ABSTRACT

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Title: Mechanisms of Photohydrodebromination of Bromoarenes

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The photohydrodebromination of brominated paracyclophanes was studied to help elucidate the possible mechanistic pathways leading to product for bromoarenes in general. Several brominated [2.2]paracyclophanes were studied to determine the effect of substitution patterns on this reaction. [2.2]Paracyclophanes were chosen for this study in order to investigate possible intramolecular excimer formation as a route to product formation. The [2.2]paracyclophanes studied were 4-bromo-, *pseudo-para*-dibromo-, and *pseudo-ortho*-dibromo[2.2]paracyclophane. 5-Bromo[3.3]paracyclophane has also been studied to determine the effect of increased ring separation on the reaction. These brominated cyclophanes showed varying efficiencies of both intermolecular and intramolecular excimer formation.

Mechanisms of Photohydrodebromination of Bromoarenes

by

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Date Thesis is presented _____ April 23, 1993 _____

Typed by _____ J. Eric Carlson _____

For Tammy and our fifteen kids

ACKNOWLEDGMENTS

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Introduction

Aromatic halides are used in a wide range of applications. For example, pentachlorophenol (PCP) is used as a wood preservative,[1] polybromobiphenyl (PBB) is used as a fire retardant,[2] and polychlorobiphenyl (PCB) is used as transformer fluid.[3] In addition to their practical applications these compounds are all environmental pollutants.

Traces of polychlorinated biphenyls (PCBs) have been reported in environmental samples since 1966[4]. There is evidence that PCBs are metabolized slowly in some organisms to their hydroxy derivatives. PCBs have an exceptionally wide range of uses due to their high dielectric constant and thermochemical stability (up to 900 °C).[3] They are used as dielectric fluids in capacitors and transformers; as industrial fluids in hydraulic systems, gas turbines, and vacuum pumps; as plasticizers in adhesives; in textiles, surface coatings, sealants, and copy paper; as heat transfer agents; and fire retardants, and fruit preservers. As a result of such wide use, these compounds have been released into the environment. All commercially available PCB mixtures are toxic to some extent; however, those containing four or fewer chlorine substituents have the highest toxicity, as reported in a study of their interaction with tissue culture cells.[5]

Polybromobiphenyls (PBBs) are also a common industrial product used as a fire retardant in thermoplastics.[2] These compounds are of particular interest because

of an accident in Michigan in 1973 and 1974 where a large quantity of commercial PBBs were mixed with livestock feed.[2] The contamination from this incident has become so widespread that, by some estimates, most residents of Michigan would, if tested, exhibit detectable levels of PBBs.[2] Unlike PCBs, studies show that PBB concentration in animal tissue decreases slowly with time or not at all.[2] The most toxic isomers of PBB have been found to be those containing one or no ortho bromines and two para bromines.[7] However, photochemical decomposition of these compounds seems to be a possible route to detoxification of these compounds in the environment.

PBBs absorb in the sunlight region (> 290 nm) with extinction coefficients ranging from 1.3 to 436 at 310 nm,[8] and undergo more rapid photodecomposition than PCB substrates.[9] Bunce et al.[10] have studied the steric effects of the photochemical reaction of mono- and dibromobiphenyls at 300 nm. They have observed that reductive debromination was the main reaction and that there was minor dimerization to quaterphenyls.

Photochemical excitation of aryl halides leads to an excited singlet state. This state has enough energy to induce carbon - halogen bond homolysis, and reaction to form products from this state (equation 1) is likely.

$$ArX \xrightarrow{h\nu} ArX^1 \longrightarrow Ar \cdot \longrightarrow \text{products} \qquad (1)$$
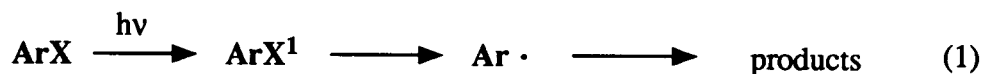
However, there can be participation from the excited triplet state. Bunce has shown that the quantum yield of intersystem crossing for chlorinated biphenyls varies from 0.4 to 1.0 for 1 to 6 chlorine atoms.[10] Therefore, dehalogenation can occur from both states. The reported quantum yield of intersystem crossing for biphenyl is 0.81.[11] Brominated biphenyls are expected to undergo efficient intersystem crossing due to the heavy atom effect. Measurement of the quantum

yield of intersystem crossing for 4-bromobiphenyl using Hammond's method[12] gave

a value of 0.98 ±0.05. This dual mechanism involving singlet and triplet reactivity

has been previously proposed by Soumillion and deWolf[13] who studied the direct

and sensitized photolysis of chlorobenzene. This dual mechanism is represented by

equation 2.

$$ArX \xrightarrow{\text{hv}} ArX^1 \longrightarrow ArX^3 \qquad (2)$$
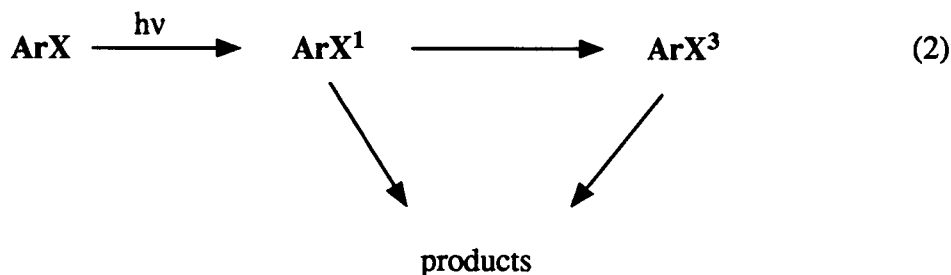
products

This simple mechanism cannot explain some of the energetic problems. The

triplet energy of 4-bromobiphenyl (66.9 kcal/mol)[14] is 12 kcal/mol lower in energy

than the phenyl C - Br bond fission energy (79.2 kcal/mol);[15] therefore, product

formation directly from the triplet state is unlikely. To help explain this reaction

from the triplet state despite the energy deficiency, Soumillionn and deWolf[13]

propose the formation of an excimer as the key step (equation 3). Freeman and Lee

have shown evidence that supports this mechanism.[16] They observed substitution

products in the micellar photochemical reaction of pentachlorobenzene which

indicate trapping of the excimer.

$$ArX \xrightarrow{\text{hv}} ArX^1 \longrightarrow ArX^3 \qquad (3)$$

$$\downarrow + ArX$$

$$ArX^{\delta -} ArX^{\delta +} \longrightarrow \text{products}$$
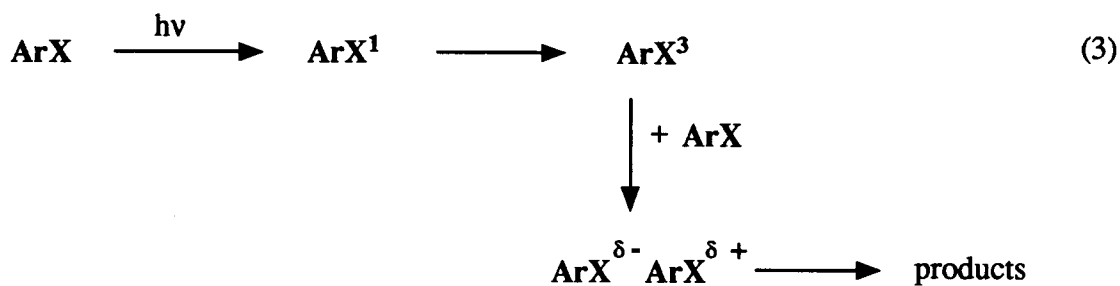
If a triplet excimer is involved then questions arise about the configuration of the excimer species. Some evidence has shown that excimer formation requires the two aromatic nuclei to lie parallel,[17] but the ground and triplet states of biphenyl are non - planar and planar respectively, and therefore very little stabilization can be gained through the excimer formation if complete face to face orientation is required.[18] However, Lim[19] has shown evidence that even skewed aryl systems exhibit excimer phosphorescence. In the case of biphenyls, excimer formation is also possible across idividual benzene rings which are arranged in parallel planes as shown below.
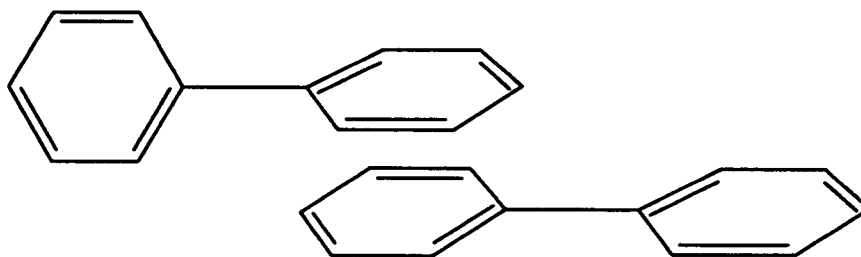
A

To elucidate the mechanism of the photohydrodehalogenation reactions of these molecules several studies have been completed. The first of these investigations involved 4-Bromobiphenyl (BpBr) and 3,4-Dibromobiphenyl (3,4-BpBr).[12] Based on the previous research and knowledge Jang conducted studies to elucidate the mechanism of the dehalogenation of bromobiphenyls. Three kinetic schemes were considered to provide a basis for the development of a mechanistic rationale. Irradiation of these bromobiphenyls at 300 nm yielded biphenyl as the sole product.

The first kinetic scheme involves the singlet state as the product determining step, Scheme I. The kinetic expression for the reciprocal of the quantum yield derived from this scheme, based on the steady state approximation, shows that the

quantum yield is independent of the substrate concentration; Thus, a plot of the reciprocal of the quantum yield versus the reciprocal of the concentration would be linear with a zero slope.

Scheme I
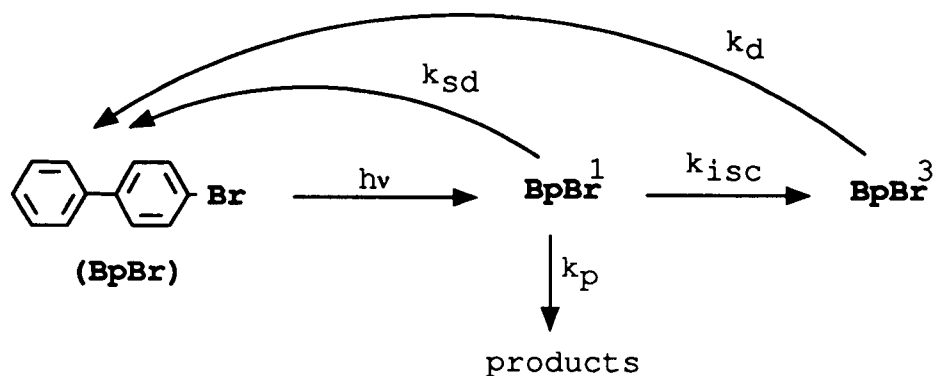
$$\frac{1}{\Phi_{prod}} = \frac{k_p + k_{isc} + k_{sd}}{k_p} \qquad (4)$$

However, it has been established that bromobiphenyls will undergo efficient intersystem crossing to the triplet state,[9,20,21] but to overcome the energy deficiency between this state and the phenyl C - Br bond fission energy, reaction via a triplet excimer has been proposed. A second kinetic scheme can be considered that involves product formation through formation of a triplet excimer, Scheme II. The kinetic expression derived from this scheme, based on the steady state approximation shows that the quantum yield is dependent on the substrate concentration; therefore, a plot of the reciprocal of the quantum yield versus the reciprocal of the substrate concentration would be linear with a positive slope.

A third kinetic scheme can be derived based on possible competition between product formation from the singlet state versus triplet state, Scheme III. If such competition were taking place, a plot of the reciprocal of the quantum yield versus the reciprocal of the substrate concentration would be curved. As the

Scheme II
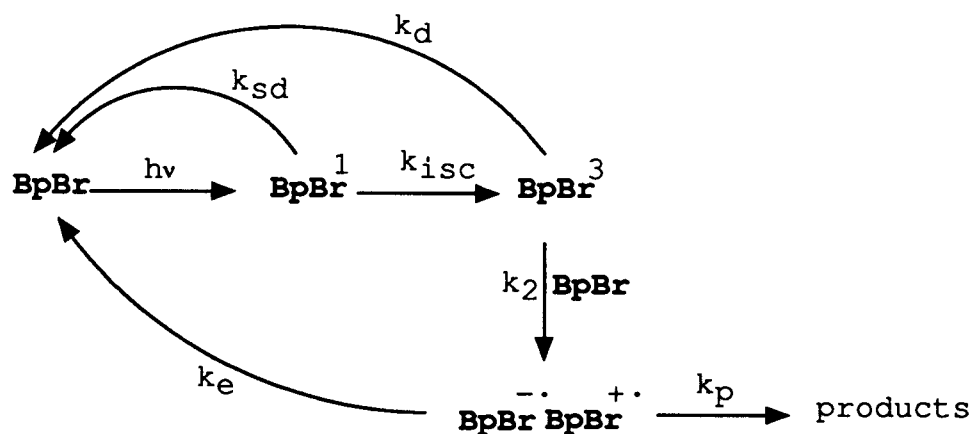
$$\Phi_{prod} = \frac{k_2 BC [\mathbf{BpBr}]}{k_d + k_2 [\mathbf{BpBr}]} \tag{5}$$

$$\frac{1}{\Phi_{prod}} = \frac{1}{B \cdot C} + \frac{k_d}{k_2 BC [\mathbf{BpBr}]} \tag{6}$$

$$\text{where} \quad B = \frac{k_p}{k_p + k_e} \qquad C = \frac{k_{isc}}{k_{isc} + k_{sd}}$$

substrate concentration increases, at some point $(k_{sp}k_2 + k_{isc}k_2 F) \gg k_{sp}k_d/[BpBr]$ and the plot would be linear with a positive slope, and as the concentration decreases, the slope would decrease and approach zero.

