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THE ELECTRONIC SPECTRUM OF (-)-S-(pS)-2,5,3',6'-TETRAHYDRO-
[2.2]-PARACYCLOPHANE-2-CARBOXYLIC ACID

THESIS

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A new, efficient route was used in the synthesis of [2.2]-paracyclophane-2-carboxylic acid. The acid was then resolved and the Birch reduction performed yielding one enantiomer of tetrahydro-[2.2]-paracyclophane-2-carboxylic acid. The ultraviolet spectrum of tetrahydro-[2.2]-paracyclophane-2-carboxylic acid in isopentane shows one absorption at 206 nm ($\epsilon_{\text{max}} = 5,271$). There are three bands observed in the circular dichroism spectrum in isopentane at 236 nm ($[\theta] = 1.8 \times 10^4$), 201 nm ($[\theta] = -16 \times 10^4$) and a positive band indicated below 180 nm but not observed. The bands were assigned and possible reasons for the occurrence of a $\pi \rightarrow \pi^*$ transition at unexpectedly long wavelengths are discussed.

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CHAPTER I

INTRODUCTION

The purpose of this study was to investigate the electronic spectrum of the Birch reduction product of [2.2]-paracyclophane-2-carboxylic acid.

The Birch reduction of [2.2]-paracyclophane and its carboxylic acid derivative are known to give the product where the olefins of one deck only partially overlap the olefins of the other deck. The arrangement of the decks in this manner makes the Birch reduction product of [2.2]-paracyclophane optically active. The Birch reduction product of [2.2]-paracyclophane-2-carboxylic acid is optically active from both the arrangement of the olefins and the asymmetric center introduced by the addition of a carboxylic acid group. The optical activity of these compounds would enable circular dichroism as well as the ultraviolet spectra to be used in interpreting the electronic transitions. The isolation of an enantiomer of the Birch reduction product of [2.2]-paracyclophane-2-carboxylic acid also lends proof to the assigned stereochemistry through the observation of olefin transitions in the circular dichroism spectrum. A new, more efficient synthetic route was used to prepare [2.2]-paracyclophane-2-carboxylic acid which is the direct precursor of tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

CHAPTER II

SYNTHESIS OF (-)-S-(pS)-2,5,3',6'-TETRAHYDRO-[2.2]- PARACYCLOPHANE-2-CARBOXYLIC ACID

Circular dichroism and ultraviolet spectroscopy were used to analyze the electronic spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane derivatives. In order to obtain the circular dichroism spectrum, it was necessary to have one of the enantiomers of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane. 2,5,3',6'-Tetrahydro-[2.2]-paracyclophane would be difficult to resolve into its enantiomeric forms since it has no appropriate functional group to use in separating the enantiomers. An appropriate functional group would be a carboxylic acid, which could be reacted with one enantiomer of an optically active base to form diastereomeric salts. Each diastereomer of this salt would exhibit different physical properties making it possible to separate the diastereomers. With one diastereomeric salt isolated, acidification of this salt would liberate one of the enantiomeric carboxylic acids.

The best route to 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid would be to make [2.2]-paracyclophane-2-carboxylic acid and then to do a Birch reduction. The Birch reduction of the [2.2]-paracyclophane system gives

the 2,5,3',6'-tetrahydro product. The presence of the carboxylic acid on the ring only serves to facilitate the Birch reduction. To separate the enantiomers, an optically active amine could be reacted with the carboxylic acid to give diastereomeric salts. The diastereomers having different solubilities could be separated by fractional recrystallization. The carboxylic acid could then be recovered by acidification of the salt. The resolved [2.2]-paracyclophane-2-carboxylic acid could then be reduced to give the desired product. This was the general approach to the synthesis of one of the enantiomers of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

The first step in the proposed synthetic route was to make [2.2]-paracyclophane-2-carboxylic acid. The starting point in the synthesis of [2.2]-paracyclophane-2-carboxylic acid was [2.2]-paracyclophane. The literature preparation of [2.2]-paracyclophane-2-carboxylic acid is difficult even though the reported yields are high (Figure 1a) (1). This preparation involves making the methyl ketone and oxidizing to the carboxylic acid. [2.2]-paracyclophane-2-methyl ketone is made via a Friedel-Crafts acylation with acetyl chloride, which goes smoothly and in moderate yields. The methyl ketone was then converted to the carboxylic acid by hypobromite oxidation but we observed that this oxidation is unreliable. This reaction is successful 15-20 per cent of the time with the yields ranging from 15 to 90 per cent.

It was felt that this was not a satisfactory route and other possible synthetic routes were then explored.

The oxidation of the methyl ketone with hypiodite was attempted unsuccessfully (Figure 1b). Another possibility considered was to make the vinyl derivative and then oxidize with ozone to the carboxylic acid (Figure 1c). The methyl ketone was reduced to the 2-(1-hydroxy) ethyl derivative with lithium aluminum hydride (2). The 2-(1-hydroxy) ethyl derivative was dehydrated in fair yields (60 per cent) to the vinyl derivative by refluxing in dried dimethylsulfoxide. The next step would be to oxidize the olefin to the carboxylic acid by ozonolysis. No attempt was made to improve the product yields for the other steps in this sequence or to do the last reaction as a better synthetic route was discovered.

The synthetic route used to make [2.2]-paracyclophane-2-carboxylic acid was to make the Grignard reagent and then to react it with carbon dioxide (Figure 1d). The Grignard reagent could not be made in the traditional manner, and another method to make the Grignard reagent using activated magnesium was successful (5). To make the carboxylic acid by the Grignard synthesis first required 2-bromo-[2.2]-paracyclophane. The bromo derivative can be made in high yields by using molecular bromine and an iron catalyst (4). The Grignard reagent was made by making activated magnesium (finely divided and absolutely dry) and adding 2-bromo-[2.2]-paracyclophane. The Grignard reagent was then

Fig. 1--Synthesis of [2.2]paracyclophane-2-carboxylic acid

carbonated on a vacuum line with an excess of carbon dioxide. The carbon dioxide was frozen on top of the Grignard reagent; as the mixture thawed, it was stirred, mixing dry carbon dioxide into the Grignard reagent. The solution was then acidified, yielding, [2.2]-paracyclophane-2-carboxylic acid in high yield through a short, reliable synthetic route.

