

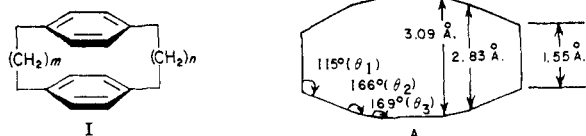
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. XVII. An Extreme Example of Steric Inhibition of Resonance in a Classically-conjugated Hydrocarbon¹BY KENNETH C. DEWHIRST² AND DONALD J. CRAM

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Reactions have been carried out on the two bridges that hold the two benzene rings of [2.2]paracyclophane face to face. Halogen, hydroxyl and carbonyl groups as well as double bonds have been introduced into these bridges. The unusual physical and chemical properties which the resulting compounds exhibit are described and rationalized.

The paracyclophanes³ (I) are of particular interest in the field of molecular structure, since their confined molecular motions permit a study of the effect of electronic interactions between unsaturated and unconjugated centers.^{3,4} The smallest of these cycles, [2.2]paracyclophane (I, $m = n = 2$), is unique as the strain in the molecule has become so large that the benzene rings have been substantially bent from planarity. The complete crystal structure of this molecule has been deter-



mined by the X-ray diffraction method.⁵ A cross section of the molecule (A) reveals it to be puckered, the benzene rings being bent some 11° from their normal planar state. The bonds joining the methylene bridges to the benzene rings are distorted 14° from their usual 180° bond angles. Clearly, strong repulsion exists between the two benzene rings which increases the bond angle between the methylene bridges and the benzene rings from what would be 90° (if the benzenes were planar) to 115°, thus leaving only 6° of strain in this angle. The remaining strain is distributed almost equally between the other two angles, θ_2 and θ_3 .

The major objective of the investigation reported here was to introduce a double bond into each of the two bridges of [2.2]paracyclophane (I, $m = n = 2$), thus shortening the methylene-methylene distances from 1.55 to 1.33 Å., and increasing the steric repulsion between the aromatic nuclei. In such molecules as II and III, the plane described by the unsaturated bridges is locked in a position orthogonal to those of the benzene rings. In III one has a fully conjugated system in a formal sense, and the question arises as to how complete an insulation of chromophores is provided by the steric inhibition of resonance inherent in the geometry. Thus the synthesis of II and III was undertaken.

(1) Part of this research was conducted under Contract AF 33-616-146 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

(2) National Science Foundation Predoctoral Fellow at the University of California at Los Angeles, 1956-1958.

(3) D. J. Cram and H. Steinberg, *THIS JOURNAL*, **73**, 5691 (1951).

(4) (a) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954); (b) D. J. Cram and R. W. Kierstead, *ibid.*, **77**, 1186 (1955); (c) D. J. Cram and N. L. Allinger, *ibid.*, **77**, 6289 (1955); (d) D. J. Cram and R. A. Reeves, *ibid.*, **80**, 3094 (1958).

(5) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

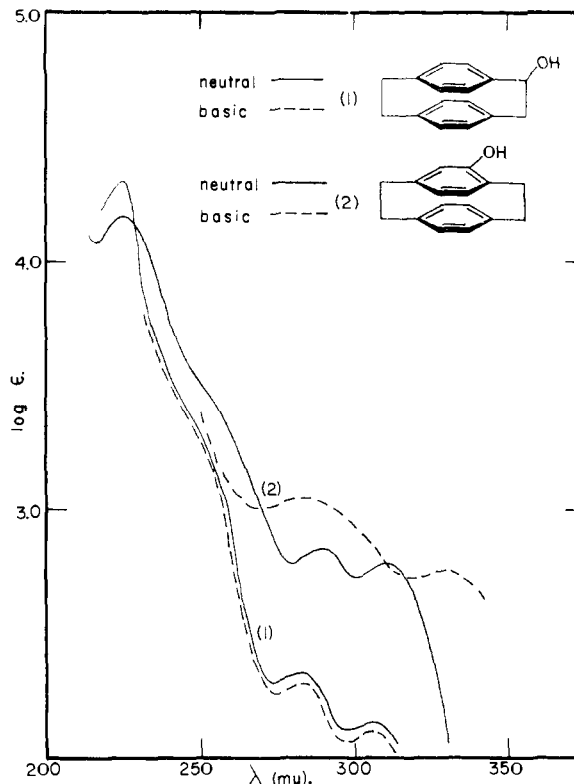


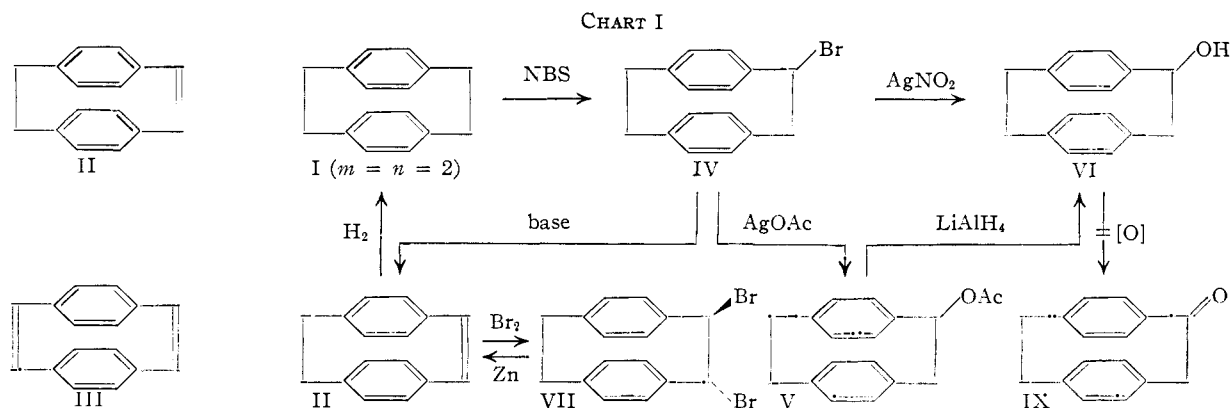
Fig. 1.—Ultraviolet spectra in 95% ethanol, Cary recording spectrometer model 11 MPS.