Studies of the dependence of the quantum yield on concentration of BpBr show that the second mechanistic scheme is the likely pathway. Other studies were conducted to help confirm this result. Quenching studies using cis-1,3-pentadiene[12], and fumaronitrile[22], were conducted. Results from these studies confirm that only the triplet excimer is responsible for product formation. A study of the intensity of the light versus the quantum yield was completed that shows that a biphotonic

Scheme III
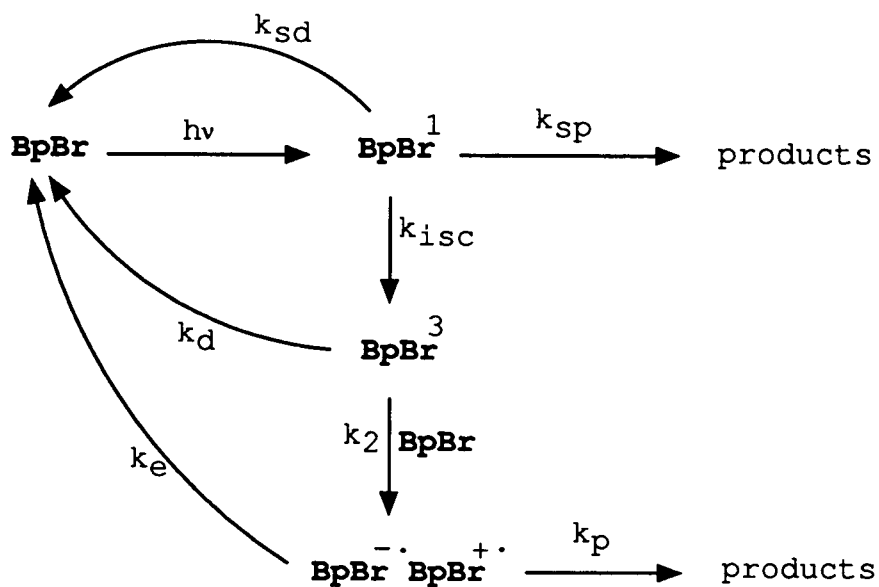
$$\frac{1}{\Phi_{prod}} = \frac{k_2 + k_d / [\mathbf{BpBr}]}{E \{ k_{sp}k_2 + k_{isc}k_2D + k_{sp}k_d / [\mathbf{BpBr}] \}} \qquad (7)$$

$$\text{where} \quad D = \frac{k_p}{k_p + k_e} \qquad E = \frac{1}{k_{sd} + k_{isc} + k_{sp}}$$

process is not occurring. A biphotonic process would have been an alternative explanation for the energy deficiency of the triplet state; absorption of a second photon could raise the molecule to a higher excited state from which products form. An extensive study of the effect of solvent polarity on the excimer formation was also conducted; however, these studies indicate only a weak polarization of the excimer species. 3,4-Dibromobiphenyl was also investigated and found to have a similar quantum yield dependence on concentration but did not exhibit any other characteristics that would help elucidate the nature of the excimer species.

Since these studies of BpBrs leave unanswered questions about the extent of polarization and conformation of excimer formation, a study of brominated [2.2]paracyclophanes was conducted. Paracyclophanes were chosen because the fixed geometry of the phenyl rings may demonstrate the presence of an intramolecular excimer. For small [n.n]paracyclophanes, where n = 2 or 3, the rings cannot rotate with respect to one another without cleavage of a bond. Perhaps a better comparison could be made with a bridged biphenyl system. "Biphenylphanes" are available through synthetic means, but their low solubility in most organic solvents makes them impractical for use in these studies. To resolve any questions about a comparison between BpBr and [2.2]paracyclophane, studies of bromobenzene were conducted. Photochemical experiments similar to those conducted on BpBr were carried out that confirm that this compound also reacts solely through a triplet excimer.

The irradiation of 4-bromo[2.2]paracyclophane (CpBr) at 300 nm yields [2.2]paracyclophane as the sole product.[12] This reaction is also believed to proceed through the triplet state. The quantum yield of intersystem crossing has been determined to be approximately one. An additional pathway is added to the kinetic scheme when considering the reaction of cyclophanes. With this molecule an

ps-o-CpBr

ps-p-CpBr

ps-m-CpBr

ps-gem-CpBr
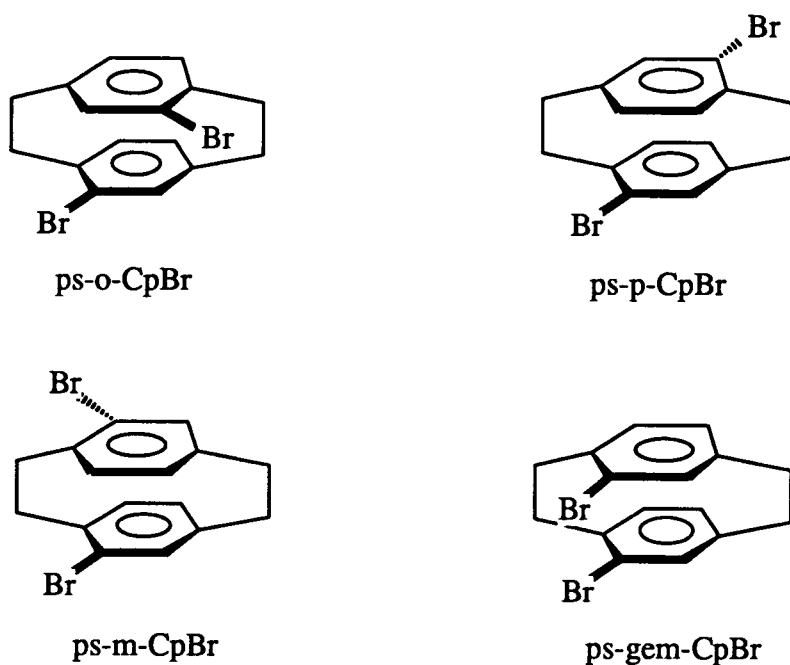
Figure I. Four Isomers of Dibromo[2.2]paracyclophane.

intramolecular process can compete with the intermolecular pathway, Scheme IV. Analysis of the expression for the quantum yield for this reaction shows that this competition is affected by the substrate concentration. If this mechanistic model is valid, as the substrate concentration increases, at some point $Gk_3 >> Fk_2/[CpBr]$ and a plot of the reciprocal of quantum yield versus the reciprocal of CpBr concentration will be linear with a positive slope, but as the concentration decreases the quantum yield will become independent of the substrate concentration and the slope will decrease and approach zero.

Using this scheme it is possible to show how the efficiency of the formation of the intramolecular excimer is effected by the substitution pattern of the bromine atoms on the adjacent rings. An increased efficiency should lead to quicker attainment of the zero slope.

Jang studied three brominated cyclophanes in order to show this effect.[12] For 4-bromo[2.2]paracyclophane (CpBr) the plot is curved and the zero slope was

Scheme IV
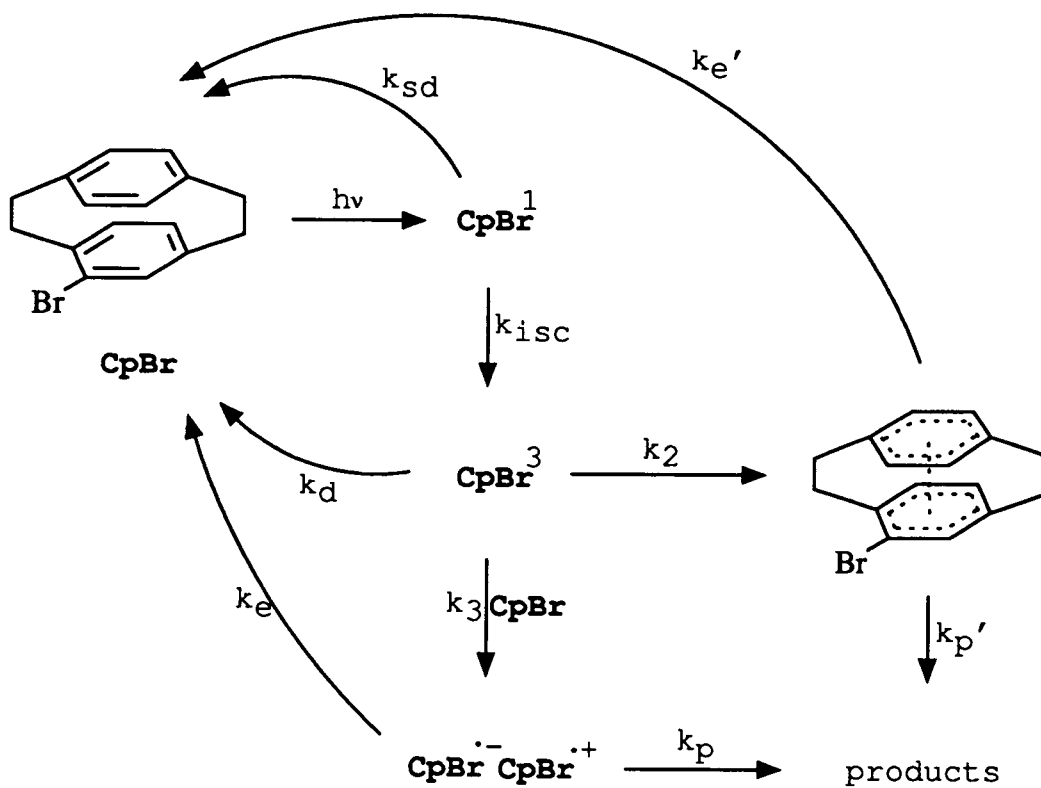
$$\frac{1}{\Phi_{prod}} = \frac{1}{\phi_{isc}} \cdot \frac{k_3 + (k_2 + k_d) / [\text{CpBr}]}{Gk_3 + Fk_2 / [\text{CpBr}]} \qquad (8)$$

where $\quad F = \dfrac{k_p'}{k_p' + k_e'} \qquad\qquad G = \dfrac{k_p}{k_e + k_p}$

attained at ca. 150 M^{-1}. In this case, an intramolecular excimer is expected to be favored because one of the rings is unsubstituted which makes it a good donor for a charge transfer complex. Two isomers of dibromo[2.2]paracyclophane have also been investigated. The concentration study of pseudo-para-dibromo-[2.2]paracyclophane (ps-p-CpBr) isomer also gives a curved plot. Finally, pseudo-ortho-dibromo[2.2]paracyclophane (ps-o-CpBr) was studied and the plot obtained was a straight line with a positive slope in the range of concentrations studied.

The questions that remain unanswered after these studies are; *i*) If the concentration range for the pseudo-ortho isomer is increased will the plot fit the expected curve? *ii*) Will there be similar correlations for other isomers of [2.2]paracyclophane, such as pseudo-meta, and pseudo-gem, and for other paracyclophanes such as brominated [3.3]paracyclophanes?

Results and Discussion.