The next steps in the synthesis of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid are the resolution of the enantiomers and the reduction of the aromatic rings (Figure 2).

Fig. 2--Synthesis of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

This sequence of steps is desirable since the tetrahydro produce is easily oxidized back to the aromatic system. It was felt that if the amount of time the tetrahydro product was exposed to the atmosphere could be minimized, then the opportunity for the rings to rearomatize would be lessened. Therefore, the first step would be to resolve the [2.2]-paracyclophane-2-carboxylic acid into its separate enantiomers.

[2.2]-Paracyclophane-2-carboxylic acid has previously been resolved with cinchonidine (1), brucine (1), and (-) α -phenylethylamine (6), with (-) α -phenylethylamine being used in this study. The carboxylic acid and the amine were dissolved in chloroform and the salt was obtained. The diastereomers were then separated by fractional recrystallization from absolute ethanol and the salt was acidified yielding (+)-[2.2]-paracyclophane-2-carboxylic acid. The conditions required for the Birch reduction of [2.2]-paracyclophane had previously been determined (9). The (+)-S-[2.2]-paracyclophane-2-carboxylic acid was easily reduced to the desired product, (-)-S-(pS)-2,5,3'6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

Experimental

General

All reagents used were reagent-grade commercial chemicals unless otherwise indicated. ℓ -(-)- α -Methylbenzylamine and spectrophotometric grade 2-methylbutane were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, 53233 and were used as received. Anhydrous aluminum trichloride, bromine and iodine were of analytical reagent grade and were purchased from Mallinckodt Chemical Works, St. Louis, Missouri, 63160. Sodium and potassium were cut into small pieces and washed free of oil with dried ether or hexane. Anhydrous ammonia (Dixie Chemical, Houston, Texas)

was of refrigeration grade and condensed directly into the reaction vessel. [2.2]-paracyclophane was donated by Dr. Joe Nugent, Tulane University, New Orleans, Louisiana and was used as received. Optical rotation data were obtained from a Rudolph Model 80 polarimeter. Circular dichroism spectra were obtained from a JASCO J-40A Automatic Recording Spectropolarimeter, while purging with nitrogen. Ultraviolet spectra were taken on a Beckman Model 25 Spectrophotometer with a one centimeter length cell. Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected for atmospheric pressure.

Purification of Dioxane (10)

A mixture of 800 ml technical grade 1,4 dioxane, 80 ml water and 10.8 concentrated hydrochloric acid was refluxed for 12 hours during which time a slow stream of nitrogen was bubbled through the solution. The solution was then cooled and potassium hydroxide pellets were added slowly with stirring until they no longer dissolved. A second layer separated and the dioxane was decanted, treated with fresh potassium hydroxide pellets and the dioxane decanted into a clean flash and refluxed with sodium for 12 hours under a nitrogen atmosphere. The solvent was distilled by fractional distillation and used immediately.

Purification of Ethanol (10)

Ethanol was refluxed continuously over calcium oxide and freshly distilled prior to use.

Purification of Tetrahydrofuran

Tetrahydrofuran was refluxed continuously over a mixture of two parts sodium to one part potassium and was freshly distilled prior to use.

2-Acetyl-[2.2]-Paracyclophane (1)

To a solution of 14.28 g of powdered anhydrous aluminum trichloride and 9.42 g of butyl chloride in 160 ml of 95 per cent sym-tetrachloroethane at -30° (dry ice in isopropanol) was added in one portion 12.28 g of [2.2]-paracyclophane. The solution turned dark red. The temperature was raised and maintained at -16° to -17°C with constant stirring for fifteen minutes. It was then cooled to -45°C as 50 ml of 1N HCl was added. The solution turned yellow with the addition of HCl. The aqueous phase was separated and extracted twice with chloroform. The organic phases were washed with water, 5 per cent NaHCO_3 and water. After drying the organic phase with anhydrous magnesium sulfate, the solvent was removed under reduced pressure. The product was collected as a white-gray solid, which was recrystallized from aqueous ethanol. The weight of the crude produce was 7.7864 g (53 per cent), mp 101-103. Another recrystallization gave a purer sample, mp 106-107 (Lit. 109.7-110.4).

[2.2]-Paracyclophane-2-Carboxylic Acid (1)

Bromine, (7.3 g) was added continuously for 20 minutes to a solution of 5.75 g of potassium hydroxide in 35 ml of water at 0° with constant stirring. A solution of 3.47 of methyl ketone prepared above in 70 ml of freshly distilled dioxane was then added to the hypobromite solution continuously for 20 minutes with continued cooling and stirring. After an additional 20 minutes, the ice-bath was removed. The solution was allowed to warm to room temperature, and stirred for another 30 minutes. Dilute sodium bisulfate solution (1 per cent) was added to destroy excess oxidizing agent. The mixture was extracted with chloroform and the aqueous phase was acidified yielding a yellowish-white solid. The very crude acid was dissolved in 100 ml of boiling acetic acid, and the undissolved salt was filtered. A little water was added to the solution and the compound crystallized. 1.2982 g were collected (37 per cent) mp 216-219. Another recrystallization yielded a sample with mp 218.5-220.5. (Lit. 223.5-224.5.)

[2.2]-Paracyclophane-2-Carboxylic Acid

Via a Hypoiodite Route

The reaction was performed as for the hypobromite reaction with no product being formed.

2-(1-Hydroxy Ethyl)-[2.2]-Paracyclophane (2)

The methyl ketone (20 g) was dissolved in 100 ml of anhydrous ether. Lithium aluminum hydride (0.31 g, a little

over four times theoretical) was added with 15 ml of anhydrous ether to an oven baked three neck flash equipped with a condenser and dropping funnel and put under a nitrogen atmosphere. The methyl ketone in ether was added to the dropping funnel and added over a 90 minute period. The solution was then allowed to stir for an additional 60 minutes. The excess lithium aluminum hydride was consumed with sodium sulfate decahydrate, giving 1.4448 g (72 per cent). Cram and Harris (2) let the same mixture stir for 30 hours for a 90 per cent yield.