Results

Preparation of the [2.2]Paracyclophane Mono-olefin (II).—The reactions carried out during the synthesis of II are summarized in Chart I. When treated with N-bromosuccinimide, [2.2]paracyclophane reacts in the presence of both peroxides and ultraviolet radiation.⁶ With 1.6 molar equivalents of brominating agent, a mixture was obtained consisting of at least 23% monobromide IV, along with starting material and higher brominated products. That the bromine entered the bridge rather than the benzene ring was demonstrated by the conversion of IV to its monoacetate V with silver acetate⁷ (75%). This acetate was reduced with lithium aluminum hydride to the corresponding hydroxy compound VI (79%). The melting point of this compound was identical to that of 4-hydroxy[2.2]-paracyclophane(VIII), and showed no depression when mixed with an authentic sample of VIII.^{4c} However, a comparison of their ultraviolet absorption spectra (Fig. 1) demonstrates the substances

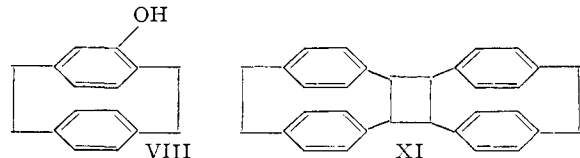
(6) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

(7) A. C. Cope and S. W. Fenton, *THIS JOURNAL*, **73**, 1668 (1951).



to be quite different, particularly with respect to the bathochromic shift observed in basic solution for phenol VIII but not for compound VI.

Hydroxy compound VI was also obtained (40%) by treatment of monobromide IV with silver nitrite in ether, presumably by hydrolysis of the initially formed nitrite ester. Oxidation of VI to monoketone IX was attempted with chromic acid,



with the Oppenauer reagent, and with manganese dioxide.⁸ In each case except the latter either starting materials, tars or non-carbonyl containing oils were obtained. The ultraviolet spectrum of the solid carbonyl compound obtained with manganese dioxide indicated that the cycle had been opened during the oxidation.

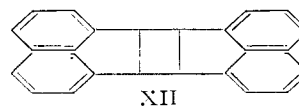
In attempts to eliminate the elements of hydrogen bromide from monobromide IV, the compound was treated with such bases as pyridine, quinoline and alcoholic potassium hydroxide at temperatures between 80 and 180°. Either starting material or tars were obtained. With potassium *t*-butoxide in refluxing *t*-butyl alcohol, IV gave monoolefin II (66%). As a preliminary to carrying out a Hofmann elimination, bromide IV was treated with dimethylamine at 160° to give a dimethylamino compound (X) of unexpected structure (see next section), and a mixture of hydrocarbons (42%) of composition C₁₆H₁₄. Through a combination of chromatographic and fractional sublimation techniques the hydrocarbon mixture gave monoolefin II, and a higher molecular weight material (XI) of the same composition, which possessed a melting point >300°.

The structure of olefin II was demonstrated by its molecular weight (Signer⁹), and by its catalytic hydrogenation to [2.2]paracyclophane. Furthermore, II added one mole of bromine to give dibromide VII, which when treated with zinc regenerated

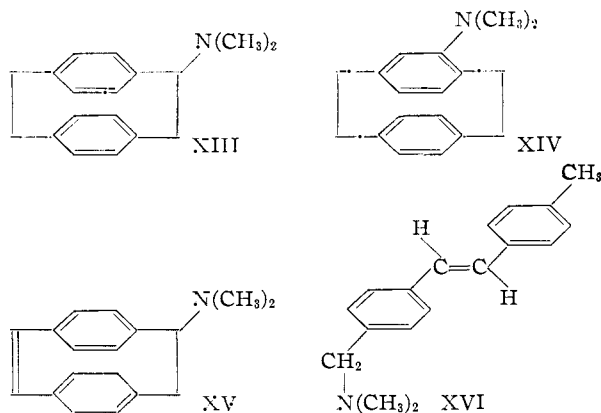
olefin II. The olefin could not be successfully condensed with butadiene in a Diels-Alder reaction.

The high melting hydrocarbon XI also possesses the composition C₁₆H₁₄, and is probably a dimer of II, as demonstrated by its high melting point, relative insolubility and Rast molecular weight of 390 (theory for dimer is 412). The compound appears to be fully saturated as demonstrated by its failure to add bromine or hydrogen in the presence of catalyst. The ultraviolet absorption spectrum of the dimer proved to be very similar to that of [2.2]-paracyclophane, a fact which suggests that the compound possesses structure XI. This structure is particularly reasonable in view of the fact that acenaphthylene which also carries a strained double bond dimerizes to form the four-membered ring compound¹⁰ XII.

The Structure of Dimethylamino Compound X.—This substance possesses the expected molecular formula C₁₈H₂₁N, but its ultraviolet absorption spectrum is quite different from that expected for structure XIII. The ultraviolet spectrum (see Fig. 2) exhibited a strong band with λ_{max} 315 (ϵ 34,000) in both acid and neutral solution, while



the infrared spectrum possessed a distinctive band at 957 cm.⁻¹ characteristic of a *trans*-olefin. The



(8) O. Mancera, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953).

(9) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941). A value of 209 (theory is 206) was obtained by this low temperature method, whereas 360 was obtained by the high temperature Rast procedure in camphor.

(10) (a) K. Dziewonski and R. Rapalski, *Ber.*, **45**, 2491 (1912); (b) J. D. Dunitz and I. Weissman, *Acta Cryst.*, **2**, 62 (1949).