Scheme V
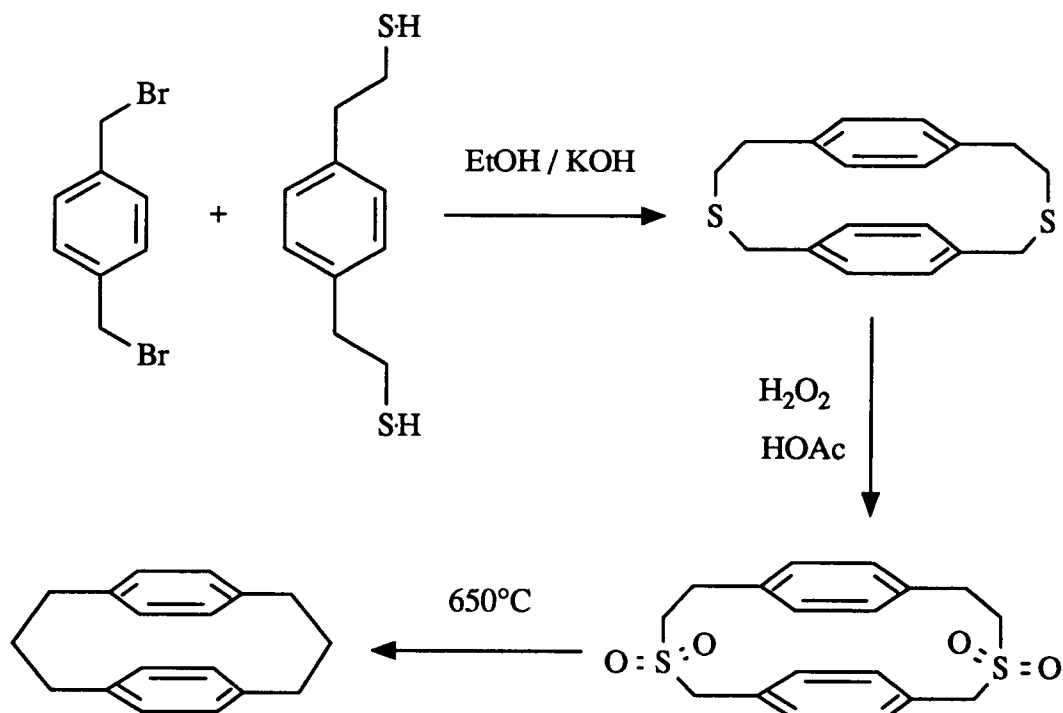
[3.3]Paracyclophane was synthesized using two methods, one which involved a coupling to form 2,13-dithia[4.4]paracyclophane followed by oxidation to the sulfone and extrusion of sulfur dioxide[23,24] (Schemes V and VI) and the other which involved coupling using tosylmethylisocyanide (Scheme VII). [3.3]Paracyclophane and the commercially available [2.2]paracyclophane were brominated following procedures similar to those described by Jang[12] (Scheme IX). *Pseudo-gem*-dibromo[2.2]paracyclophane was synthesized following methods described by Cram[25] for giving pseudo-geminal substitution (Scheme VIII). There was, however, no literature method for the final step, which provided some challenge. After trying the Cristol-Firth modification of the Hunsdiecker reaction

Scheme VI

Scheme VII

Scheme VIII

1.)CH₃COCl, AlCl₃, -30 °C
  1,1,2,2-tetrachloroethane
2.) H⁺, -40 °C

1.) 5% aq. NaOCl
  NaOH, 0 °C
2.) aq. HCl

Fe⁰, Br₂, CH₂Cl₂

SOCl₂

2-Mercaptopyridine-N-oxide
CBrCl₃, AIBN

Scheme IX

Fe^0, Br$_2$, CH$_2$Cl$_2$

n = 2 or 3

Fe^0, 2eq. Br$_2$, CH$_2$Cl$_2$

n = 2 or 3
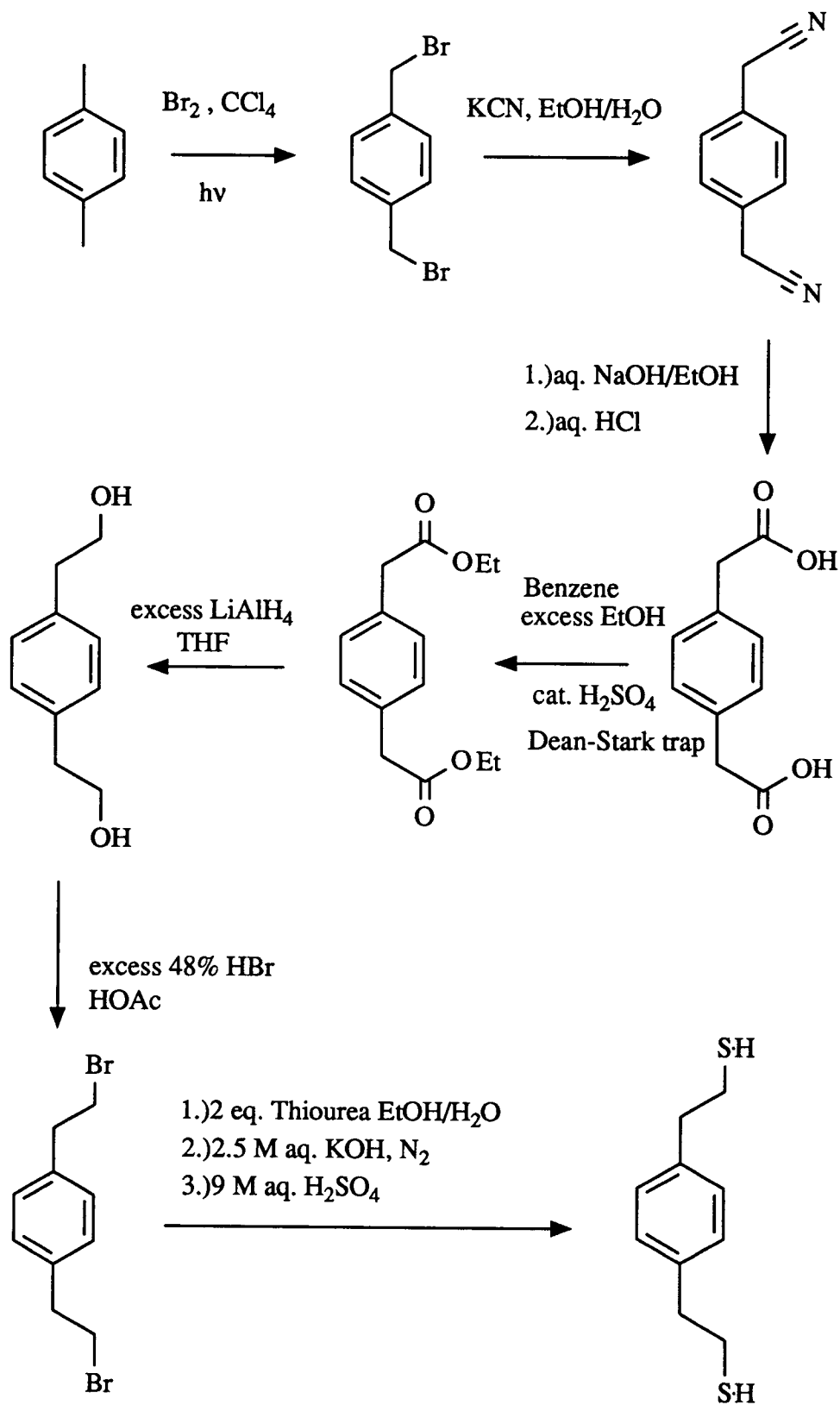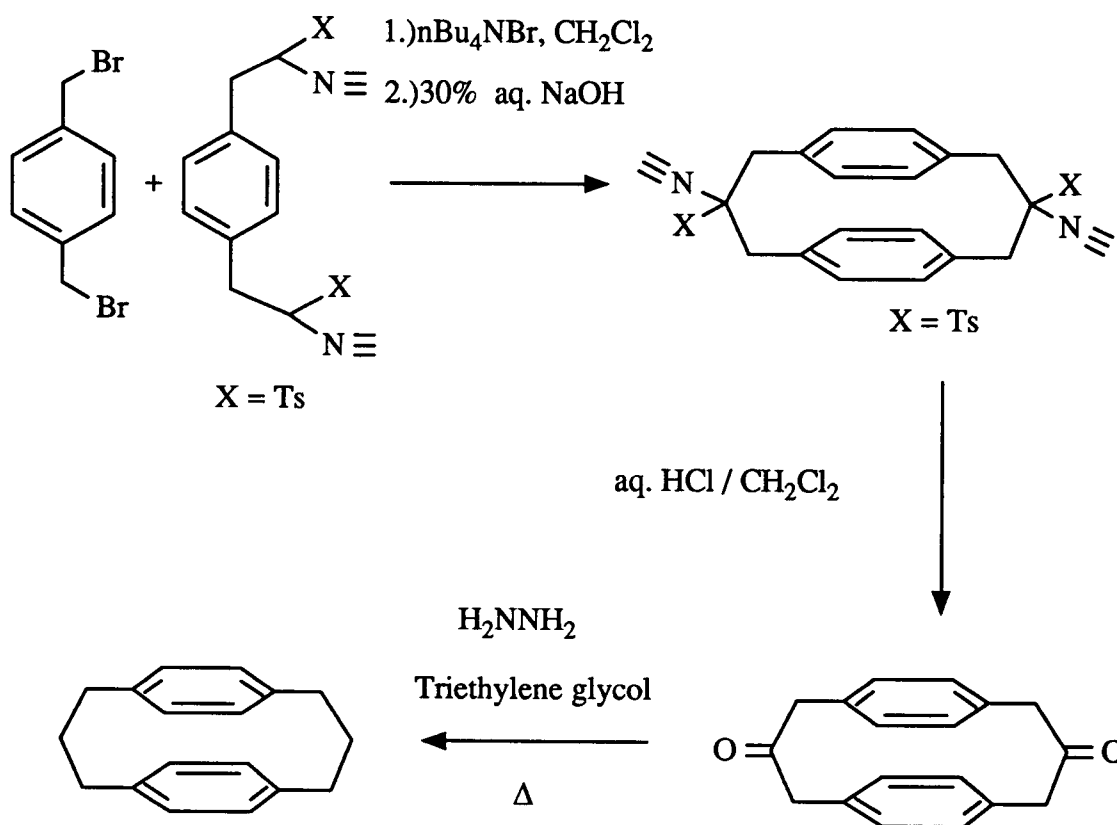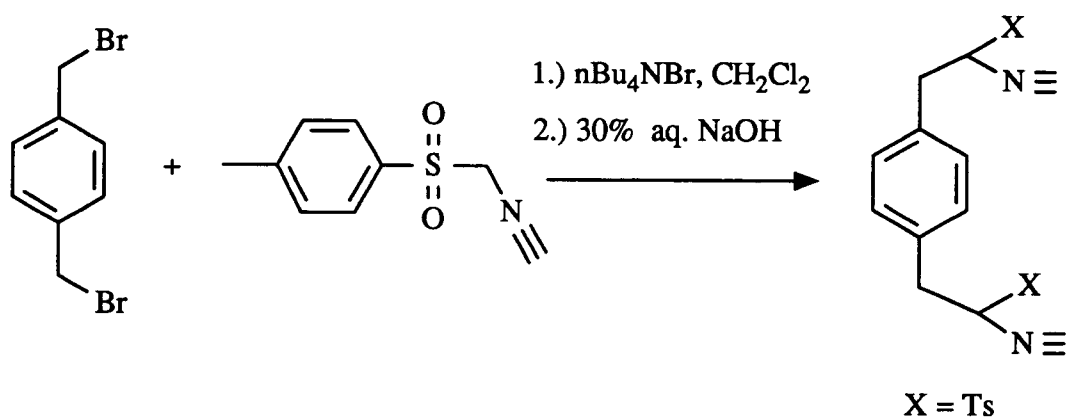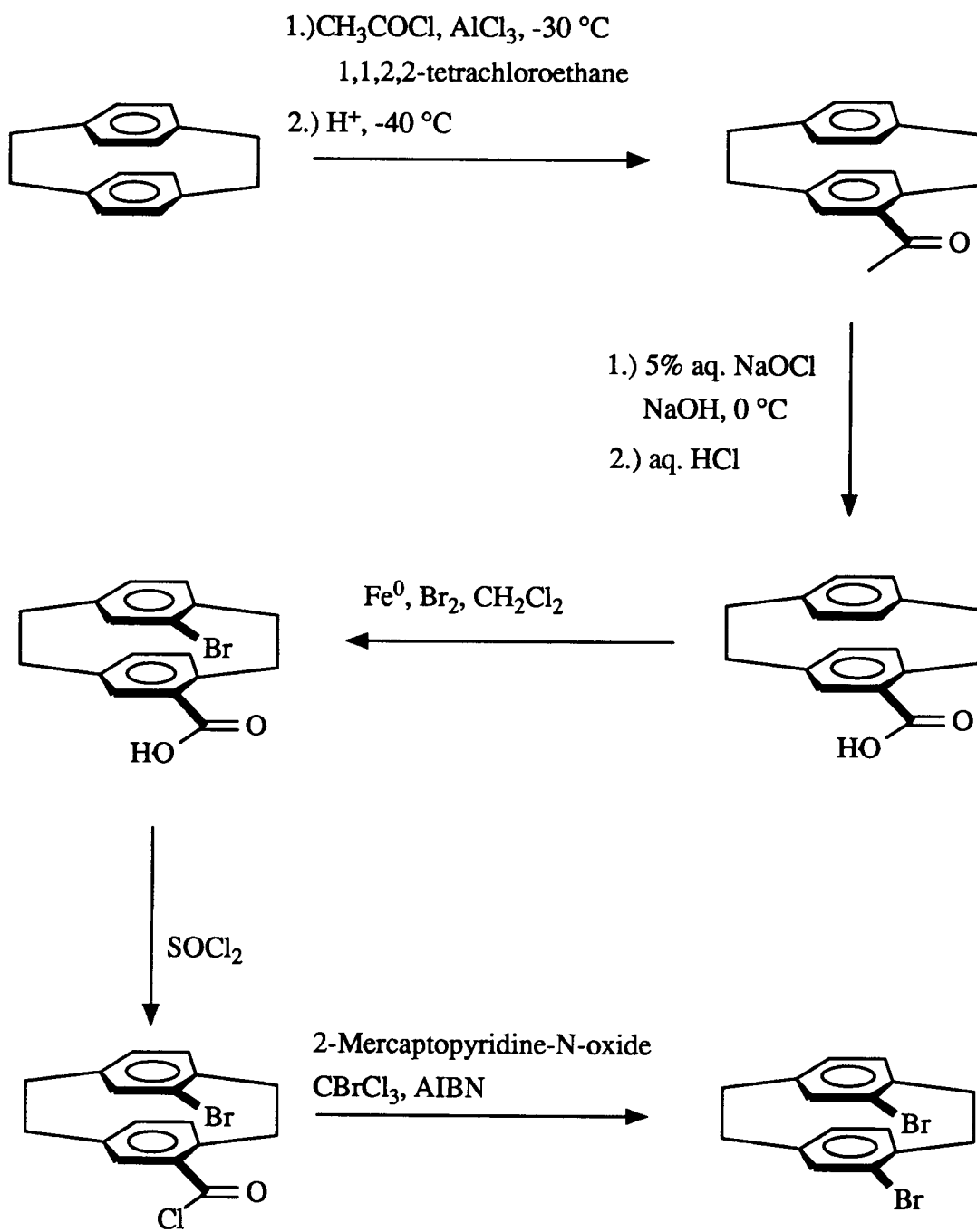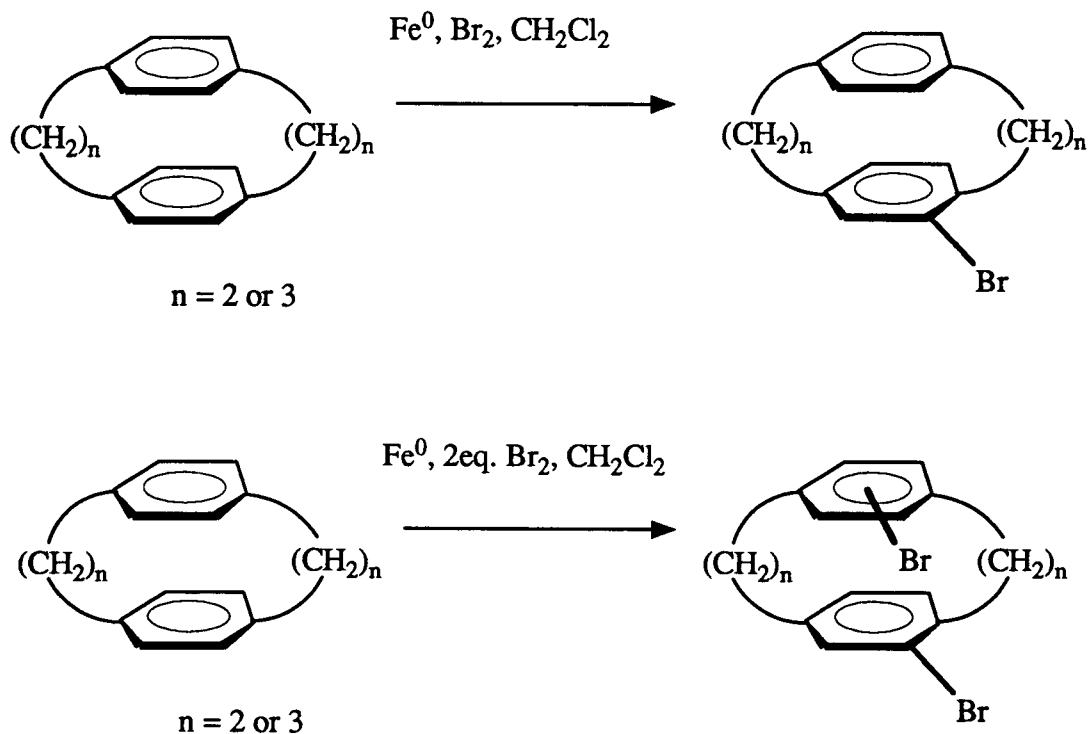
and a photochemical version of that reaction, the Barton radical process proved successful,[26] although the yield was low (6%).

