14 mg, 0.018 mmol), and 5 mL of *N*-methylpyrrolidone in a nitrogen-filled drybox. The suspension was stirred rapidly, and 2 mL of water was added. The reaction mixture was evacuated three times and placed in an 80 °C oil bath for 24 h. Purification by flash column chromatography on silica gel eluted with hexane yielded **19** as a white solid (82.2 mg, yield 78%); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.66 (d, 2H), 7.46 (m, 3H), 7.32 (m, 2H), 7.03 (d, 1H), 3.43 (t, 2H), 3.25 (t, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 146.4, 142.9, 138.2, 134.7, 128.7, 127.9, 127.2, 126.9, 124.3, 121.4, 30.8, 29.5; HRMS (EI, 70 eV) calcd for $C_{14}H_{12}$, 180.0939; found, 180.0936.

1,4-Bis(phenylethynyl)benzene (20). Compound **20** was prepared from dibromobenzene (1.0 g, 4.24 mmol), phenylacetylene (1.02 mL, 9.33 mmol), copper iodide (16 mg, 0.08 mmol), triethylamine (50 mL), triphenylphosphine (133 mg, 0.5 mmol), and Pd[(dba)$_2$] (50 mg, 0.08 mmol), using the procedure for **15**. The resultant solid was recrystallized (toluene), yielding **20** as white crystals (956 mg, yield 80%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.52 (s, 4H), 7.35 (m, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 132.0, 131.9, 128.8, 128.7, 123.3, 91.8, 89.2. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.78; H, 5.05.

Diphenyl Fumarate (22). Compound **22** was synthesized from fumaryl chloride (2.0 g, 9.3 mmol), phenol (1.83 g, 19.0 mmol), triethylamine (3 mL), and methylene chloride (30 mL), using the procedure for **4**. Flash column chromatography (3:1 hexane/tetrahydrofuran) provided **22** as an off-white solid (745 mg, yield 30%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.45 (t, 4H), 7.28 (d, 2H), 7.22 (s, 2H), 7.18 (d, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 163.0, 150.5, 134.4, 129.5, 126.2, 121.2. Anal. Calcd for $C_{12}H_{16}O_4$: C, 71.64; H, 4.51. Found: C, 71.27; H, 4.39.

Compound 23. A 1-mL culture tube was charged with **4** (36.3 mg, 0.105 mmol) and benzmaleimide (26.0 mg, 0.150 mmol), stoppered, and bathed in refluxing ethylene glycol for 20 h. The melt was cooled, yielding a reddish glassy solid, and dissolved in methylene chloride. Purification by flash column chromatography on silica gel eluted with tetrahydrofuran/hexane (1:1) followed by recrystallization from hexane/methylene chloride (5:1) provided compound **23** as white crystals (27 mg, yield 50%): ^{1}H NMR (360 MHz, toluene-d_8) δ 7.89 (s, 2H), 7.28 (d, 3H), 7.10 (m, 18), 4.28 (br, d, 2H), 2.71 (br, s, 2H), 2.62 (br, d, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 177.5, 165.1, 150.6, 138.6, 132.9, 131.3, 129.5, 129.1, 128.6, 126.3, 126.2, 125.5, 121.6, 39.7, 30.3; HRMS (EI, 70 eV) calcd for $C_{32}H_{23}NO_6$, 517.1525; found, 517.1530.

Compound 24. A 1-mL culture tube was charged with **10** (51.3 mg, 0.164 mmol) and benzmaleimide (37.8 mg, 0.218 mmol), stoppered, and bathed in refluxing ethylene glycol for 20 h. The melt was cooled, yielding a tan glassy solid, and dissolved in methylene chloride. Purification by flash column chromatography on silica gel eluted with tetrahydrofuran/hexane (1:1) followed by recrystallization from hexane/methylene chloride (5:1) provided **24** as white crystals (40 mg, yield 64%): ^{1}H NMR (360 MHz, benzene-d_6) δ 7.75 (d, 4H), 7.58 (t, 2H), 7.40 (t, 6H), 7.35 (m, 1H), 7.33 (s, 2H), 7.04 (d, 2H), 3.34 (m, 2H), 3.30 (m, 1H), 3.25 (m, 1H), 3.08 (m, 1H), 3.03 (m, 1H); ^{13}C NMR (90 MHz, benzene-d_6) δ 196.9, 177.3, 139.9, 136.9, 135.7, 133.8, 131.7, 130.2, 129.1, 128.6, 128.5, 126.2, 126.1, 39.8, 27.1; HRMS (EI, 70 eV) calcd for $C_{32}H_{23}NO_4$, 485.1627; found, 485.1623.

Acknowledgment. This research is funded by the U.S. Army (Contract DAAK60-92-K-0005). J.S.M. acknowl-

edges support from the NSF Young Investigator Program, Grant CHE-9257050 (1992–1997).

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