2-Vinyl-[2.2]-Paracyclophane (3)

A solution of 1.3144 g of 2(1-hydroxyethyl)-[2.2]-paracyclophane and 1.5 ml of freshly distilled dimethylsulfoxide was heated at 160° for five hours. The solution was then poured into 100 ml of a 5 per cent HCl solution, and a solid separated. The mixture was extracted with benzene and dried over anhydrous magnesium sulfate. The benzene was removed under reduced pressure. The resulting gummy solid was taken up in carbon tetrachloride and the solid precipitated on the addition of absolute ethanol, giving 0.7276 g (60 per cent).

2-Bromo-[2.2]-Paracyclophane (4)

Bromine (1.4 ml) in 25 ml carbon tetrachloride was added dropwise with stirring over 25 minutes to a mixture of 5.2 g [2.2]-paracyclophane, 0.05 g Fe powder and 500 ml

methylene chloride. The mixture was then stirred 30 minutes. Water (500 ml) was added and the solution was stirred for an additional 15 minutes. The organic layer was separated and washed twice with a dilute sodium bisulfite solution, water and brine. The organic layer was dried over anhydrous magnesium sulfate and the solvent removed by rotatory evaporation. The crude product was recrystallized from acetic acid and water to yield shining white plates, giving 6.0575 g after sintering (84.16 per cent), mp 132-134.5 (Lit. 132-134).

[2.2]-Paracyclophane-2-Carboxylic Acid

Via Activated Grignard

Magnesium (1.5 g), a catalytic amount of iodine and 10 g of 1-chlorobutane was added to a three-neck round bottom flash equipped with a dropping funnel, mechanical stirrer and condenser all under an argon atmosphere. The mixture was heated until a white solid was formed (magnesium chloride) and white smoke was present in the flask (octane). About 250 ml of dry tetrahydrofuran was added, along with 3.2 grams of potassium. The tetrahydrofuran was brought to reflux and stirred. After 3 hours a small aliquot was tested to make sure all potassium was consumed. 2-Bromo-[2.2]-paracyclophane (2,3691 g) was dissolved in approximately 50 ml of dry tetrahydrofuran and dripped into the solution. The solution was stirred for a half hour and allowed to reflux for 16 hours. The solution was then

poured into a flash with a stirring bar and a tetrahydrofuran vapor blanket, degassed and placed on a vacuum line. The solution was frozen and a large excess (1.75 grams) of carbon dioxide was then frozen on top of the Grignard reagent. The flash was packed in dry ice and stirred. When the dry ice had sublimed, and mixture was removed from the vacuum line, a little water added and the tetrahydrofuran evaporated. The remaining solution was then poured into 200 ml of a 5 per cent HCl solution. Sodium chloride was added and the solution was extracted with ether. The ether layer was then extracted with brine and 10 per cent NaOH. The 10 per cent NaOH layer was acidified yielding a white fluffy solid, 1.0218 g (97.5 per cent), after sintering, mp 219-221 (Lit. 223.5-224.5).

Resolution of [2.2]-Paracyclophane-2-
Carboxylic Acid

2.2 -Paracyclophane-2-carboxylic acid (0.551 g) and 0.2884 g of ℓ -(-)- α -methylbenzyl amine were stirred in 20 ml of chloroform for one hour. Ether was added and the solution was placed in an ice bath for 48 hours. The solution was filtered and the filtrate washed with ether yielding 0.7316 g of a dusty white salt. The salt was dissolved in 12 ml of anhydrous ethanol and was allowed to precipitate in an ice bath. Thereby 0.2041 g of salt was obtained and dissolved in 3.4 ml of absolute ethanol and allowed to precipitate, with 0.17 g of salt being

recovered, $[\alpha]_D = +95.44$ (0.68, CHCl_3). The salt was stirred in a mixture of chloroform and dilute hydrochloric acid. The chloroform layer was separated and extracted with 10 per cent NaOH. The aqueous extraction was acidified and cooled in an ice bath. The aqueous solution was extracted with chloroform and the chloroform removed on the rotatory evaporator giving the free carboxylic acid, $[\alpha]_D = +164.1$ (0.372, CHCl_3).

2,5,3',6'-Tetrahydro-[2.2]-Paracyclophane-2-
Carboxylic Acid (7)

(+)-2-Carboxy-[2.2]-paracyclophane (0.0654 g) was dissolved in 30 ml of dry tetrahydrofuran and placed in a 250 ml three-neck flask equipped with a magnetic stirrer. About 75 ml of liquid ammonia was added. Sodium (0.120 g) and 1.2 ml dry ethanol were added over a period of 30 minutes. After the blue color from sodium disappeared the solution was stirred for 3 hours, and then 0.45 g ammonium chloride and 20 ml water were cautiously added. The mixture was stirred for an additional hour. The entire reaction was done under an argon atmosphere. A little water was added and the flask was cooled in an ice bath. The solution was then made acidic with concentrated hydrochloric acid. The remaining tetrahydrofuran was removed on the rotatory evaporator. The solution was extracted with chloroform. The chloroform layer was washed with cold water and dried over anhydrous magnesium sulfate. The chloroform was removed

by rotatory evaporation leaving .0635 g (95.6 per cent) of white crystals. The crystals were washed with petroleum ether, mp 157.5-159 (Lit. (7) 158-159) $[\alpha]_D = -101$ (0.326 CHCl_3).