To answer some of the questions posed in the previous section about the conformation of a triplet excimer, further studies have been carried out on several compounds. In all of the studies, irradiation times were kept short to avoid secondary reactions; the extent of reaction was kept below 10%. If the extent of reaction is kept low the quantum yield of reaction can be calculated either by loss of starting material or by the appearance of product, in these studies quantum yield was calculated using the former method. In order to determine if the *pseudo-ortho* isomer will exhibit intramolecular excimer formation a concentration study was conducted at a much more dilute range. In this case, the irradiation was carried out at 254 nm. In such photochemical studies one must be able to assume that the

Table I Photolysis of 4-Bromo[2.2]paracyclophane
in Acetonitrile (254nm)

[CpBr]$_i$[a] (M)	1/[CpBr]$_i$ (M^{-1})	ϕ_{react}[b]	1/ϕ_{react}
0.05042	19.8	5.32*10^{-4}	1880
0.03329	30.0	1.25*10^{-4}	7987
0.02017	49.6	7.07*10^{-5}	14137
0.01995	50.1	6.96*10^{-5}	14374
0.01051	95.2	6.49*10^{-5}	15419
0.00690	145	5.48*10^{-5}	18235
0.00504	198	5.41*10^{-5}	18499
0.00504	199	4.90*10^{-5}	20415
0.00396	253	4.70*10^{-5}	21281
0.00345	290	4.15*10^{-5}	24097
0.00303	331	4.05*10^{-5}	24707

[a] Initial concentration of 4-bromo[2.2]paracyclophane.

[b] Quantum yield of reactant (4-bromo[2.2]paracyclophane)
disappearance: average of two determinations.

sample absorbs all of the incident light, but for dibromo[2.2]paracyclophanes the extinction coefficient at 300 nm was low (ca. 2,000) so the assumption could not be made for dilute solutions. At 254 nm the extinction coefficient is much higher (30,000) allowing the assumption to be made. The wavelength was changed to 254 nm in all the following studies.

The irradiation of 4-bromo[2.2]paracyclophane at 254 nm in acetonitrile yielded [2.2]paracyclophane as the only product (Table I, Figure II), and irradiation of *pseudo-para*[2.2]paracyclophane at 254 nm in acetonitrile yielded 4-bromo-

Table II Photolysis of pseudo-para dibromo[2.2]paracyclophane
in Acetonitrile (254nm)

[CpBr]$_i^a$ (M)	1/[CpBr]$_i$ (M^{-1})	ϕ_{react}^b	1/ϕ_{react}
0.01950	51.3	1.76*10^{-4}	5684
0.01300	76.9	8.18*10^{-5}	12231
0.00889	112	8.08*10^{-5}	12373
0.00712	141	7.22*10^{-5}	13859
0.00593	169	7.11*10^{-5}	14060
0.00445	225	6.77*10^{-5}	14772
0.00356	281	6.45*10^{-5}	15495
0.00297	337	6.54*10^{-5}	15281
0.00255	392	5.93*10^{-5}	16865

[a] Initial concentration of pseudo-para dibromo[2.2]paracyclophane.

[b] Quantum yield of reactant (pseudo-para dibromo[2.2]paracyclophane)
disappearance: average of two determinations.

[2.2]paracyclophane as the only product (Table II, Figure III). The concentration

studies of these compounds show that plots of the reciprocal of the quantum yield

versus the reciprocal of concentration are curved. This indicates that these

compounds fit the proposed mechanistic scheme (Scheme IV). The quantum yields

for these reactions do not correlate precisely with the previous studies but the

general trends remain intact.

Irradiation of *pseudo-ortho*[2.2]paracyclophane at 254 nm in acetonitrile

yielded 4-bromo[2.2]paracyclophane as the only product (Table III, Figure IV). The

concentration study conducted for this compound expands the concentration range to

extend to higher dilution. The plot obtained from this study shows that the slope

Table III Photolysis of pseudo-ortho dibromo[2.2]paracyclophane
in Acetonitrile (254nm)

$[CpBr]_i^a$ (M)	$1/[CpBr]_i$ (M^{-1})	ϕ_{react}^b	$1/\phi_{react}$
0.00568	176	$5.59{*}10^{-5}$	17898
0.00455	220	$5.12{*}10^{-5}$	19518
0.00398	251	$4.70{*}10^{-5}$	21270
0.00341	293	$4.52{*}10^{-5}$	22101
0.00284	352	$4.57{*}10^{-5}$	21877
0.00227	440	$4.61{*}10^{-5}$	21707
0.00170	587	$4.43{*}10^{-5}$	22597
0.00114	880	$3.45{*}10^{-5}$	28957
0.00057	1760	$2.76{*}10^{-5}$	36229

[a] Initial concentration of pseudo-ortho dibromo[2.2]paracyclophane.
[b] Quantum yield of reactant (pseudo-ortho dibromo[2.2]paracyclophane)
disappearance: average of two determinations.

does approach zero, but at a much lower concentration than CpBr and ps-p-CpBr.
This result seems to indicate that the formation of the intramolecular excimer is
inefficient.

The final study completed involved a brominated [3.3]paracyclophane.
Irradiation of 5-bromo[3.3]paracyclophane ([3.3]CpBr) at 254 nm in acetonitrile
yielded [3.3]paracyclophane ([3.3]Cp) as the only product (Table IV, Figure V).
This molecule was studied in an effort to determine whether the distance between
rings has an effect upon the photochemistry of cyclophanes. Crystallographic
studies show that the average distance between the rings of Cp is 2.5 Å, and is 3.0 Å
for [3.3]Cp.[27] The concentration study conducted for this compound gives a curved

Table IV Photolysis of 5-Bromo[3.3]paracyclophane
in Acetonitrile (254nm)

[CpBr]$_i$[a] (M)	1/[CpBr]$_i$ (M^{-1})	ϕ_{react}[b]	1/ϕ_{react}
0.04676	21.4	$2.01{*}10^{-4}$	4984
0.03117	32.1	$2.74{*}10^{-5}$	36546
0.01870	53.5	$2.38{*}10^{-5}$	42011
0.01249	80.1	$2.09{*}10^{-5}$	47807
0.00935	107	$2.00{*}10^{-5}$	49972
0.00468	214	$1.55{*}10^{-5}$	64652
0.00312	231	$1.07{*}10^{-5}$	93328

[a] Initial concentration of 4-bromo[2.2]paracyclophane.

[b] Quantum yield of reactant (4-bromo[2.2]paracyclophane)
disappearance: average of two determinations.

plot. This indicates that mechanistic scheme IV is also valid for this compound. This study will not be able to be repeated at 300 nm because of the very low absorbance of [3.3]CpBr at that wavelength (extinction coefficient ca. 0).