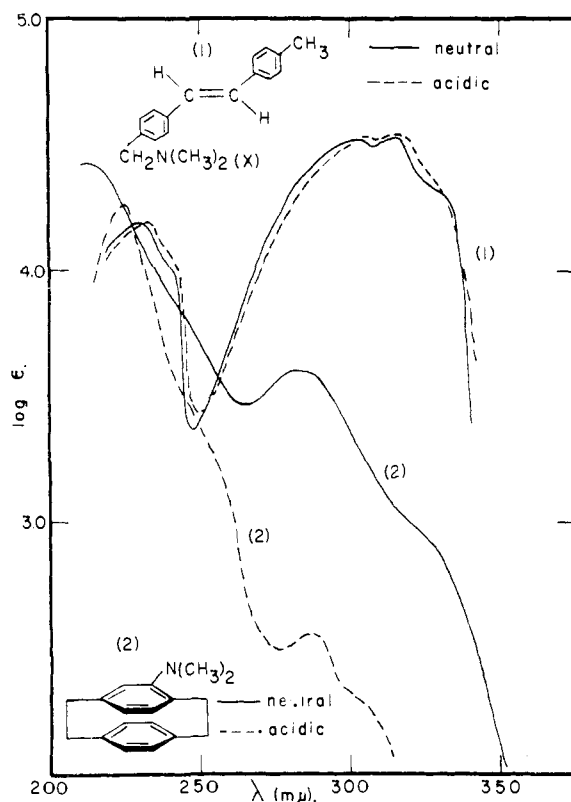
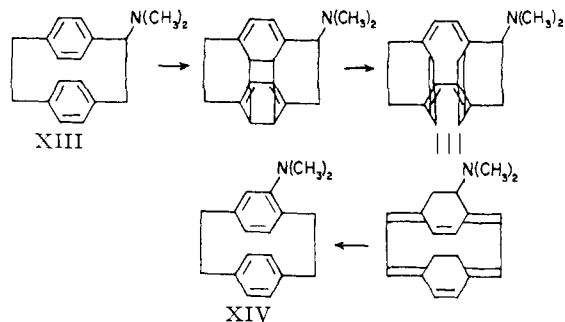


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrometer model 11 MPS.

nuclear magnetic resonance spectrum¹¹ showed three peaks with δ^{12} values of +1.8, -1.7 and -3.1 with relative areas of 5-1-5, respectively. The pK^* of the conjugate acid of amine X was found¹³ to be 7.43.

The symmetry properties of XIII are such that by a thermal isomerization a compound possessing structure XIV might arise, as shown in the formulation.¹⁴ However, this structure is inconsistent with the pK^* value¹⁵ for X, as well as the



(11) Measured in 5 mm. o.d. tubes of either pure liquids or saturated solutions in carbon tetrachloride (10-20%) with Varian Associates high resolution spectrometer (V-4300B) at 40 mc. and 12 in. magnet equipped with super stabilizer.

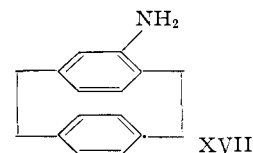
(12) In parts per million, referred to water.

(13) We are indebted to Dr. E. Heilbronner of the Eidg. Technische Hochschule, Zürich, for his kindness in providing this value. The measurements were made by microtitration in 80% methyl Cello-solve-20% water [see W. Simon, *Helv. Chim. Acta*, **39**, 290 (1956)].

(14) For an example of a similar thermal rearrangement, see G. Wittig, G. Koenig and K. Clauss, *Ann.*, **593**, 127 (1955).

(15) N. F. Hall and M. R. Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

ultraviolet spectrum,¹⁶ particularly with that in acid solution (see Fig. 2). To definitely rule out structure XIV for compound X, XIV was synthesized by methylation of the known compound XVII,^{4c} and was found to be different from X.



Structure XV, or some similar structure with rearranged double bonds, might have arisen by base-catalyzed isomerization of XIII to relieve steric

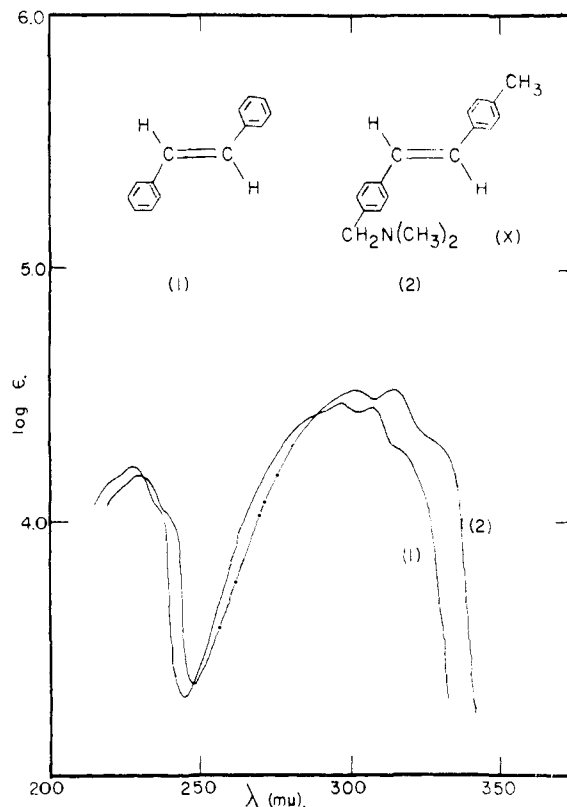


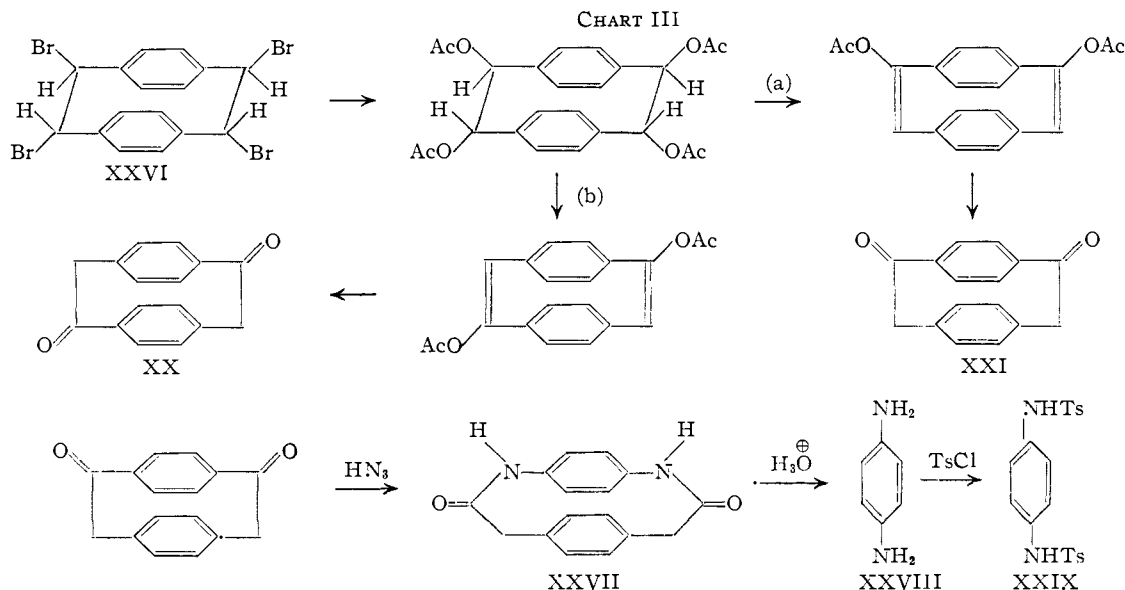
Fig. 3.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrometer model 11 MPS.

strain in the system. However, no arrangement of double bonds, considering the orthogonal geometry of the system, could possibly give rise to an intense absorption band in the 320 mμ region of the ultraviolet absorption spectrum, as was observed in X.