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CHAPTER III

INTERPRETATION OF THE ELECTRONIC SPECTRUM OF 2,5,3',6'- TETRAHYDRO-[2.2]-PARACYCLOPHANE-2- CARBOXYLIC ACID

Absorption in the ultraviolet region of the electromagnetic spectrum depends on the electronic structure of the molecule. Absorption of energy is quantized and results in the movement of electrons from ground state orbitals to higher energy excited state orbitals. Energy absorption in the ultraviolet region produces changes in the electronic energy of a molecule resulting from transitions of valence electrons. The absorption spectrum arising from a single electronic transition should consist of a single discrete line since the energy of absorption in the ultraviolet is quantized. However, a discrete line is not obtained since rotational and vibrational sublevels lie under the electronic absorption. In complex molecules, the multiplicity of vibrational sublevels and the closeness of their spacing cause the discrete bands to coalesce and form absorption bands. Transitions frequently occur from the ground electronic state to many different vibrational levels of a particular excited electronic state. Such transitions may give rise to vibrational fine structure in the electronic transition.

Transitions in the ultraviolet region are concerned with the movement of electrons. In the very short time required for an electronic transition to take place, the atoms in a molecule do not change their positions appreciably. This phenomenon is referred to as the Franck-Condon principle. Since the electronic transition is rapid, the molecule will have the same geometry in the excited state as it had in the ground state at the moment of absorption.

The principal characteristics of an absorption band are its position and intensity. The position of absorption corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition. The intensity of an absorption is expressed by its molar absorptivity, from the following equation:

$$A = \epsilon cb$$

where A is absorbance, ϵ is molar absorptivity, c is concentration and b is pathlength. The intensity of an absorption band in the ultraviolet spectrum is usually expressed as the molar absorptivity at maximum absorption, $\epsilon_{\max}$ or $\log \epsilon_{\max}$. Strong ultraviolet bands are electric dipole allowed. Magnetic dipole and electric quadrupole are observed as very weak bands and become important only when electric dipole transitions are forbidden.

Circular dichroism is also concerned with electronic transitions, except that optically active compounds are required for absorption. Circular dichroism is the

phenomenon in which optically active substances absorb right and left circularly polarized light differently. Plane polarized light consists of two circularly polarized components of equal intensity corresponding to right- and left-handed helices. If plane polarized light is passed through a sample for which the refractive indices of the left and right polarized components differ, the components will upon recombination give plane polarized radiation in which the plane of polarization has been rotated. All optically active substances exhibit circular dichroism in the region of appropriate electronic absorption. Whenever circular dichroism is observed in a sample, the resulting radiation is not plane polarized but is elliptically polarized. Only the chromophore that absorbs at the given wavelength contributes to that circular dichroism bond. In order for an electronic transition to give rise to optical activity, the transition must be both electric and magnetic dipole allowed. In circular dichroism, two systems of describing absorptions are used. The differential dichroic absorption:

$$\Delta\epsilon = \epsilon_L - \epsilon_R$$

with ϵ_L and ϵ_R being the molar extinction coefficients for the left and right circularly polarized light. Another commonly used unit is molecular ellipticity $[\theta]$ which is related to differential dichroic absorption, $\Delta\epsilon$, by

$$[\theta] = 3300\Delta\epsilon.$$

Further information contained in the circular dichroism spectrum are the absolute sign of absorption and the rotatory strength, R . R is the rotational strength of an electronic transition given by

$$R = \rho\mu \cos\theta$$

where ρ is the scalar product of the electric dipole transition moment, μ is the scalar product of the magnetic dipole transition moment and θ is the angle between the direction of the two moments.

There are several ways in which a circular dichroism spectrum can be helpful in characterizing electronic states. The circular dichroism ellipticity can be positive or negative. This property is often instrumental in resolving close lying or overlapping electronic transitions, when the two bands have opposite signs. Also, since the quantities ϵ and $\Delta\epsilon$ depend on different matrix elements, the absorption and circular dichroism spectrum contours are quite different; the absolute quantities of ϵ and $\Delta\epsilon$ at the peaks have different ratios depending on the transition. The ratio

$$g = \frac{\Delta\epsilon}{\epsilon}$$

is the anisotropy factor. This ratio is a measure of the magnitude of the magnetic dipole transition moment relative to the electric dipole transition movement. A relatively large value of g is obtained for transitions which were magnetic dipole allowed (electric dipole forbidden) in the

unsubstituted symmetric chromophore whereas a small value of g is indicative of the opposite case.

In elucidating the electronic spectrum of a molecule, it is very useful to have access to the circular dichroism spectrum in addition to the ultraviolet spectrum. There are different requirements for absorption in each of these methods. An electric dipole allowed transition is required for a strong ultraviolet absorption. In the case of circular dichroism, an absorption requires a transition have magnetic and electric dipole components. Circular dichroism and ultraviolet are used in the same region of the electromagnetic spectrum and complement each other. More transitions are usually visible in the circular dichroism spectrum. These two methods along with analogies to similar systems will be used to explain the electronic spectrum of the tetrahydro-[2.2]-paracyclophane system.

2,5,3',6'-Tetrahydro-[2.2]-paracyclophane-2-carboxylic acid (Figure 1) exists as a pair of enantiomers and is resolvable. This makes both the circular dichroism and the ultraviolet spectra available for the interpretation of the electronic spectra. Previously only the ultraviolet spectra were available to aid in the understanding of the tetrahydro-[2.2]-paracyclophane systems. It had been observed that the ultraviolet spectra consisted of an end absorption extending from 200 nm to 260 nm and 200 nm to 250 nm for 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid (1)

and 2,5,3',6'-tetrahydro-[2.2]-paracyclophane (Figure 3), respectively (2). This end absorption had been incorrectly used in determining the stereochemical relationship between the olefins in each of the decks of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane. It had been postulated that the low energy end absorption was due to the olefin groups overlapping each other (Figure 4). With the olefin groups in this position, it was postulated that there would be significant interaction, such as that seen in conjugated olefins, giving rise to this low energy band (2). The stereochemical relationship has since been determined through an NMR study of the tetraepoxide derivative of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid. It was found that the olefins were in fact staggered (Figure 4) and the postulation of significant interaction between the decks should not account for this low energy band (1). The circular dichroism spectrum corroborates the NMR study of the staggered olefin configuration. In the staggered configuration, the olefins are in a dissymmetric environment without the presence of the acid moiety and should give a strong olefinic absorption. With the overlapping configuration, the acid moiety is needed to provide a dissymmetric environment and at most a weak olefinic absorption would be expected. Since, in fact a strong olefinic absorption is observed then this adds further evidence for the assignment for the staggered configuration (Figure 5). An even stronger proof would be to

Fig. 3.--a) 2,5,3',6'-Tetrahydro-[2.2]-paracyclophane
b) 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

Fig. 4.--Possible stereochemistry of tetrahydro-[2.2]-paracyclophane a) olefins overlapping b) olefins staggered.