A somewhat qualitative interpretation of the kinetic data can be made using the kinetic scheme for cyclophanes (Scheme IV). Phosphorescence decay times (τ_p) for these brominated [2.2] and [3.3]paracyclophanes were measured in ethanol at 77 K. Based on Scheme IV these lifetimes represent the reciprocal of the sum of k_2 and k_d.

$$\tau_p = 1 / (k_2 + k_d) \tag{9}$$

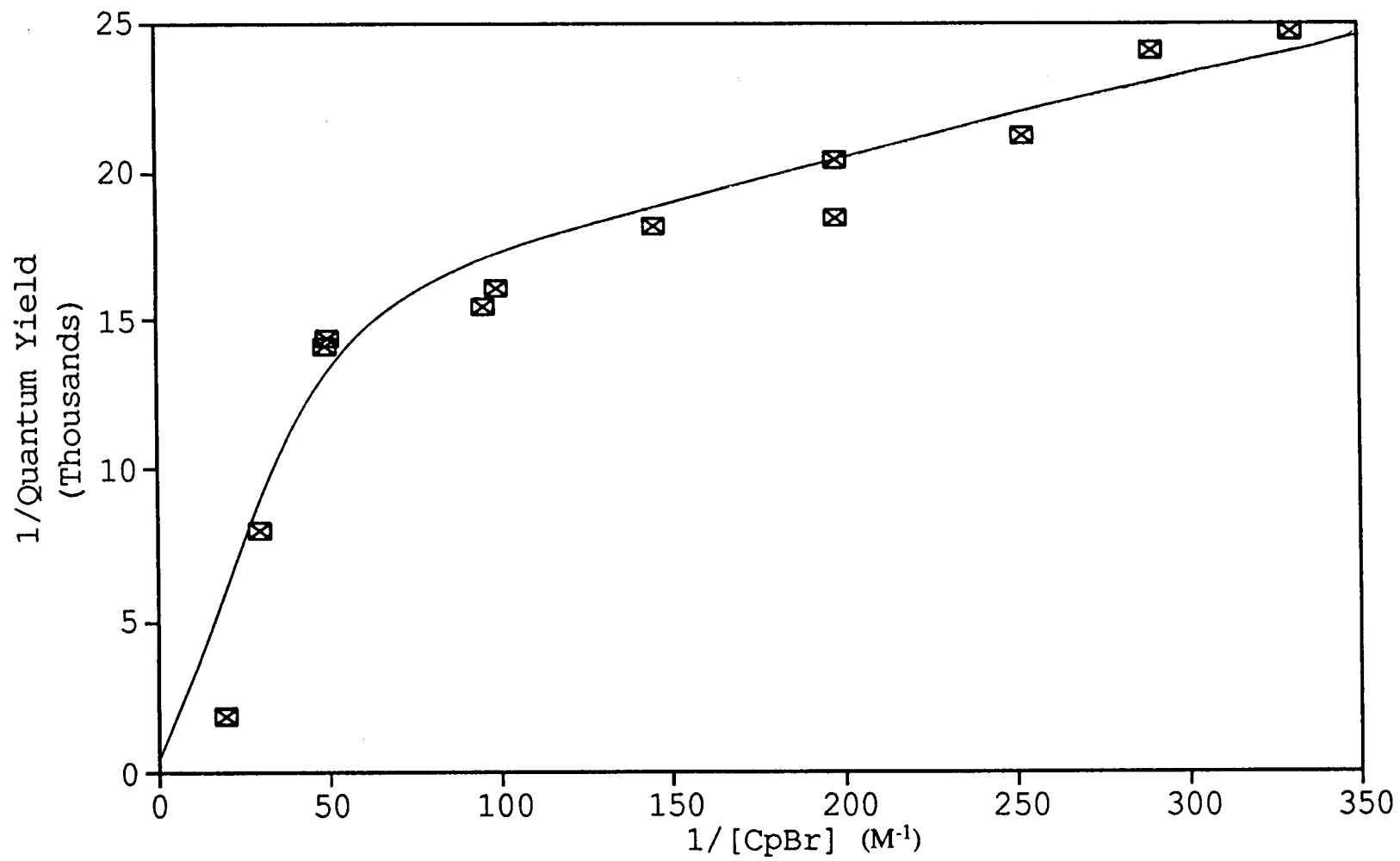Also, based on Scheme IV, an expression for the reciprocal of ϕ_{prod} (equation

Figure II Photolysis of 4-Bromo[2.2]paracyclophane in Acetonitrile at 254 nm
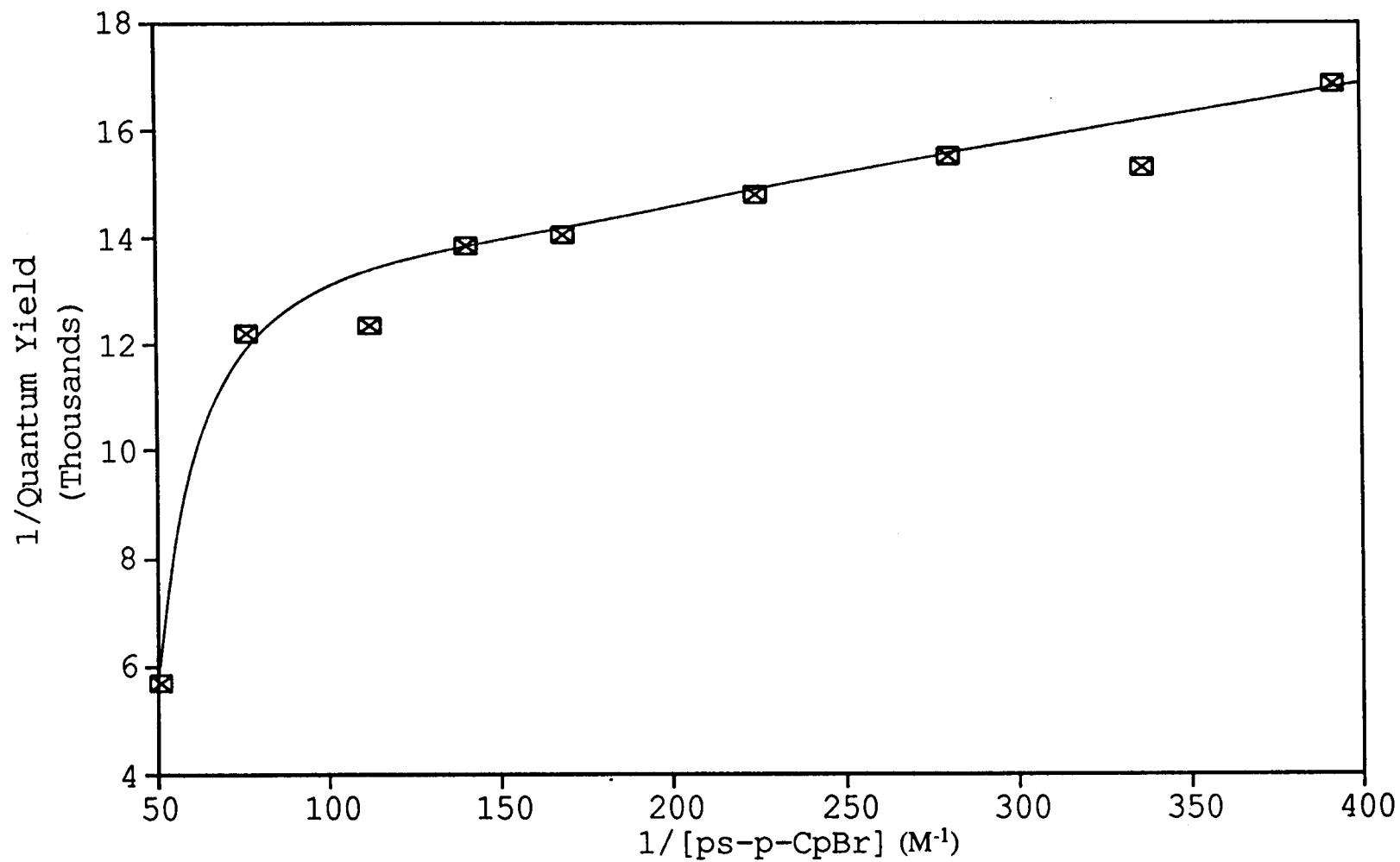
Figure III Photolysis of pseudo-para-Dibromo[2.2]paracyclophane in Acetonitrile at 254 nm
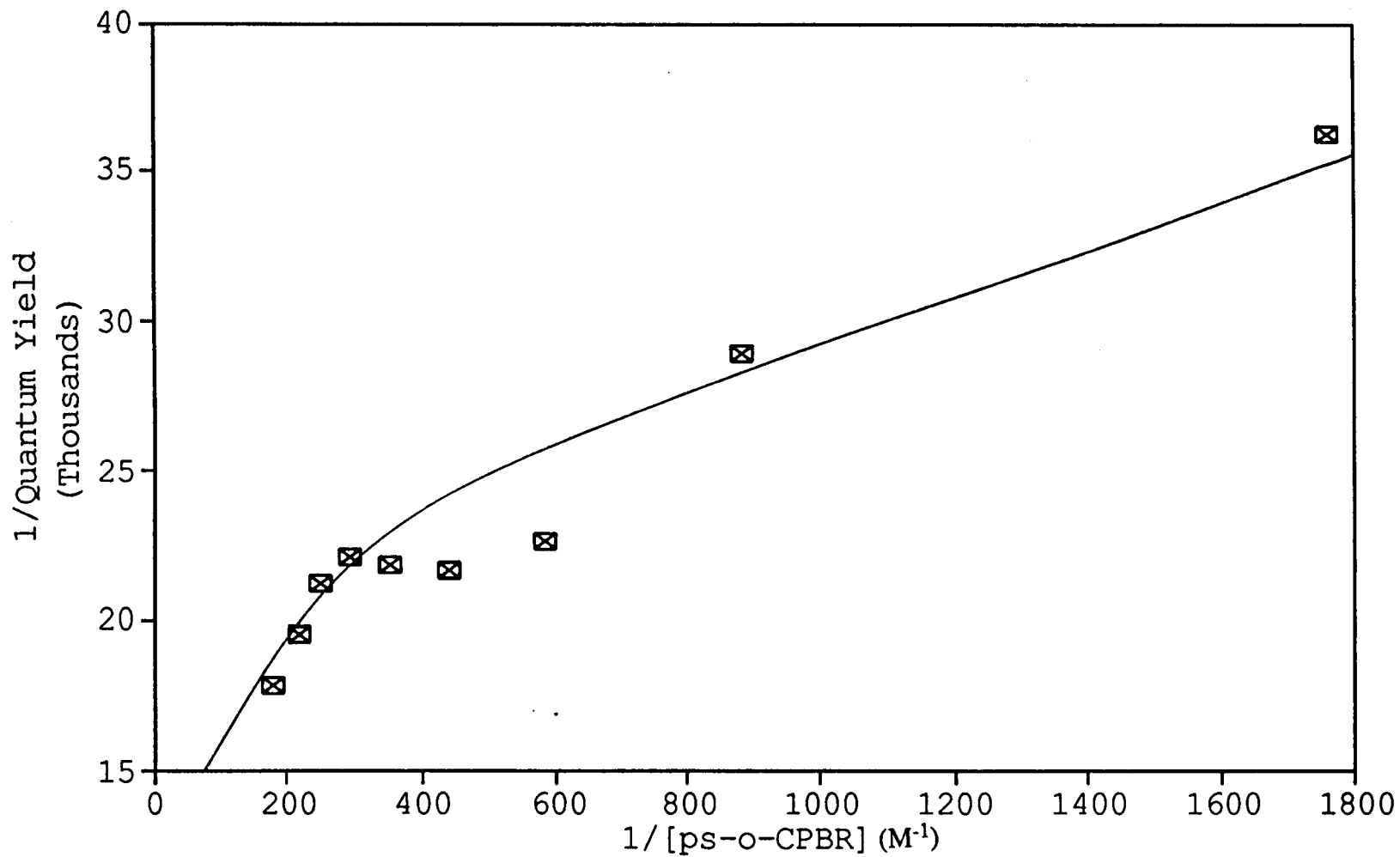
Figure IV Photolysis of pseudo-ortho-Dibromo[2.2]paracyclophane in Acetonitrile at 254 nm
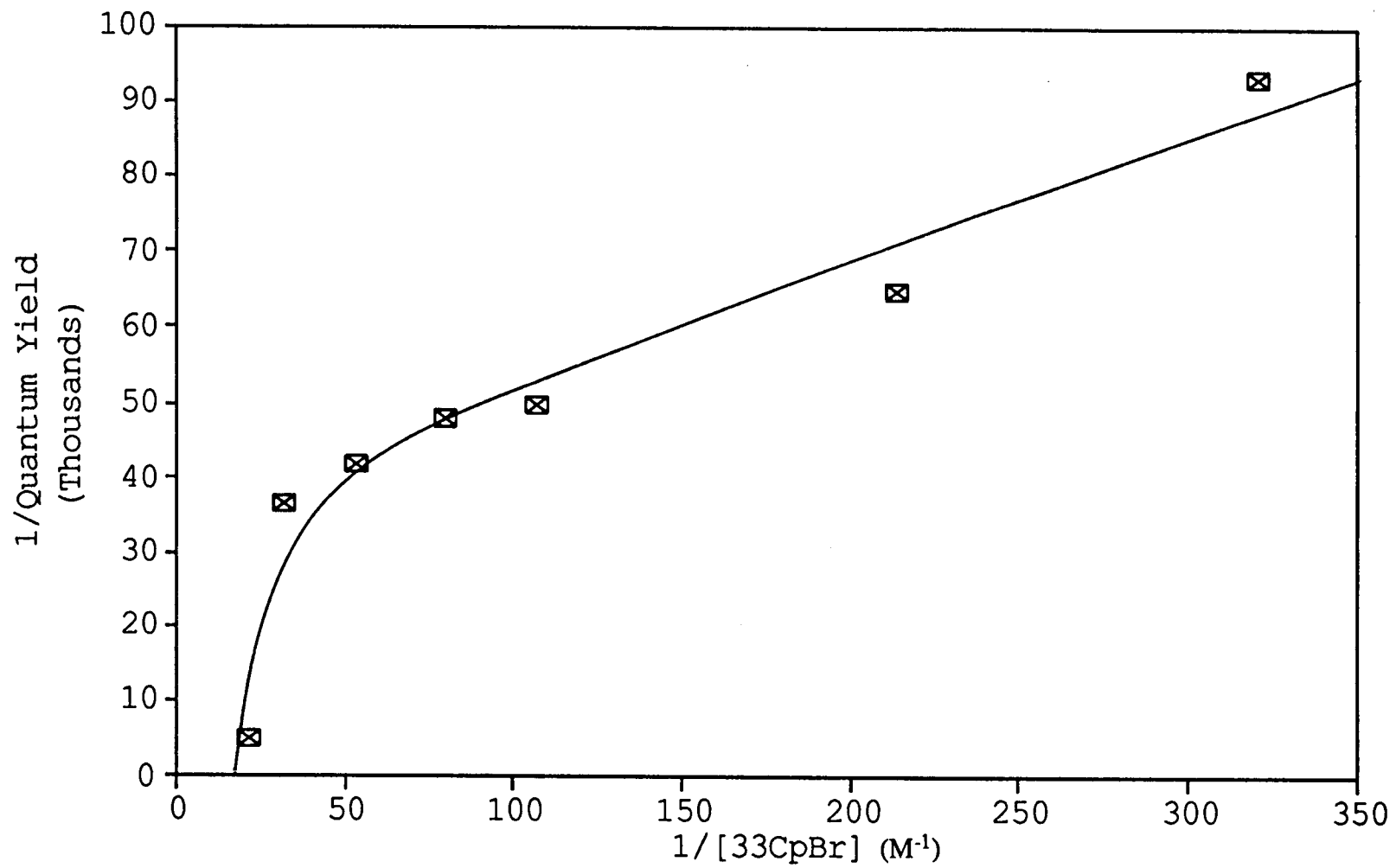
Figure V Photolysis of 5-Bromo[3.3]paracyclophane in Acetonitrile at 254 nm