Structure XVI for compound X is consistent with all of the data. As indicated in Fig. 3, the ultraviolet absorption spectra of X and *trans*-stilbene show a marked resemblance to one another. The small shifts of the bands to longer wave lengths and higher intensities in passing from *trans*-stilbene to structure XVI are just what are expected from the effect of two *p*-methyl substituents¹⁷ on the spectrum of this *trans*-olefin. Structure XVI for compound X also explains the band at 957 cm.⁻¹

(16) L. Daub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

(17) R. N. Beale and E. M. F. Roe, *ibid.*, **74**, 2303 (1952).



amounting to 46%. The chromatographic behavior of these compounds was somewhat unusual, as the order of elution observed was tetrabromide-tri-bromide-pentabromide. The isomeric tetrabromides will be referred to as A (m.p. 220.4–221.2°) and B (m.p. 213.8–214.4°).

Attempts were made to convert A and B into diolefin III directly. When A was refluxed for 3 days with sodium iodide in acetone, no iodine was liberated and 76% of the starting material was recovered. Tetrabromide B was treated with zinc in ethanol, but only intractable products were obtained. With dibutyl ether as solvent, a 71% yield of [2.2]paracyclophane was obtained. Similarly, with sodium in isopropyl alcohol [2.2]paracyclophane was the main product.²⁰

The *gem*-arrangement of the bromine atoms in A and B was demonstrated by the reactions formulated in Chart II. Each tetrabromide with silver acetate in acetic acid gave a unique diketone in about 65% yield. Each of these diketones was reduced to its corresponding diol from which the tosylate was prepared. Each of these derivatives with potassium *t*-butoxide gave the desired diolefin III. Thus an over-all yield of 14% of III was obtained with [2.2]paracyclophane as starting material.

The Structures of Tetrabromides A and B.—The isolation of two distinct, pure, monomeric²¹ diketones derived from the two tetrabromides provides strong evidence that the tetrabromides possess structures XVIII and XIX. The only plausible path for the formation of these diketones from *vic*-tetrabromides such as XXVI would involve acetolysis, elimination of acetic acid and hydrolysis of the resulting enolacetate, followed by ketonization as formulated in Chart III. This series of

transformations is highly unlikely for the following reasons: (1) Loss of acetic acid from a tetraacetate under the mild conditions used for the reaction is highly unlikely, particularly in view of the stability of monoacetate V under the same conditions. (2) To obtain *only one ketone* from each of the two tetrabromides would require the elimination reactions to go completely in one direction for one tetraacetate, and only in the other direction for the other isomer. The symmetry properties of the possible stereomers of these tetraacetates are completely incompatible with this type of selectivity, and a mixture of diketones would be expected from each tetrabromide should the structures of Chart III apply. (3) Addition of bromine to diolefin III gave a mixture of diastereomeric *vic*-tetrabromides (XXVI) which when treated with zinc reverted smoothly to diolefin III. In contrast, tetrabromides A and B did not give III under the same conditions. The physical properties of the *vic*-tetrabromides were different from tetrabromides A and B.

Clearly tetrabromides A and B possess structures XVIII and XIX, but the question remains as to which is which. It has been shown²² that the $=\text{C}-\text{H}$ out-of-plane bending frequency in aromatic compounds is a function not only of the number and position of substituent groups, but also of the electronegativity of the groups. Within a series of compounds with the same positions substituted (e.g., 1,4-disubstituted), the more electronegative the groups, the higher the bending frequency. The structures of the two diketones XX and XXI suggest that XX should exhibit a single band in this spectral region, and XXI should have two bands of lower intensity corresponding to the two differently substituted benzene rings. The infrared spectrum of the diketone derived from tetrabromide A shows a single band at 808 cm^{-1} , whereas that derived from tetrabromide B shows two bands, a doublet at 806 and 815 cm^{-1} and a

(20) With zinc and ethanol, or with sodium and isopropyl alcohol, the rigid 9,10-(11,12-dichloroethano)-phenanthrene system undergoes elimination [S. J. Cristol and N. L. House, *THIS JOURNAL*, **74**, 2193 (1952)].

(21) These ketones gave molecular weight values near dimer by the Rast method, but the more reliable Signer method gave values of 247 and 227 for XX and XXI, respectively (theory is 236).

(22) R. D. Kross, V. A. Fassel and M. Margoshes, *THIS JOURNAL*, **78**, 1332 (1956).

singlet at 832 cm^{-1} . Thus tetrabromide A probably possesses structure XVIII, and B, structure XIX.

Conclusive proof of the correctness of this assignment is supplied by the following degradative sequence. The diketone prepared from tetrabromide B was treated with a solution of hydrazoic acid in trifluoroacetic acid²³ to give diamide XXVII. Hydrolysis of this amide gave *p*-phenylenediamine, identified as its bis-*p*-toluenesulfonate XXIX.

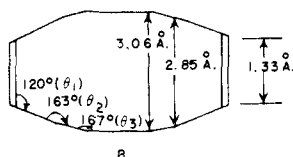
Discussion

The Geometry of Diolefin III.—The interesting question arises as to the nature of the alteration of geometry that occurs when two double bonds are introduced into [2.2]paracyclophane. In the parent hydrocarbon (see cross section A), the steric repulsions between the benzene rings expand the bond angle $\left(\begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \searrow \quad \nearrow \\ \text{Ar} \end{array}\right)$ from the normal 109°

to 115°. The change of this angle from a normal of 109° to a normal of 120° $\left(\begin{array}{c} \text{CH}=\text{CH} \\ \searrow \quad \nearrow \\ \text{Ar} \end{array}\right)$ in passing

to diolefin III might be expected to release strain. However, the $\text{CH}_2\text{-CH}_2$ bond distance of 1.55 Å. in [2.2]paracyclophane is probably decreased to 1.33 Å. in III, thereby bringing the benzene rings closer together. A crude prediction of the geometry of III is found in diagram B. This model is based on the following assumptions: (a) the $\text{CH}=\text{CH}$ bond angle is 120° and the $\text{CH}=\text{CH}$

bond length is 1.33 Å.; (b) the $\text{CH}_2\text{-Ar}$ bond lengths are 1.54 Å.; (c) the angle strain is distributed throughout the other bond angles in the same ratio as in the parent [2.2]paracyclophane. Thus the geometric requirements of the molecule



may be satisfied by increasing the strain in θ_2 and θ_3 by 3 and 2°, respectively, with very little alteration of the benzene ring separation.