Fig. 5a--Circular dichroism spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid in isopentane.

Fig. 5b--Ultraviolet spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid in isopentane.

Fig. 5c--Circular dichroism spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid in ethanol.

Fig. 5d--Ultraviolet spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid in ethanol.

decarboxylate and in this case the staggered decks should be optically active and the overlapping decks would not be optically active. No attempt was made to decarboxylate 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid since it was felt that the conditions required for decarboxylation would rearomatize the ring containing the carboxylic acid, or possibly both rings (Figure 6).

Fig. 6--Proposed products for decarboxylation of tetrahydro-[2.2]-paracyclophane-2-carboxylic acid.

2,5,3',6'-Tetrahydro-[2.2]-paracyclophane easily rearomatizes and would probably lose a hydrogen from a methylene to form an aromatic ring instead of replacing the carboxylic acid with a hydrogen. In order to isolate one of the enantiomers of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane, it would require special techniques for decarboxylation or possibly another synthetic pathway.

In studying the electronic spectrum of tetrahydro-[2.2]-paracyclophane-2-carboxylic acid, circular dichroism and ultraviolet absorption spectroscopy were employed.

In taking the electronic spectrum of the tetrahydro-[2.2]-paracyclophane system, the method of choice would be

to take the spectrum in the vapor phase. Unfortunately a polymer is formed under these conditions and the spectrum of the polymer is the same as that for p,p'-dimethyl-bibenzyl. This indicates that there has been cleavage of a methylene bridge and rearomatization of the benzene moiety. Therefore, the ultraviolet and circular dichroism spectra were taken in solution. In this study, it was found that for 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2 carboxylic acid the ultraviolet spectra consisted of a peak at 206.3 nm in isopentane. The circular dichroism spectrum had peaks at 236 nm, 201 nm and with another peak indicated below 180 nm. From the circular dichroism spectrum, it can be seen that the electronic spectrum consists of three transitions (Table I).

TABLE I

ULTRAVIOLET AND CIRCULAR DICHROISM ABSORPTIONS FOR 2,5,3',6'-TETRAHYDRO-[2.2]-PARACYCLOPHANE-2-CARBOXYLIC ACID IN
A) ISOPENTANE AND B) ETHANOL

CD			UV	
λ (nm)	$[\theta] \times 10^4$	$\Delta\epsilon$	λ (nm)	$\epsilon_{\max}$
A) 236 201 180	-1.825 -16.38 ?	-5.529 -49.64 ?	206.3	5271
B) 205	-15.28	-46.33	208.2	5915

The lowest energy transition is tentatively assigned as a $\pi \rightarrow 3s(\sigma^*)$ (Figure 7) Rydberg-like transition. This transition was identified as $\pi \rightarrow 3s$ on the basis of its weakness relative to the next lower energy transition (3) and its apparent shift upon a change of solvents (3, 4). For isolated olefins, this Rydberg-like transition has been observed to be on the lower energy wing of the first low energy transition (4). In ethanol, the Rydberg-like transition appears to have shifted under the first low energy transition where it is not readily observable. In isopentane, the Rydberg-like transition is observed as a shoulder on the stronger absorption at 201 nm. A method to aid in establishing this as a Rydberg transition would be to observe its circular dichroism spectrum upon progressive cooling. Progressive cooling will blue shift a Rydberg band but will not shift other transitions (3). This was not done since the equipment necessary for taking the circular dichroism spectrum at different temperatures was not available.

The next two transitions observed in the circular dichroism (isopentane) are an oppositely signed couplet. One band of the couplet is observed at 201 nm with the other band indicated below 180 nm. The ultraviolet spectrum should have bands corresponding to those seen in the couplet. The first band in the ultraviolet is seen at 206.3 nm (isopentane) and the second is probably below 180 nm where it is not observed (3). This couplet is assigned to mixing of

Fig. 7--The olefin chromophore a) coordinate frame
 b) Rydberg united-atom 3s orbital c) π_y^* orbital d) π_y
 orbital e) π_x^* orbital f) π_x orbital (taken from reference 3).

$\pi x \rightarrow \pi x^*$ and $\pi x \rightarrow \pi y^*$ (Figure 7). An oppositely-signed circular dichroism couplet comes from the interaction of the collinear transition moments in a chiral molecule when one is an electric and the other a magnetic multipole of the same order. It has been implied that the oppositely signed couplet of chiral olefins arises from the mixture of an electric- and a magnetic- dipole zero-order excitation through perturbation. For ethylene the $\pi x \rightarrow \pi x^*$ transition, with a Z-polarized electric dipole moment, is accompanied by a near-degenerate quadrupole transition, and if this is $\pi x \rightarrow \pi y^*$ or $\pi y \rightarrow \pi x^*$, it could have the XY- component of an electric quadrupole and the Z-component of a magnetic dipole as the leading transition moments (3). On energy grounds, in chiral alkenes $\pi x \rightarrow \pi y^*$ is virtually degenerate with $\pi x \rightarrow \pi x^*$, easily allowing mixing. The couplet in chiral olefins arises mostly from the mixing of the zero-order excitations $\pi x \rightarrow \pi x^*$ and $\pi x \rightarrow \pi y^*$ (3). The absorption bands in both the ultraviolet and the circular dichroism are expected to have similar areas and the bands which come from the virtual degeneracy of the $\pi x \rightarrow \pi x^*$ and $\pi x \rightarrow \pi y^*$ transitions in substituted olefins (3). The absence of spectra below 180 nm makes this hard to determine, but the trends are present. The major absorption around 200 nm and the absorption indicated below 180 nm are assigned to a mixing of the $\pi x \rightarrow \pi x^*$ and $\pi x \rightarrow \pi y^*$ transitions.