8) has been derived using steady state kinetics and is represented in a different form:

$$\frac{1}{\phi_{prod}} = \frac{1}{\phi_{isc}} \cdot \frac{k_3 + \dfrac{k_2 + k_d}{[CpBr]}}{k_3 G + \dfrac{k_2 F}{[CpBr]}} \tag{10}$$

As described earlier, when $Gk_3 \gg Fk_2/[CpBr]$, the latter quantity may be neglected to simplify equation (10). The resulting expression is the equation of a line where a plot of $1/[CpBr]$ vs. $1/\phi_{prod}$ will be linear with a positive slope:

$$\frac{1}{\phi_{prod}} = \frac{1}{\phi_{isc} G} + \frac{k_2 + k_d}{\phi_{isc}k_3 G[CpBr]} \tag{11}$$

Therefore, the linear portion will have

$$\text{intercept} \quad = \quad 1 / \phi_{isc} G \tag{12}$$

$$\text{slope} \quad = \quad (k_2 + k_d) / \phi_{isc} Gk_3 \tag{13}$$

Since $\phi_{isc} = 1$,

$$\text{intercept} \quad = \quad 1 / G \tag{14}$$

$$\text{slope / intercept} \quad = \quad (k_2 + k_d) / k_3 \tag{15}$$

Substituting for $(k_2 + k_d)$ from equation (9), we obtain,

$$\text{slope / intercept} \quad = \quad 1 / \tau_p k_3 \tag{16}$$

Using this analysis, the rates of intermolecular excimer formations, k_3, could be calculated for each of the brominated paracyclophanes (Table V).

Due to competing intramolecular charge-transfer complex formation, as substrate concentration decreases, $1/\phi_{prod}$ becomes independent of the concentration which causes the overall plot to curve with a decreased slope. The regions of the plots that approach a zero slope represent the concentration regions where intramolecular charge transfer is dominant. So, as $1/[CpBr]$ approaches infinity, equation (10) may be simplified to give the following equation:

$$\frac{1}{\phi_{prod}} = \frac{1}{\phi_{isc}} \cdot \frac{k_2 + k_d}{k_2\,F} \tag{17}$$

Since $\phi_{isc} \approx 1$,[12]

$$\text{intercept} \quad = \quad (k_2 + k_d)\,/\,k_2\,F \tag{18}$$

Substituting for equation (9),

$$\text{intercept} \quad = \quad 1\,/\,\tau_p\,k_2\,F \tag{19}$$

Substituting for τ_p allows the calculation of $k_2 F$.

At the point where the plot curves and the slope approaches zero,

$$G\,k_3\,[CpBr] = k_2\,F \tag{20}$$

From this analysis it is possible to calculate the concentration where the rate of intramolecular and intermolecular excimer formation coincide (Table V). For CpBr, ps-p-CpBr, ps-o-CpBr, and [3.3]CpBr the values obtained are 0.0196, 0.0068, 0.0021, and 0.0186 respectively. For the series of [2.2]paracyclophanes these results indicate that the efficiency of intramolecular charge transfer complex formation is effected by the substitution pattern of the bromines. The values for CpBr and [3.3]CpBr are similar, which indicates that the distance between the rings has little effect on this characteristic.

In this analysis ps-p-CpBr exhibits the highest rate of intermolecular excimer formation (k_3), followed by CpBr, ps-o-CpBr, and [3.3]CpBr. In the last case this rate is very slow (10^5 slower) compared to the [2.2]paracyclophanes. The reason for this is not entirely clear; however, the results from the irradiation of [3.3]CpBr have not been repeated so interpretation of these data is not conclusive.

These results seem to be consistent with presence of an intramolecular excimer, or charge transfer complex; furthermore, the results suggest that alignment in a *pseudo-para* geometry is more favorable than a *pseudo-ortho* alignment for

Table V Rate Constants Obtained from Kinetic Studies

	CpBr	ps-p-CpBr	ps-o-CpBr	[3.3]CpBr
intercept = $(1/G)$	1098	3042	392	1
G	9.1×10^{-4}	3.3×10^{-4}	2.6×10^{-3}	1
slope	392	102	37	1,025
$\dfrac{\text{slope}}{\text{intercept}} = \dfrac{k_2 + k_d}{k_3}$	0.3570	0.0335	0.0944	1,025
τ_p (sec)	2.9×10^{-3}	24.4×10^{-3}	22.8×10^{-3}	82.9×10^{-3}
$k_2 + k_d$ (sec^{-1})	345	41	44	12
k_3 (sec$^{-1} \times$ M^{-1})	967	1,223	465	0.0118
intercept $= \dfrac{k_2 + k_d}{k_2 F}$	20,000	15,000	25,000	55,000
$k_2 F$	0.0172	0.0027	0.0018	2.19×10^{-4}
[CpBr][a]	0.0196	0.0068	0.0021	0.0186

[a] Concentration where $Gk_3[CpBr] = k_2 F$

intramolecular excimer formation. Additional work needs to be conducted on these and other brominated cyclophanes to provide convincing conclusions about the conformation of such excimers.

Experimental

Materials: 4-Bromo[2.2]paracyclophane (CpBr), *pseudo-para*-
dibromo[2.2]paracyclophane (ps-p-CpBr), *pseudo-ortho*-dibromo-
[2.2]paracyclophane (ps-o-CpBr), and 5-bromo[3.3]paracyclophane were
synthesized and purified according to the procedures cited below.

General Procedure for Photolysis: Irradiation of the samples in duplicate
was carried out in a Rayonet merry-go-round reactor (The Southern New England
Co.) equipped with eight lamps (254 nm) while being cooled by an overhead fan to
ca. 30 °C. The photolysis samples (1 mL) were placed in quartz tubes (Ace glass,
170 mm × 15 mm), each screwed to a teflon or nylon adapter bushing containing a
Pyrex glass sliding stopper valve and degassed through three or four freeze-pump-
thaw cycles. The tubes were sealed under vacuum and irradiated at 254 nm for the
desired time (Table VI). Quantum yields of reactants were determined by using
three azoxybenzene[28] actinometer solutions (1 mL each).

Product Analyses: Photolysis mixtures were analyzed by GLC on a Varian
3400 capillary gas chromatograph equipped with an FID, a 30 m × 0.35 mm
capillary column (Alltech) and a Spectra Physics 4290 integrator. The capillary
column used was an SE-54 (5% phenylmethylsilicone). The column and GLC
conditions for product analysis are summarized in Table VI. Helium was used as a
carrier gas at 30 mL/min. The photoproducts were identified by comparing their GC
retention times with those of authentic samples and using mass spectral analysis
carried out with a Hewlett-Packard 5971 mass spectrometer equipped with a

Table VI Irradiation time and GLC Conditions for Product Analysis

| Substrate | Irradiation Time (Min) | Column | | Standard | Injector/Detector Temperature (°C) |
		Type	Temperature[a]		
CpBr	30	SE-54	150/1/10/250	$C_{20}H_{42}$	300/325
ps-p-CpBr	10	SE-54	150/1/10/250	$C_{22}H_{46}$	300/325
ps-o-CpBr	10	SE-54	150/1/10/250	$C_{22}H_{46}$	300/325
[3.3] CpBr	20	SE-54	150/1/10/250	$C_{20}H_{42}$	300/325

[a]Initial temp./Holding time/Rate of increase in °C per min/Final temp.

Hewlett-Packard 5890 capillary gas chromatograph. The internal standards used in the determination of yields of photoproduct are also listed in Table VI.

Synthesis of 4-Bromo[2.2]paracyclophane (CpBr):[29] Iron powder (144 mg) was added to a solution of bromine (1.0 mL, 18.5 mmol) in 68 mL of carbon tetrachloride and stirred for 1 h at room temperature. [2.2]Paracyclophane (3.12 g, 15 mmol) in 125 mL of dry dichloromethane was added and the stirring was continued for 4 h. The reaction was quenched by adding dilute (approximately 10%) aq. sodium hydrogensulfite solution. The reaction mixture was washed with saturated aq. sodium chloride solution and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel with a mixture of hexane and chloroform in 9 : 1 ratio. The relatively pure product was further purified by fractional crystallization using hexane and a fraction of benzene (80% yield): mp 133-134 °C, 133-134 °C[29]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.01 (m, 6H), 3.45 (m, 2H), 6.50 (m, 4H), 7.15 (dd, 1H, J = 7.9 Hz, 1.9); ^{13}C NMR (300 MHz, CDCl$_3$) δ 33.348, 34.785, 35.443, 35.813, 126.935, 128.651, 131.431, 132.216, 132.878, 133.275, 135.018, 137.214, 139.074, 139.294, 141.574; MS (m/e) 288, 286 (M$^+$), 184, 182, 104 (100).

Synthesis of _pseudo-para_-Dibromo[2.2]paracyclophane:[30,31] A solution of 4.62 g (28.8 mmol) of bromine in 40 mL of carbon tetrachloride was prepared; 3 mL of this solution was stirred with 40.0 mg of iron powder in 30 mL of dichloromethane for 1 h. An additional 50 mL of dichloromethane was added and the solution was heated to reflux. [2.2]Paracyclophane, 3.00 g (14.4 mmol), was added and the remainder of the bromine solution was added dropwise over a period of 3.5 h. After completion of the bromine addition, the mixture was heated at reflux

for 30 min. The cooled reaction mixture was quenched with 10% aq. sodium hydrogensulfite solution, then washed with saturated aq. sodium chloride solution and dried with anhydrous magnesium sulfate. After removal of the solvent, the mixture was purified by silica gel chromatography using hexane as eluent. The first fraction, which contained the pseudo-para isomer, was collected and recrystallized from hot hexanes to give pure pseudo-para-dibromo[2.2]paracyclophane (27% yield): mp 250-253 °C, 250-251 °C[30,31]; ^{1}H NMR (300 MHz, CDCl$_3$), δ 2.85 (m, 4H), 3.14 (m, 2H), 3.48 (ddd, 2H), 6.42 (d, 2H, 7.8 Hz), 6.51 (d, 2H, 1.5 Hz), 7.14 (dd, 2H, 7.8 Hz, 1.6); ^{13}C NMR (300 MHz, CDCl$_3$) δ 32.817, 35.352, 126.726, 128.252, 134.108, 137.313, 138.518, 141.150; MS (m/e) 368, 366, 364 (M$^+$), 184, 182 (100), 103 and 77.