Steric Modification of Spectral Properties.

The effect of steric inhibition of resonance on the ultraviolet absorption spectra of unsaturated organic molecules varies considerably with the character of the unsaturated functions whose conjugation with one another is being modified. With such systems as biphenyl, styrene or stilbene, steric constraints that prohibit coplanarity of the whole system of double bonds move those bands of the spectrum associated with the chromophore as a whole to shorter wave lengths and lower intensities.²⁴ In the case of systems which contain the acetophenone absorbing unit, the values of λ_{max} re-

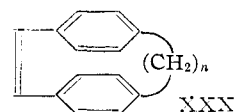
(23) P. A. S. Smith, *THIS JOURNAL*, **70**, 320 (1948).

(24) (a) L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936); (b) M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940).

main essentially constant while those of the extinction coefficient decrease as the phenyl and carbonyl groups are forced from a coplanar configuration by steric factors.²⁵ These facts are compatible with the idea that in this type of system, only that fraction of molecules whose carbonyl and phenyl groups are nearly coplanar can undergo excitation. In the molecules prepared in the present investigation, the orthogonal relationship between the benzene rings and any chromophore placed in the side chain should represent the limit of chromophoric insulation by rotation about carbon-carbon bonds.

Figure 4 records the ultraviolet spectra of [2.2]-paracyclophane, monoolefin II and diolefin III. In these spectra, the successive introduction of double bonds caused little change in the over-all spectrum, in agreement with expectation. The small differences that are observed are easily accounted for by small differences in the amounts of distortion of the benzene rings of the three systems from a planar geometry.

It is interesting to compare the spectra (Fig. 5) of monoolefin II and its open-chain structural analog, *cis*-stilbene.¹⁷ These spectra are entirely different, and represent the extremes of system XXX. The preparation of a few compounds with values of *n*



higher than 2 and an examination of their spectra should prove instructive.

Figure 6 records the spectra of diketones XX and XXI. An inspection of the curves reveals that diketone XX has a band at 235 $m\mu$ (ϵ 12,500) which has degenerated to a shoulder in XXI. The position and intensity of these bands (when corrected to take into account both carbonyls) are compatible with the absorption of a moderately hindered benzoyl chromophore. However, the complete lack of such resonance interaction in the case of the olefinic compounds makes this assignment unlikely. An examination of the values for λ_{max} of the brominated [2.2]paracyclophanes (see Table II) shows that the successive introduction of bromine atoms into the methylene bridges produces a corresponding shift of the 225 $m\mu$ band (associated with the benzene chromophore) toward longer wave lengths. Since resonance interactions between the halogens and the aromatic rings are impossible in these compounds, the shifts must be attributed to the inductive effect of the bromine atoms. Such an inductive effect by the carbonyl groups could also shift the benzene absorption band to the observed 235 $m\mu$, which is close to the positions of the bands for the tetrabromides (236 $m\mu$).²⁶

Supporting evidence for this point is obtained

(25) E. A. Braude and P. Soudheimer, *J. Chem. Soc.*, **3754**, 3773 (1955).

(26) The magnitudes of the inductive effects of a ketonic carbonyl group and a *gem*-dibromomethylene probably do not differ greatly from one another. Thus the pK_a 's of the following compounds are as follows: $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, 4.88; $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$, 3.58; $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{H}$, 4.02; $\text{Br}_2\text{CHCH}_2\text{CO}_2\text{H}$, 3.31 (estimated from model compounds). See H. C. Brown in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, pp. 578-579.

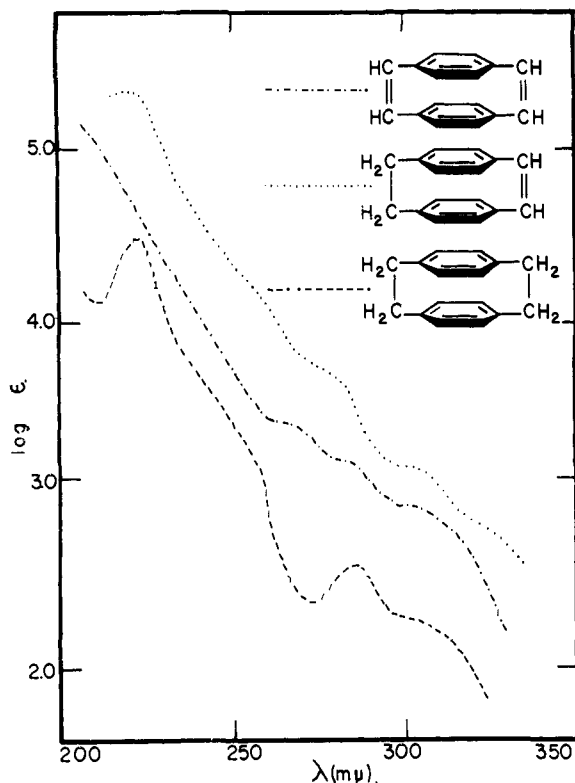


Fig. 4.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrometer model 11 MPS. The upper two spectra are displaced upward on the ordinate by successive increments of 0.5 log unit.