Another band which is expected to be present in both the ultraviolet and the circular dichroism is the carboxylic

acid absorption. Carboxylic acids usually absorb weakly between 200-210 nm when they are not conjugated (5, 6). There is an indication that the carboxylic acid $n \rightarrow \pi^*$ absorption is buried under the stronger $\pi \rightarrow \pi^*$ absorption of the olefin in the same region. The intensity of the absorption in this region is greater for 2,5,3',6' tetrahydro [2.2]-paracyclophane-2-carboxylic acid than for 2,5,3',6'-tetrahydro-[2.2]-paracyclophane (1). The carboxylic acid would be expected to show a circular dichroism absorption since it is located in a dissymmetric environment. Since there is no resolved 2,5,3',6'-tetrahydro-[2.2]-paracyclophane available, it is not possible to compare the circular dichroism spectra. Since in the ultraviolet, intensities are additive, the increased absorption of the acid compared to the same compound lacking the acid, this is taken as evidence that the acid $n \rightarrow \pi^*$ lies under the stronger $\pi \rightarrow \pi^*$. The major absorption around 200 nm also experiences a blue shift upon going from a polar to a nonpolar solvent, which does not indicate a $n \rightarrow \pi^*$ transition but is indicative of a $\pi \rightarrow \pi^*$ transition. Also the weak circular dichroism band at 236 nm is not assigned as a red-shifted acid $n \rightarrow \pi^*$ transition since this study has established that 1,4-dihydrobenzoic acid shows no absorption above 200 nm (11). This effectively rules out the assignment of the 236 nm absorption as originating from an $n \rightarrow \pi^*$ transition. The $n \rightarrow \pi^*$ transition of the acid is therefore believed to lie under the strong $\pi \rightarrow \pi^*$ transition on the high energy side of the band.

The rotational and dipole strengths and the anisotropy factor were not determined because the overlapping of these bands makes it difficult to determine these values from experimental data. The Rydberg band appears to be on the order of 0.1 the strength of the first major low energy band but it is partly obscured by the low energy wing of this band. The occurrence of both the acid $n \rightarrow \pi^*$ and the first low energy olefin transition make it difficult to separate the two transitions. The values for the highest energy olefin transition cannot be obtained since the complete band is not observed.

The ultraviolet spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid absorbs at 208.2 nm in ethanol and 206.3 nm in isopentane. This is a lower energy absorption than might be expected. The $\pi \rightarrow \pi^*$ transition of trisubstituted ethylenes absorb around 184 nm (4, 9). A 1,4 cyclohexadiene moiety is present in 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid. 1,4 Cyclohexadiene absorbs at 156 nm which is a higher energy absorption than the $\pi \rightarrow \pi^*$ transition of ethylene which absorbs at 165 nm (10). This would indicate that 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid should absorb at wavelengths lower than 188 nm. Since it in fact absorbs at longer wavelengths, then there must be other interactions in this system.

The first step in looking at 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid would be to look at

the four olefins as independent chromophores. This is the classical way of approaching non-conjugated olefins (5). The first item of note is that each olefin is a trialkyl substituted ethylene, which typically absorbs at 184 nm (4, 9). It is known that alkyl substitution of an olefin will shift the $\pi \rightarrow \pi^*$ absorption to lower energy (4, 5, 9, 10) (Tables II and III).

TABLE II
OBSERVED ULTRAVIOLET ABSORPTIONS FOR METHYL-SUBSTITUTED ETHYLENES

Number of Methyl Groups	$\pi x \rightarrow \pi y^*$ (N $\rightarrow$ V) (nm)	$\pi \rightarrow 3s$ (N $\rightarrow$ R) (nm)
0	164	174
1	174	185
2(1,1)	186	201
2(1,2-cis)	175	206
2(1,2-trans)	178	204
3	184	216
4	188	230

TABLE III
COMPARISON OF λ_1 and λ_2 AS OBSERVED IN THE CD OF CHIRAL ENDOCYCLIC OLEFINS SHOWING DOUBLE EXTREMA AND THE EXPECTATION VALUES (λ) OF THE UVmax AND THE $\pi x \rightarrow 3s$ SHOULDER (9)

Substitution	CD - λ_1 (nm)	UV - λ_{max} (nm)	CD - λ_2 (nm)	$\pi x \rightarrow 3s$ (nm)
Di	185 $\pm$ 5(?)	188	200 $\pm$ 3	208
Tri	189 $\pm$ 7	195	206 $\pm$ 5	216
Tetra	199 $\pm$ 6	203	216 $\pm$ 6	228

Therefore alkyl substitution could account for part of the reason that 2,5,3',6'-tetrahydro-[2.2]-paracyclophane systems absorb at long wavelengths.

A possible effect that could account for the long wavelength $\pi \rightarrow \pi^*$ transition is twisting around a double bond. Steric strain can be most efficiently relieved by twisting of the double bond in olefins. The steric interference raises the potential energy of both the ground and excited states about $\theta = 0^\circ$, this effect is probably larger in the ground than in the excited state because of the larger bond order of the ground state. The transition thus requires less energy moving it to longer wavelengths (12) 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid is not predicted to have twisted olefin groups. This prediction is based on comparison to other compounds, the flexibility of the 1,4 cyclohexadiene moiety and the lack of very bulky groups on the olefins. The groups immediately around the olefins in 2,5,3',6'-tetrahydro-[2.2]-paracyclophane are methylenes which are relatively small groups. The 1,4-cyclohexadiene rings found in 2,5,3',6'-tetrahydro-[2.2]-paracyclophanes can easily flex and are not forced into rigid conformation which would strain the double bonds. A trisubstituted olefin endocyclic to a somewhat constrained cyclohexane ring is α -pinene. Electron diffraction studies indicate that the double bond of α -pinene is not distorted

(20). There is apparently enough flexibility in the ring and the substituents small enough that there is no steric strain placed on the double bond. A compound with a 1,4 cyclohexadiene ring locked into a rigid conformation is anti-7-norbornenyl p-bromobenzoate which has a very slight twist (1°) of the double bond (21). The olefins in 2,5,3',6'-tetrahydro-[2.2]-paracyclophane are certainly not in as strained a system as is present in anti-7-norbornenyl p-bromobenzoate and should not have any twisting of its olefin groups. From looking at these various factors, twisting of the olefin groups should not account for the long wavelengths absorption of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane.