Synthesis of *pseudo-ortho*-Dibromo[2.2]paracyclophane: The conditions for the bromination were altered slightly to favor the pseudo-ortho compound. A solution of bromine (5 mL, 0.10 mol) in 130 mL of carbon tetrachloride was prepared, 6 mL of the solution was stirred with 140 mg of iron in 50 mL of methylene chloride and 50 mL of carbon tetrachloride for 1 h. After addition of 100 mL of carbon tetrachloride, the mixture was heated to reflux and [2.2]paracyclophane (10 g, 0.05 mol) was added. The remainder of the bromine solution was added dropwise over 3.5 h and the entire mixture was heated at reflux for an additional hour. The reaction mixture was cooled to room temperature, quenched with aq. sodium bisulfite solution and washed with saturated aq. sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The product mixture was first separated by column chromatography (silica gel/hexane). The first fraction contained dibromides, from which the *pseudo-ortho* compound was isolated using a chromatotron (1 mm silica

plate/hexane). The first fraction collected contained the *pseudo-para* dibromide and the second fraction contained the desired *pseudo-ortho* dibromide. Approximately 500 mg of 80% pure pseudo-ortho compound was collected. (12% yield): mp 198-200 °C, 204-207 °C[26,27]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.79 (m, 2H), 3.04 (m, 4H), 3.43 (m, 2H), 6.51 (m, 4H), 7.17 (s, 2H); MS (m/e) 368,366,364 (M$^+$), 184, 182 (100), 103 and 77.

Synthesis of 4-Acetyl[2.2]paracyclophane:[25] A solution of 5.77 g of anhydrous aluminum chloride and 3.77 g of acetyl chloride in 45 mL of 1,1,2,2 tetrachloroethane was stirred under an inert atmosphere and cooled to -30 °C with a dry ice-isopropanol bath. [2.2]Paracyclophane, 5.00 g (24 mmol), was added quickly while keeping the reaction temperature below -15 °C. The reaction mixture was stirred for 30 min at -30 °C then cooled to -40 °C, and 18 mL of 1 N aq. hydrochloric acid was added dropwise. Then 50 mL of chloroform was added, and the organic layer was washed with one 50 mL portion of water, two 50 mL portions of aq. sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The product was isolated by short path vacuum distillation to give 3.76 g of a beige solid. (63% yield): bp. 140-145 °C/ 0.15 torr; mp 105 - 107 °C, 106.8 - 108.2 °C[25]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.45 (s, 3H), 2.83 (m, 1H), 2.95 - 3.24 (m, 6H), 3.95 (m, 1H), 6.33 - 6.68 (m, 6H), 6.90 (s, 1H).

Synthesis of 4-Carboxy[2.2]paracyclophane:[25] A solution of 87 g of aq. sodium hypochlorite solution (5.25%, bleach) and 1.81 g of sodium hydroxide was stirred and cooled to 0 °C. A solution of 1.00 g (4 mmol) of 4-acetyl-[2.2]paracyclophane in 21 mL of dioxane was added dropwise over 15 min, and the reaction mixture was allowed to warm to room temperature and was stirred for an

additional 12 h. The reaction was quenched with a solution of 0.5 g of sodium

hydrogensulfite in 50 mL of water. The aqueous layer was acidified with 1 N aq.

hydrochloric acid and the product was extracted with three 50 mL portions of

chloroform. The organic layer was washed with water and dried over anhydrous

sodium sulfate. After evaporation of the solvent, the product was recrystallized

from acetic acid to give 0.57 g of a white solid (57% yield): mp 220 - 224 °C, 223.5

- 224.5 °C[30]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.81 - 3.22 (m, 7H), 4.20 (m, 1H), 6.46

- 6.61 (m, 5H), 6.20 (dd, 1H), 7.27 (d, 1H).

Synthesis of *pseudo-gem*-Bromocarboxy[2.2]paracyclophane:[25] A

solution of 0.50 g (2 mmol) of 4-carboxy[2.2]paracyclophane and 100 mg of iron

powder in 25 mL of dichloromethane was stirred and heated to reflux. A solution of

0.34 g (2.1 mmol) of bromine in 6 mL of carbon tetrachloride was added dropwise

over 1 h and the mixture was heated at reflux for an additional 5 h. The reaction

was quenched with aq. sodium hydrogensulfite solution, washed with water, and

dried over anhydrous sodium sulfate. After evaporation of the solvent, 0.44 g of a

white solid was obtained. (67% yield): mp 275 - 280 °C; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 3.02 - 3.25 (m, 6H), 3.58 (p, 1H), 4.52 (p, 1H), 6.72 (m, 4H), 6.85 (dd,

1H), 7.44 (d, 1H), 10.82 (broad s, 1H).

Synthesis of *pseudo-gem*-Bromochloroformyl[2.2]paracyclophane: A

solution of *Pseudo-gem*-bromocarboxy[2.2]paracyclophane (0.20 g, 0.70 mmol) in

thionyl chloride (0.6 g, 5 mmol) was stirred and heated at 60 °C for 4 h. The excess

thionyl chloride was evaporated and the product was dried in a vacuum desiccator

giving 0.20 g of a beige solid. (81% yield): mp 140 - 144 °C; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 3.02 - 3.25 (m, 6H), 3.50 (m, 1H), 4.13 (m, 1H), 6.76 (m, 4H), 7.01 (dd,

1H), 7.62 (d, 1H).

Synthesis of *pseudo-gem*-Dibromo[2.2]paracyclophane: This isomer was prepared using a procedure described by Barton.[26] 2-Mercaptopyridine-N-oxide sodium salt hydrate (0.04 g, 0.29mmol) was dissolved in $CBrCl_3$ (3 mL), stirred and heated to 100 °C in an oil bath. A solution of *pseudo-gem*-bromochloroformyl-[2.2]paracyclophane (0.100 g, 0.29 mmol) and azo-bis-isobutyronitrile (0.03 g, 0.10 mmol) in $CBrCl_3$ (3 mL) was added and the mixture was stirred at 100 °C for 3 h. The products were concentrated and chromatographed on silica gel with 1:4 chloroform:hexanes. The first fraction collected was concentrated without further purification, which gave 0.70 mg of a beige solid (6% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 3.00 (m, 6h), 3.70 (m, 2H), 6.51 (m, 4H), 6.77 (d, 2H); MS (m/e) 368, 366 (M^+), 364, 184, 182 (100), 103, 77; HRMS, EI for $C_{16}H_{14}Br_2$ (M - 1^+) calcd 363.94632, found 363.94630.

Synthesis of 1,4-Bis(bromomethyl)benzene: A solution of 61 mL (0.50 mol) of *p*-xylene in 200 mL of carbon tetrachloride was stirred in a large flask. The flask was irradiated with a sun lamp as 54 mL (1.00 mol) of bromine was added dropwise over 30 min. The lamp remained on until no more bromine was observed. The solvent was then evaporated to give a large amount of white solid. The desired product was extracted with petroleum ether (40-60 °C) using a soxhlet extractor. The solid obtained after evaporation of the petroleum ether was recrystallized in toluene and methanol to give 35 g of a white crystalline solid (27% yield): mp. 141-145 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.45 (s, 4H), 7.35 (s, 4H).

Synthesis of 1,4-Bis(cyanomethyl)benzene:[32] A solution of 12 g (0.18

mol) of potassium cyanide in 30 mL of water was added to 100 mL of ethanol and

heated to reflux with stirring. Solid 1,4-bis(bromomethyl)benzene (25 g, 0.09 mol)

was added and the mixture was heated at reflux for 1 h. The mixture was then

filtered hot to remove an unidentified yellow solid. The remaining solution was

diluted with 200 mL of water and the product was extracted with diethyl ether. The

organic layer was then separated, washed with saturated aq. sodium chloride

solution and dried over magnesium sulfate. After evaporation of the solvent the

product was recrystallized from methylene chloride and hexane to give 7.4 g of

white crystals. (54% yield): mp 96 - 98 °C, 94 - 96 °C[32].

Synthesis of 1,4-Bis(carboxymethyl)benzene:[33] A solution of 10.00 g (64

mmol) of 1,4-bis(cyanomethyl)benzene and 8.00 g of sodium hydroxide in 60 mL of

methanol and 30 mL of water was heated at reflux for 3 h. The mixture was then

cooled and the solvent was evaporated. The remaining solid was acidified with 10%

aq. hydrochloric acid, filtered and oven dried to give 9.50 g of a white powder. (77%

yield): mp. 246 - 252 °C, 249 - 251 °C[33].

Synthesis of 1,4-Bis(ethoxycarbonylmethyl)benzene:

1,4-Bis(carboxymethyl)benzene (10.00 g, 50 mmol), 50 mL of 95% ethanol, 100 mL

benzene and several drops of concentrated sulfuric acid were stirred and heated to

reflux in a flask fitted with a condenser and a Dean-Stark trap. As the reaction

progressed, the water produced in the reaction was collected in the trap. The

reaction mixture was heated at reflux until the insoluble starting material was no

longer visible (approximately 24 h). The solvent was then evaporated and the crude

product was recrystallized from ethanol/water (near room temp) to give a white

crystalline solid (70% yield): mp 65-69 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.23 (t, 6H), 3.56 (s, 4H), 4.11 (q, 4H), 7.22 (s, 4H).

Synthesis of 1,4-Bis(2-hydroxyethyl)benzene:[34]

A solution of 3.00 g of lithium aluminum hydride in 50 mL of dry tetrahydrofuran was added dropwise to a solution of 5.20 g of 1,4-bis(ethoxycarbonylmethyl)benzene in 50 mL of dry tetrahydrofuran over a period of 1 h. The mixture was allowed to stir overnight (approximately 12 h) under a stream of dry argon. The progress of the reaction was monitored by TLC. When the reaction was complete, the reaction was cooled in an ice bath and ethyl acetate was added dropwise over 30 min to quench the excess LAH. The mixture was acidified with 10% hydrochloric acid and the product extracted with ethyl acetate. After evaporation of the solvent, the crude product was recrystallized from ethanol to give a white crystalline solid (90% yield): mp. 85-87 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.73 (br. s, 2H), 2.82 (t, 4H), 3.83 (t, 4H), 7.16 (s, 4H).

Synthesis of 1,4-Bis(2-bromoethyl)benzene:[32]

1,4-Bis(2-hydroxyethyl)benzene (4.135 g, 24.90 mmol) was heated at reflux in 25 mL of 48% hydrobromic acid for 24 h. The mixture was neutralized with aq. sodium bicarbonate solution and the product was extracted with ethyl acetate. After evaporation of the solvent the product was purified by column chromatography (silica gel/chloroform). The first fraction was collected and the solvent was evaporated to give a white solid (63% yield): mp 63-65 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.14 (t, 4H), 3.53 (t, 4H), 7.15 (s, 4H).

Synthesis of 1,4-Bis(2-mercaptoethyl)benzene:[23]

1,4-Bis(2-bromoethyl)benzene (5.20 g, 18 mmol) and thiourea (3.00 g, 36 mmol) were heated to reflux in 95% aq. ethanol for 2.5 h. The solvent was then evaporated and a solution of 20.0 g of KOH in 150 mL of water was added to the resulting salt and the mixture was heated at reflux for 7 h under a constant stream of argon. The mixture was cooled in an ice bath, and acidified with 9 M aq. sulfuric acid. Finally, the product was extracted with benzene and the solvent evaporated to give a light yellow oil, 2.8 g (80% yield): bp. 125-127 °C/1 torr; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.55 (t, 4H), 2.89 (t, 4H), 3.38 (s, 4H), 6.78 (s, 8H).

Synthesis of 2,13-dithia[4.4]-paracyclophane:[23] A solution of 2.64 g (10 mmol) of 1,4-bis(bromomethyl)benzene and 1.98 g (10 mmol) of 1,4-bis-(2-mercaptoethyl)benzene was added dropwise to a refluxing solution of 1.78 g of KOH in 1 L of 95% aq. ethanol under a constant stream of argon. The addition was complete after 12 h. The mixture was heated at reflux for an additional 12 h and then concentrated. The residue was chromatographed on silica gel with benzene-hexane (1:1) to give a white crystalline solid, 500 mg (20% yield): mp 177-180 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.55 (t, 4H), 2.89 (t, 4H), 3.38 (s, 4H), 6.78 (s, 8H).

Synthesis of 2,13-dithia[4.4]paracyclophane 2,2,13,13-tetraoxide:[23] A solution of 1.79 g (5.96 mmol) of 2,13-dithia[4.4]paracyclophane, 2.5 mL of 30% hydrogen peroxide, and 10 mL of acetic acid was heated to 100 °C in an oil bath and allowed to reflux for 6 h. The product was filtered and dried to give 2.06 g of an off-white powder (94% yield): mp 320 °C (dec.); FT-IR (KBr pellet) 1115, 1261, 1304 cm^{-1}.