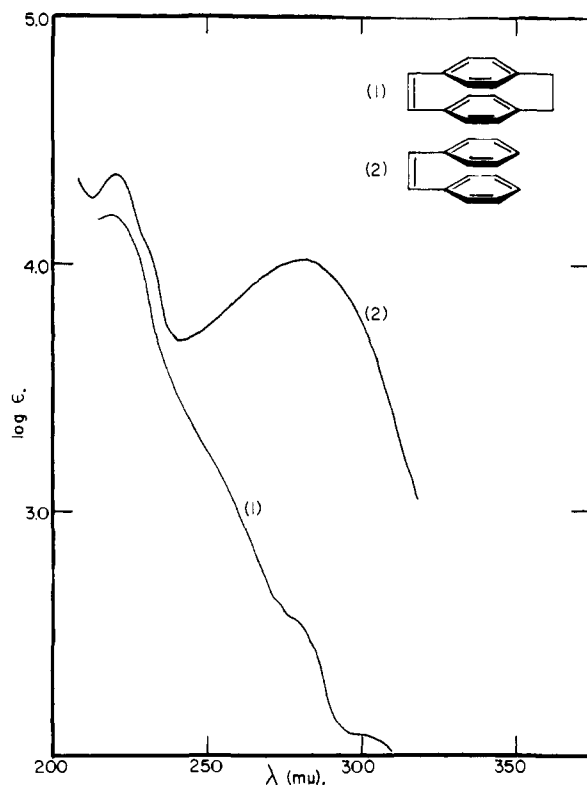


Fig. 5.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrometer model 11 MPS.

from the ultraviolet spectra of the corresponding 2,4-dinitrophenylhydrazone derivatives, the principal absorption bands of which were sufficiently far removed from the general absorption of the [2.2]paracyclophane system so that they could be easily interpreted. The position of this band has been shown²⁷ to be a function of the extent of conjugation of various chromophores with the original carbonyl group. Aromatic ketones have values for λ_{\max} near 380 $m\mu$ which fall to a lower limit of 360 $m\mu$ for aliphatic ketones. The value of 365 $m\mu$ obtained for both diketone derivatives indicates little, if any, conjugation between the carbonyl and phenyl groups.

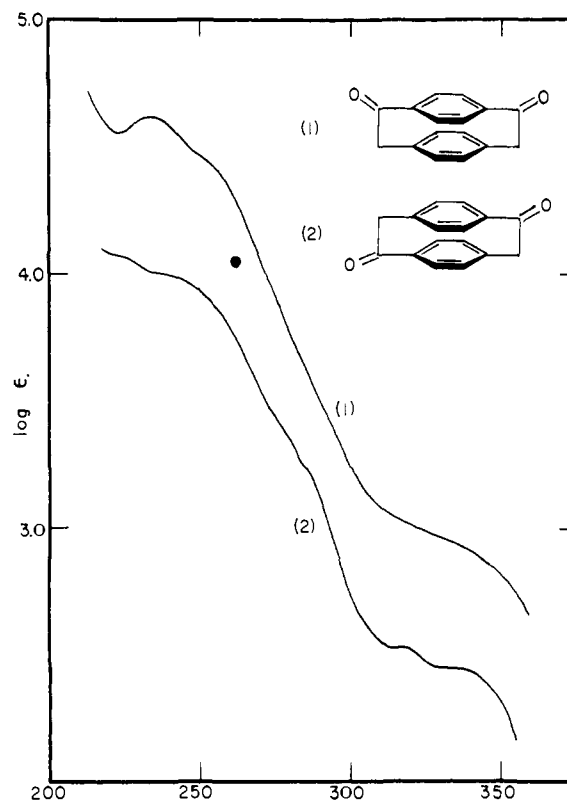


Fig. 6.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrometer model 11 MPS. Spectrum 1 is displaced upward on the ordinate by 0.5 log unit.

In contrast to the abnormalities of the ultraviolet spectrum, the infrared band associated with the carbon-oxygen stretching frequency occurred at 1685 cm^{-1} (potassium bromide pellet) in the two diketones XX and XXI, a position normal for aromatic ketones.²⁸ There are at least two factors other than conjugation, however, which might cause the absorption frequency to occur this low. (1) Crystal packing and medium effects in the solid phase might be responsible. For example, a concentrated solution of *p*-hydroxyacetophenone²⁸ absorbs at 1653 cm^{-1} , while in a Nujol mull the band is shifted to 1636 cm^{-1} . (2) Steric strain associated with the C-C-C angle of the carbonyl groups might shift the absorption to lower fre-

(27) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

(28) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 119.

quencies. This effect probably is responsible for the low absorption frequency of other large ring ketones (cyclodecanone determined in the liquid phase in this Laboratory had a value of 1700 cm.^{-1}).

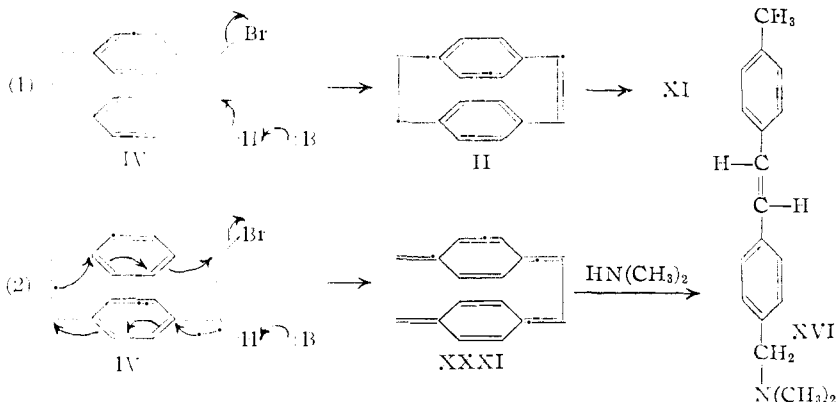
Steric Modification of Chemical Properties.—Catalytic reduction of [2.2]paracyclophane itself

TABLE II
ULTRAVIOLET ABSORPTION DATA FOR THE BROMINATED DERIVATIVES OF [2.2]PARACYCLOPHANE^a

Compound	λ_{max} , $m\mu$	ϵ
[2.2]Paracyclophane	225	25,000
1-Bromo[2.2]paracyclophane (IV)	226	19,500
<i>trans</i> -1,2-Dibromo[2.2]paracyclophane (VI)	227	16,300
Tribromo[2.2]paracyclophane	233	18,300
1,1,9,9-Tetrabromo[2.2]paracyclophane (XX)	236	19,000
1,1,10,10-Tetrabromo[2.2]paracyclophane (XXI)	236	20,500
1,2,9,10-Tetrabromo[2.2]paracyclophane (XXVI)	236	19,500
Pentabromo[2.2]paracyclophane	239	20,000

^a Spectra were determined on a Cary recording spectrophotometer, model 11 PMS in 95% ethanol.