The mixing of excited states in chiral olefins appears to be responsible for absorptions at long wavelengths. The α -(-)-Pinene CD absorption shows transitions at 201 nm and 177 nm (3). α -(-)-Pinene would be expected to show a strong $\pi \rightarrow \pi^*$ absorption at 184 nm, as would be expected for a nonchiral trisubstituted olefin (12) (Table II). For α -(-)-Pinene it has been suggested that the couplet of oppositely signed CD bands in the far ultraviolet regions arise from the mixing of the excited states under either a static or a dynamic perturbation of the symmetric olefin chromophore by dissymmetrically located substituents (2). The perturbation of the olefin chromophore in chiral olefins gives two $\pi \rightarrow \pi^*$ transition of almost equal intensity with one appearing at longer than expected wavelengths.

Another important interaction can be seen from examining 1,4 cyclohexadiene, since this group is found as a part of the 2,5,3',6'-tetrahydro-[2.2]-paracyclophane system. The $\pi \rightarrow \pi^*$ transition for 1,4 cyclohexadiene is located at 156 nm and for ethylene at 165 nm (10). 1,4 Cyclohexadiene absorbs at higher energy because of the parallel electric dipole interaction of the isolated olefins. This shift is predicted from the vector addition of the electric dipoles. This interaction would tend to shift the $\pi \rightarrow \pi^*$ transition to lower energy (10). 2,5,3',6'-Tetrahydro-[2.2]-paracyclophane-2-carboxylic acid contains 1,4 cyclohexadiene moieties with a significant difference. 1,4 Cyclohexadiene itself is flat (12) whereas the 1,4 cyclohexadiene moiety in 2,5,3',6'-tetrahydro-[2.2]-paracyclophane systems is puckered (1, 14). The puckering of this moiety relieves the steric strain present in the parent compound (15). 2,5-[2.2.2]-Bicyclooctadiene and 2,5-[2.2.1]-bicycloheptodiene will be examined as models for the effects of puckering on a non-conjugated cyclohexadiene. 2,5-[2.2.2]-Bicycloheptadiene absorbs at 198 nm (16) and 2,5-[2.2.1]-bicycloheptadiene absorbs at 211 nm (17). Both of these molecules contain a puckered cyclohexadiene ring. These molecules absorb at much longer wavelengths than does flat 1,4 cyclohexadiene. None of these molecules is optically active ruling out mixing of the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ excited states. A possible explanation is that the puckered conformation is somewhat unstable thus

raising the energy of the ground state. This would make the transition energy smaller in going from the ground to the excited state giving a lower wavelength absorption. This possible puckering effect can also be seen in 2-[2.2.2]-bicyclooctene and 2-[2.2.1]-bicycloheptene as these molecules absorb at 190.3 nm and 195 nm respectively (16, 17). These absorptions are at longer wavelengths than would be expected for 1,2 cis-disubstituted ethylenes which absorb at 175 nm (9) (Table II). These ideas are further supported by CNDO/2 calculations done in this study on flat and puckered 1,4 cyclohexadiene. These calculations indicate the ground state of flat 1,4 cyclohexadiene is much more stable than that for puckered 1,4 cyclohexadiene. As can be seen in Table IV, flat 1,4 cyclohexadiene is predicted to absorb at higher energy than ethylene as it is observed to do experimentally (10). 1,4-Cyclohexadiene puckered 20° into the "boat" conformation is predicted to absorb at much longer wavelengths than ethylene. These calculations were used to predict trends and not to calculate the energy of the observed $\pi \rightarrow \pi^*$ transitions. The calculations correctly predicted flat 1,4 cyclohexadiene to lie at approximately eight nanometers lower wavelength than ethylene but does not predict the wavelength of absorption as seen experimentally. CNDO/2 calculations predict that the $\pi \rightarrow \pi^*$ transition of nonconjugated cyclohexadiene is shifted to longer wavelengths when forced into the "boat"

TABLE IV

CNDO/2 CALCULATIONS FOR GROUND AND πx^* EXCITED STATES AND WAVELENGTH OF $\pi x \rightarrow \pi x^*$ ABSORPTION FOR FLAT 1,4 CYCLOHEXADIENE, PUCKERED 1,4 CYCLOHEXADIENE AND ETHYLENE

	1,4 Cyclohexadiene		Ethylene
	Flat	Puckered (20°)	
Ground State (In Atomic Units)	-47.5765	-46.5791	-17.0677
πx^* Excited State (In Atomic Units)	-47.1196	-46.2353*	-16.6442
Energy Difference (In Atomic Units)	0.4569	0.3438	0.4235
Calculated Wavelength Of Absorption (nm)	99.7	132.5	107.6

*Energy not satisfied; excited at 15 iterations.

conformation. This comes about because of a smaller energy difference for the ground and excited states for puckered 1,4 cyclohexadiene than that found for the same states in flat 1,4 cyclohexadiene. The CNDO/2 calculations carried out on 1,4 cyclohexadiene puckered 20° into the "boat" conformation indicate that the ground state is raised much high in energy than in the excited state. This puckering effect is relative to the more stable flat conformation. The energy difference between the ground and excited states is smaller for the puckering than for the flat ring giving rise to a lower energy $\pi x \rightarrow \pi x^*$ transition.

An additional consideration of 1,4 cyclohexadiene in the "boat" conformation is that of rear lobe interaction. Rear lobe interaction has been postulated to explain the anomalous NMR coupling constants of norbornene. It was postulated that the rear lobes of the bond significantly interacted with the rear lobes of the carbon hybrid orbitals on carbons 5 and 6 (18) (Figure 8).