Synthesis of [3.3]Paracyclophane: 2,13-Dithia[4.4]paracyclophane

2,2,13,13-tetraoxide was converted to [3.3]paracyclophane using flow system

pyrolysis as described by Boekelheide.[24] The tetraoxide (500-1000 mg) was placed

in an aluminum boat in a long quartz tube. The tube was evacuated and placed

through two furnaces, one at 300 °C and the other at 600 °C. A valve at one end

provided a steady stream of dry nitrogen to flow at 1.25 mm Hg. The other end of

the tube was fitted with a cold finger trap onto which the product was condensed.

After 6 h the tube was removed from the oven and the crystalline product was

collected from the cold finger. The product was chromatographed on silica gel with

pet. ether (40-60 °C), then recrystallized from methanol to give white crystals (25%

yield): mp 102-104 °C, 104.3-105.3 °C[23]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.05 (p,

4H) 2.70 (broad s, 8H), 6.66 (s, 8H).

Synthesis of 5-bromo-[3.3]paracyclophane: The procedure followed is

similar to the bromination of [2.2]paracyclophane.[29] Iron powder (5 mg) was added

to a solution of bromine (0.2 mL, 3.8 mmol) in 5 mL of carbon tetrachloride and

stirred for 1 h at room temperature. [3.3]Paracyclophane (100 mg, 0.42 mmol) in 3

mL of dichloromethane was added and the stirring was continued for 24 h.

Additional bromine solution was added during this period if GC analysis showed

low conversion to product. The reaction was quenched by adding 10% aq. sodium

hydrogensulfite solution. The reaction mixture was washed with saturated aq.

sodium chloride solution and the organic layer was dried over anhydrous magnesium

sulfate. After evaporation of the solvent, the residue was chromatographed on silica

gel with hexanes. The collected product was further purified by fractional

crystallization from ethanol. (70% yield): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.85 - 2.07

(m, 2H), 2.31 (m, 1H), 2.54 - 2.80 (m, 8H), 3.06 (, 1H), 6.67 (m, 5H), 6.89 (s, 1H), 7.01 (d, 1H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 29.456, 35.020, 35.410, 35.860, 127.460, 129.442, 132.146, 137.036, 138.210, 138.443, 140.852; HRMS, EI for C$_{18}$H$_{19}$Br (M - 1$^+$) calcd 314.06706, found 314.06706.

Synthesis of Dibromo-[3.3]paracyclophane: A solution of bromine (0.04 mL, 0.80 mmol) in 5 mL of carbon tetrachloride was prepared, and 0.1 mL of this solution was stirred with iron powder (1.2 mg) in 5 mL of carbon tetrachloride for 1 h. Then the mixture was heated to reflux and [3.3]paracyclophane (100 mg, 0.40 mmol) was added. The remainder of the bromine solution was added dropwise over 3.5 h and the entire mixture was heated at reflux for an additional hour. After cooling the reaction mixture to room temperature, it was quenched with 10% aq. sodium bisulfite solution, and washed with saturated aq. sodium chloride solution. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated. The residue was chromatographed on silica gel with hexane. The collected dibromides were further purified using a chromatotron (silica gel/hexanes). The compounds eluted in several fractions. Fraction 1 contained a mixture of compounds one of which crystallized from hexanes to give a pure dibromo isomer (A) (57% yield): mp. 199-204 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.89 (m, 2H), 2.32 (m 2H), 2.60 (m, 4H), 2.76 (m, 2H), 3.08 (m, 2H), 6.64 (d, 2H, J = 1.4 Hz),6.89 (d, 2H, J = 7.8 Hz), 6.95 (d, 2H, J = 1.4 Hz); ^{13}C NMR (300 MHz, CDCl$_3$) δ 26.775, 34.629, 35.415, 124.033, 126.784, 132.661, 133.185, 136.752, 141.088; MS (m/e) 396, 394 (100, M$^+$), 392 , 315, 313, 197, 117, 105, 77; HRMS, EI for C$_{18}$H$_{18}$Br$_2$ (M - 1$^+$) calcd 391.97762, found 391.97762. Fraction 2 contained a single dibromo isomer (B): mp. 102-105 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.89 (m 2H), 2.28 (m, 2H), 2.63 (m,6H), 3.07 (m, 2H), 6.67 (dd, 2H, J = 7.8 Hz, 1.6 Hz),

6.76 (d, 2H, J = 7.8 Hz), 7.25 (d, 2H, J = 1.6 Hz); MS (m/e) 396, 394, 392 (100, M$^+$), 315, 313, 197, 117, 105, 77; HRMS, EI for $C_{18}H_{18}Br_2$ (M - 1$^+$) calcd 391.97762, found 391.97762. Fractions 3 and 4 gave unidentified compounds.

Synthesis of 1,4-Bis(2-isocyano-2-toluenesulfonylethyl)benzene:[35] A 7.5

N aq. NaOH solution (40 mL) was added dropwise to a solution of p-toluenesulfonylmethyl isocyanide (TosMIC) (9.872 g, 0.05 mol), 1,4-bis(bromomethyl)benzene (6.746 g, 0.025 mol), and n-Bu$_4$NI (3.868 g, 0.01 mol) in CH_2Cl_2 (40 mL) with vigorous stirring at 5 °C. After being stirred for 4 h at 5 °C, the reaction mixture was filtered with suction to collect the precipitated product which was used in the following reaction without further purification. A powdery yellow solid was collected, 12.071 g (48% yield): mp 170 - 177 °C, 175 - 176 °C[35]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.48 (s, 6H), 2.98 (dd, 2H), 3.60 (dd, 2H), 4.56 (dd, 2H), 7.22 (s, 4H), 7.65 (q, 8H).

Synthesis of 2,11-Diisocyano-2,11-ditosyl[3.3]paracyclophane:[35] A 7.5 N

aq. NaOH solution (50 mL) was added dropwise to a solution of 1,4-bis(2-isocyano-2-tosylethyl)benzene (4.92 g, 10.0 mmol), 1,4-bis(bromomethyl)benzene (2.64 g, 10.0 mmol), and n-Bu$_4$NI (0.75 g, 2.0 mmol) in CH_2Cl_2 (500 mL) with vigorous stirring at room temperature. The reaction was stirred for 24 h at room temperature before separating the CH_2Cl_2 layer, and washing twice with 200 mL portions of water and once with saturated aq. NaCl solution. After drying over anhydrous $MgSO_4$, the solvent was evaporated to give a heavy syrup. Benzene (30 mL) was added to the residue, and the product crystallized from the resulting solution after being allowed to stand overnight. Tiny yellow needles were collected with vacuum filtration, (0.297 g, 0.5 mmol) (5%

yield): mp 173 - 178 °C, 177 - 179 °C[35]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.49 (s, 6H), 3.38 (q, 8H), 6.75 (m, 4H), 7.11 (m, 4H), 7.72 (q, 8H).

Hydrolysis of 2,11-diisocyano-2,11-ditosyl[3.3]paracyclophane:[35]

Concentrated hydrochloric acid (1 mL) was added dropwise to a solution of 2,11-diisocyano-2,11-ditosyl[3.3]paracyclophane (577 mg, 1.00 mmol) in CH$_2$Cl$_2$ (30 mL) with stirring at room temperature. The mixture was stirred for 1 h, then the CH$_2$Cl$_2$ layer was separated, and washed with two 30 mL portions of 7.5 N NaOH solution and two 30 mL portions of water. After drying over anhydrous MgSO$_4$, the solvent was evaporated and the residue was chromatographed on silica gel. Elution with benzene removed the tosylsulfinic acid, followed with benzene/AcOEt (1:1) to elute the product, 2,11-dioxo[3.3]paracyclophane. A white solid was collected after evaporation of the solvent (192 mg, 0.7 mmol) (75% yield): mp 274 - 278 °C, 276 - 278 °C[35]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.67 (s, 8H), 6.83 (s, 8H).

Synthesis of [3.3]paracyclophane:[35]

A suspension of 2,11-dioxo-[3.3]paracyclophane (192 mg, 0.70 mmol), KOH (750 mg, 13.2 mmol), and hydrazine hydrate (1.26 g, 25.0 mmol) in diethylene glycol (20 mL) was heated slowly (1 h) from 100 °C without a condenser to allow water to evaporate. When the temperature reached 190 °C the condenser was returned and the mixture was stirred at that temperature for an additional 3 h. After being cooled the mixture was poured into water (200 mL) and the product was extracted with CHCl$_3$. To separate the product from excess diethylene glycol, the mixture was chromatographed on silica gel with hexanes. Product collected was a white solid (82 mg, 0.35 mmol) (48% yield): mp 102 - 104 °C, 104.3 - 105.3 °C[33]; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.05 (q, 4H), 2.70 (broad s, 8H), 6.66 (s, 8H).

Bibliography

1. Cirelli, D. P. In *Pharmacology and Environmental Toxicology*; Plenum: New York, NY, 1978; pp 13-18.

2. a) Miller, F. D.; Brilliant, L. B.; Copeland, R. *Bull. Environ. Contam. Toxicol.* **1984**, *32*, 125.

    b) Totter, W. J. *Bull Environ. Contam. Toxicol.* **1977**, *18*, 726.

3. Zabik, M. J. In *PCBs: Human and environmental Hazzards*; D'Itri, F. M.; Kamrin, M. A., Eds.; Woburn, MA, 1983; pp141-163.

4. Safe, S.; Huntzinger, O. *Nature* **1971**, *232*, 641.

5. Ingalls, R. B.; Wolfe, W.; Kharasch, N. *Abstracts of Papers*, 164th Meeting of the American Chemical Society: Washington, DC, 1964; p 6D.

6. Robertson, L. W.; Parkinson, A.; Safe, S. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 175.

7. Robertson, L. W.; Chittim, B.; Safe, S. H.; Mullin, M. D.; Pochini, C. M. *J. Agric. Food Chem.* **1983**, *31*, 454.

8. Ruzo, L. O.; Sundstrom, G.; Huntzinger, O.; Safe, S. *J. Agric. Food Chem.* **1976**, *24*, 1062.

9. Ruzo, L. O.; Zabik, M. J. *Bull Environ. Contam. Toxicol.* **1975**, *13*, 181.

10. Bunce, N. J.; Hayes, P. J.; Lemke, M. E. *Can. J. Chem.* **1983**, *61*, 1103.

11. Sandros, K. *Acta. Chemi. Scand.* **1969**, *23*, 2815.

12. Jang, J-S. Ph. D. Thesis, Oregon State University, 1990.

13. Soumillion, J. P.; De Wolf, B. *J. Chem. Soc. Chem. Comm.* **1981**, 436.

14. O'Donnell, C. M.; Harbaugh, K. F.; Fisher, R. P.; Winefordner, J. D. *Analyt. Chem.* **1973**, *45*, 609.

15. Egger, K. E.; Cocks, A. T. *Helv. Chim. Acta.* **1973**, *56*, 1516.

16. Freeman, P. K.; Lee, Y. S. *J. Am. Chem. Soc.* **1992**, *57*, pp.

17. Hirayama, F. J. *Chem. Phys.* **1965**, *42*, 3163.

18. Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.

19. Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8.

20. Bunce, N. J.; Safe, S.; Ruzo, L. O. *J. Chem. Soc. Perkins Trans. I* **1975**, 1607.

21. Pederson, C. L.; Lohse, C. *Acta. Chem. Scand. B* **1975**, *33*, 649.

22. a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

    b) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.

    c) Wettack, F. S.; Renkes, G. D.; Renkly, M. G.; Turro, N. J.; Dalton, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 1318.

23. Otsubo, T.; Kitasawa, M.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515.

24. Sherrod, S. A.; daCosta, R. L.; Barnes, R. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1565.

25. Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1955**, *77*, 6289.

26. Barton, D. H. R.; Lacher, B.; Zard, S. Z. *Tetrahedron Lett.* **1985**, *26*, 5939.

27. Gantzel, P. K.; Trueblood, K. N. *Acta. Cryst.* **1965**, *18*, 958.

28. Bunce, N. J.; LaMarre, J.; Vaish, S. P. *Photochem. Photobiol.* **1984**, *39*, 531.

29. Otsubo, T.; Horita, H.; Koizumi, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1677.

30. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

31. Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527.

32. Titley, A. F. *J. Chem. Soc.* **1928**, 2751.

33. Ruggli, P.; Busselmaker, B. B.; Müller, W. *Helv. Chim. Acta.* **1935**, *18*, 619.

34. Augustinsson, K. B.; Hasselquist, H. *Acta. Chim. Scand.* **1963**, *17*, 953.

35. Sasaki, H.; Kitagawa, T. *Chem. Pharm. Bull.* **1983**, *31*, 2868.