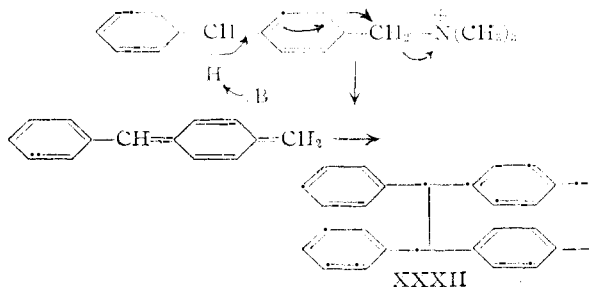
already has been demonstrated to assume an unusual course^{4c} in the sense that four moles of hydrogen were absorbed much faster than the last two moles. Isolation of product after four moles of hydrogen had been consumed gave a crystalline and non-conjugated diene. This unusual effect was attributed^{4c} to a release of steric strain in passing from [2.2]paracyclophane to the relatively un-



strained diene. Diolefin III exhibited a somewhat similar behavior when hydrogenated. The first mole of hydrogen was absorbed somewhat faster than the second, a fact consistent with an expected proportionately greater increase in steric strain in passing from [2.2]paracyclophane to monoolefin II to diolefin III.

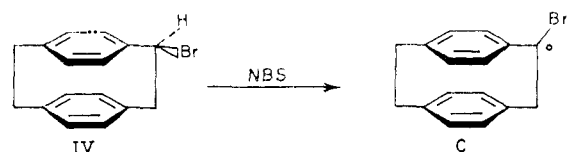
The aminative ring-cleavage of monobromide IV when treated with dimethylamine represents a second abnormal transformation encountered with this strained ring system. An elimination reaction could assume either of two courses with this system, as formulated. Reaction course 1 is the usual 1,2-elimination reaction, while 2 represents a vinylogous fragmentation reaction leading to octaene XXXI. A number of such fragmentation reac-

tions recently have been reported²⁹; for example, treatment of *cis*- or *trans*-1,4-dibromocyclohexane with zinc in dioxane results in the formation of 1,5-hexadiene in good yield. Octaene XXXI is then visualized as adding dimethylamine 1,12 to give the observed product XVI. The formation of 1,2-diphenyl[2.2]paracyclophane (XXXII)³⁰ probably occurs by a similar mechanism. In this case, however, cyclization without dimerization cannot occur. The interesting possibility also exists that all three products of the reaction of IV with dimethylamine involve octaene XXXI as an intermediate; monoolefin II arising by simple cyclization of XXXI and four-membered ring compound XI resulting from dimerization of XXXI.



The formation of *gem*- rather than the usual *vic*-tetrabromides³¹ when [2.2]paracyclophane was treated with N-bromosuccinimide represents a third abnormal reaction associated with this ring system. The generally accepted mechanism for this reaction³² involves a free radical chain. The decided reluctance of [2.2]paracyclophane to enter

into reaction with N-bromosuccinimide except under drastic conditions undoubtedly reflects the fact that much of the resonance stabilization of the benzyl radical in this system is lost due to steric inhibition of resonance. One of the factors contributing to the abnormal course of the reaction is the steric strain associated with the system. In passing from cycle carrying a bromine in a methylene bridge (e.g., IV) to the radical C, more compression strain should be relieved than when hydro-



gen was abstracted from a benzyl carbon not carrying a halogen.

Experimental

Boiling points and melting points are corrected.

(29) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

(30) H. W. Bersch, *Angew. Chem.*, **69**, 237 (1957).

(31) References to examples of the formation of vicinal bromides are as follows: reference 14; F. D. Greene, W. A. Remers and J. W. Wilson, *This Journal*, **79**, 1416 (1957).

(32) G. P. Bloomfield, *J. Chem. Soc.*, 114 (1914).

1-Bromo[2.2]paracyclophane (IV).—A mixture of [2.2]-paracyclophane (17.5 g.), 22.4 g. of *N*-bromosuccinimide and 1400 ml. of CCl_4 were refluxed overnight. The warm solution was filtered to remove succinimide, and evaporated to dryness. The residue was crystallized from benzene to give 4.8 g. (27%) of starting material, m.p. 264–274°. The filtrates were adsorbed on a column of neutral alumina of activity 1.³³ Elution with pentane gave two main fractions: starting material, 0.90 g. (5%), and 1-bromo[2.2]-paracyclophane, 5.4 g. (22%), m.p. 114–117°. Elution of the column with 5% ether–pentane gave only mixtures which were combined to give a total of 2.7 g. For analysis, a small sample of the monobromide was recrystallized from ethanol–water, m.p. 121.4–122.0°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{Br}$: C, 66.91; H, 5.26. Found: C, 67.11; H, 5.46.

The mixture of bromides (800 mg.), silver acetate (1.2 g.) and 100 ml. of dry acetic acid were heated under reflux for 4 hours. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was dissolved in benzene and chromatographed on neutral alumina. Elution of the column with 20% ether–pentane gave a very small amount of material which, after recrystallization from ethanol–water, melted at 222–224°. This material gave no 2,4-dinitrophenylhydrazine test, and the ultraviolet spectrum showed no bands of interest. Elution of the column with 70% ether–pentane gave two main fractions; the first melted from 142–150°, and the second from 104–114°. Recrystallization of these fractions did not improve the melting points; they were analyzed.

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_4$: C, 74.05; H, 6.22. Found (material, m.p. 142–150°): C, 73.71; H, 6.34. Material, m.p. 104–114°: C, 73.68; H, 5.92.

1-Acetoxy[2.2]paracyclophane (V).—Monobromide IV (1.0 g.), silver acetate (0.63 g.) and 100 ml. of dry acetic acid were refluxed for 4 hours. The warm mixture was filtered to remove silver bromide, and the filtrate was evaporated *in vacuo*. The contents of the flask were cooled, diluted with water, and filtered. Crystallization of the solid from ethanol–water gave 700 mg. (75%) of V, m.p. 95–98°. For analysis, a small sample was recrystallized 4 times from ethanol–water, m.p. 104.6–105.2°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.17; H, 6.81. Found: C, 80.86; H, 7.03.