Fig. 8--a) Rear lobe interaction of 2-[2.2.1]-bicycloheptene b) rear lobe interaction of 2,5-[2.2.1]-bicycloheptadiene.

This rear-lobe interaction could account for the long wavelength absorption for 2-[2.2.1]-bicycloheptene through

hyperconjugation with the carbon orbitals. This could be extended to 2-[2.2.2]-bicyclooctene. The higher energy absorption may be due to the fact the orbitals are further apart and overlap is not as great. If this is possible for a puckered cyclohexene, than overlap should be more efficient for a puckered 1,4-cyclohexadiene (Figure 5). Both 2,5-[2.2.2]-bicyclooctadiene and 2,5-[2.2.1]-bicycloheptadiene absorb at longer wavelengths than do their mono-olefin counterparts. The difference in the diene absorption could be that the π -bonds are closer in 2,5-[2.2.1]-bicycloheptadiene giving more efficient overlap and lowering the energy of the $\pi \rightarrow \pi^*$ transition. The "puckering effect" can be attributed to the energy difference between ground and excited states becoming smaller and to rear lobe interaction.

The last interaction which must be considered is the interaction between the decks of the 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid. Interaction between decks is significant in paracyclophane system as can be seen by looking at the spectra of several paracyclophanes with various sizes of methylene bridges. Interaction is significant for the smaller paracyclophanes but when the number of methylenes in each bridge reaches four, then the spectrum becomes similar to that found for the open chain analog *p,p'*-bibenzyl (19). As the decks are moved farther apart, the interaction between decks is lessened. There is

evidence for some interaction between the decks of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane systems. CNDO/2 calculations (Table V) on the two ethylenes (as in Figure 9) indicate that

Fig. 9--Orientation of ethylenes used in CNDO/2 calculations of interdeck interaction.

they are more stable than two ethylenes with the same geometry but much further apart. It would be hard to differentiate between ring pucker and interdeck interaction because as the molecule is expanded the ring will no longer be puckered. This same argument could also be applied to [2.2]-paracyclophane systems. For these reasons it would be hard to separate these effects and determine what contribution interdeck interaction would make to the electronic spectra. Based on CNDO/2 (Table I) calculations there should be some interdeck interaction but its nature would be hard to determine experimentally.

TABLE V

CNDO/2 CALCULATIONS FOR THE ENERGY OF GROUND STATES
OF TWO ETHYLENES SITUATED AT VARIOUS
DISTANCES AS SEEN IN FIGURE SIX

Distance Between Ethylenes (Å)	Energy (Atomic Units)
2.83	-34.1372
3.55	-34.1345
4.27	-34.1347
5.76	-34.1348
10.0	-34.1348

When complex systems are considered, there can be many factors affecting the spectra. One possible factor is the substitution of the olefin chromophore. Another is the mixing of the $\pi x \rightarrow \pi x^*$ and $\pi x \rightarrow \pi y^*$ transitions because of the dissymmetric environment of the olefins. The parallel electric dipole interaction as found in 1,4 cyclohexadiene would also make a contribution. Puckering raising the ground state in energy and rear lobe interaction of non-conjugated dienes also could play a part. Finally, there is the unknown contribution of interdeck interaction. These are the possible interaction making contributions to the electronic spectrum of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane system. The exact contribution of each interaction is not known and the nature of each contribution cannot be positively determined.

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CHAPTER IV

SUMMARY

2,5,3',6'-Tetrahydro-[2.2]-paracyclophane-2-carboxylic acid exhibits an electronic spectrum very similar to that found for other endocyclic trisubstituted olefins (1) (Table III). Even though the wavelengths of the transitions do not fall within the typical values, the pattern is the same. The differences can be attributed to some of the effects discussed earlier. The effect of alkyl substitution on olefins is well established and undoubtedly is a cause for the long wavelength $\pi \rightarrow \pi^*$ transitions. Puckering could make a contribution to the long wavelength absorption found in endocyclic olefins and should have an even stronger effect in 2,5,3',6'-tetrahydro-[2.2]-paracyclophanes as discussed earlier. Mixing of states makes an important contribution to the spectra of chiral olefins but it is not known how this will affect the shifting of the $\pi \rightarrow \pi^*$ transition. Although mixing of states probably affects the spectrum since chiral alkyl substituted olefins absorb at longer wavelengths than do achiral alkyl substituted olefins. The interaction of the parallel electric dipoles in the 1,4 cyclohexadiene moieties should move the $\pi \rightarrow \pi^*$ transition to higher energy. Twisting of double bonds is not believed to occur and therefore should not make a

contribution to the spectrum. Interaction between decks of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane should probably be minimal and should have little or no effect on the electronic spectrum. The long wavelength absorption of 2,5,3',6'-tetrahydro-[2.2]-paracyclophane is attributed to a $\pi \rightarrow \pi^*$ transition red shifted by mixing of orbitals, substituent and puckering effects and with a smaller blue shift contribution from parallel dipole interaction. The low energy side of this band is extend to longer wavelengths since a $\pi \rightarrow 3s$ Rydberg-like transition is partially hidden under this low energy wing. The combination of these two bands is the reason for the long wavelength reach of this compound. The absorption bands for 2,5,3',6'-tetrahydro-[2.2]-paracyclophane-2-carboxylic acid were assigned as follows: a) 236 nm as $\pi \rightarrow 3s$, b) 201 nm as $\pi_x \rightarrow \pi_x^*$, c) the absorption indicated below 180 nm as $\pi_x \rightarrow \pi_y^*$. The $n \rightarrow \pi^*$ absorption of the carboxylic acid is believed to lie under the $\pi_x \rightarrow \pi_x^*$ transition probably on the high energy side of this band. 2,5,3',6'-Tetrahydro-[2.2]-paracyclophane-2-carboxylic acid obeys the +XYZ sector rule for the long wavelength absorption and the +XYZ sector rule for the short wavelength absorption of the CD couplet (2).

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