1-Hydroxy[2.2]paracyclophane (VI).—Monoacetate V (466 mg.) in 25 ml. of ether was added over a period of 10 minutes to 150 mg. of lithium aluminum hydride in 75 ml. of ether, and the resulting solution was refluxed for an additional hour. Ethyl acetate was then added to decompose the excess hydride followed by sufficient dilute hydrochloric acid to dissolve the complex. The phases were separated, and the ether layer was washed successively with dilute acid, sodium bicarbonate and water. The ether layer was then dried, evaporated, and the residue was crystallized from benzene–hexane to give 295 mg. (79%) of product, m.p. 226–229°. For analysis, a small sample was recrystallized 3 times from ethanol–water to give VI, m.p. 228.0–231.0°. A sample of this compound, m.p. 226–229°, upon admixture with a sample of 4-hydroxy[2.2]paracyclophane,⁴⁶ m.p. 221–226°, melted at 225–229°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$: C, 85.67; H, 7.19. Found: C, 85.55; H, 7.19.

Treatment of 1-Bromo[2.2]paracyclophane with Silver Nitrite.—Monobromide IV (200 mg.), silver nitrite (130 mg.) and 50 ml. of anhydrous ether were stirred at room temperature for 48 hours. The mixture was then filtered and evaporated to give 130 mg. of material, m.p. 181–196°. This material could not be purified by recrystallization, and was insoluble in sodium hydroxide solution. Chromatography of the solid on activity IV alumina,³³ however, gave 30 mg. of starting material and 60 mg. (39%) of the 1-hydroxy[2.2]paracyclophane, m.p. 225–229°. A mixed melting point of this sample with an authentic sample of VI of the same melting point gave a value of 225–229°.

Attempted Syntheses of 1-Keto[2.2]paracyclophane (IX).—Attempts to prepare IX by the oxidation of alcohol VI failed. With chromic acid, only tars were obtained. With aluminum isopropoxide, no reaction occurred. Manganese dioxide opened the ring of alcohol VI.

Reaction of 1-Bromo[2.2]paracyclophane with Dimethylamine.—Monobromide IV (1.0 g.), 1 ml. of benzene and 20 ml. of dimethylamine were placed in a sealed tube and heated at 160° for 20 hours. At the end of this time, the dimethylamine was distilled and dilute sodium hydroxide was added. This mixture was extracted with ether, and the ether phase was evaporated. The residue was dissolved in benzene and adsorbed on a column of neutral alumina of activity I.³³ Elution of the column with pentane gave 300 mg. of a mixture of hydrocarbons (42%), m.p. 200–250°, which later proved to be a mixture of monomer II and dimer XI. Elution of the column with ether gave 310 mg. of crude dimethylamino compound XVI, m.p. 93–98°. Recrystallization of this material from ethanol–water gave 205 mg. (24%) of product, m.p. 102–103°. For analysis, a small sample of the hydrocarbon XI was twice recrystallized from ethanol–water, m.p. >>300°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84; mol. wt., 206. Found: C, 93.12; H, 6.97; mol. wt. (Rast), 390.

For analysis, a small sample of dimethylamino compound XVI was twice recrystallized from ethanol–water, m.p. 105.0–105.4°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}$: C, 86.00; H, 8.42; mol. wt., 251. Found: C, 86.19; H, 8.21; mol. wt., 256 (Rast).

The physical properties of this amine are listed in the Discussion section. When dissolved in CCl_4 and allowed to stand for several days, a small amount of material crystallized, m.p. 270–272°. The ultraviolet spectrum of this compound was identical to that of XVI. Not enough material was obtained for an investigation of its structure.

The crude hydrocarbon fraction was crystallized from a quantity of benzene such that about one-quarter of the material crystallized. The filtrate was adsorbed on a column of 50 g. of neutral alumina of activity I,³³ and eluted with pentane. Fractions 1–10 (50 ml. each) were combined to give 100 mg. of material (II), m.p. 195–201°. This procedure was repeated twice to give 25 mg. of II, m.p. 193–195°. For analysis, a small sample was twice recrystallized from benzene–hexane, m.p. 196.8–198.2°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84; mol. wt., 206. Found: C, 93.11; H, 6.93; mol. wt., 360 by Rast, 209 by Signer.

[2.2]Paracyclophane Monoolefin (II).—Monobromide IV was dissolved in 50 ml. of 1 *M* potassium *t*-butoxide solution and the solution was refluxed for 11 hours. The mixture was cooled, poured into 300 ml. of water, and extracted twice with ether. The ether layer was washed with water, dried, and evaporated. Chromatography of the residue on neutral alumina gave 500 mg. (66%) of product II, m.p. 194–196°. Recrystallization of this material from benzene–hexane raised the melting point to 196.0–197.0°. A mixed-melting point of this substance with monoolefin prepared previously was 195–197°.

Catalytic Hydrogenation of [2.2]Paracyclophane Monoolefin.—Monoolefin II, 4.0 mg., was placed in a low pressure hydrogenation apparatus with 20 ml. of ethanol and 1 mg. of platinum oxide. The mixture was stirred in an atmosphere of hydrogen for one day, filtered, and the filtrate was concentrated to give 2.5 mg. (63%) of [2.2]paracyclophane, m.p. 282–285°. A mixed-melting point with an authentic sample of melting point 286–288° was 284–287° and the infrared spectra of the two samples were identical.

Catalytic Hydrogenation of the [2.2]Paracyclophane Monoolefin Dimer.—Compound XI, 20 mg., was hydrogenated as in the above procedure for 2 days to give 7 mg. of starting material, m.p. >>300°, and 5 mg. of unknown material, m.p. 80–190°.

trans-1,2-Dibromo[2.2]paracyclophane (VII).—To 50 mg. of monoolefin II in 3 ml. of chloroform was slowly added 40 mg. of bromine in 4 ml. of chloroform. The mixture was allowed to stand for 15 min. and then concentrated on a steam-bath. The concentrate was adsorbed on a column of neutral alumina of activity I³³ and eluted with 15% ether–pentane to give 60 mg. (68%) of product, m.p. 154–158°. For analysis, a small sample of VII was twice recrystallized from ethanol–water, m.p. 163–165°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{Br}_2$: C, 52.49; H, 3.85. Found: C, 52.70; H, 3.95.

Debromination of trans-1,2-Dibromo[2.2]paracyclophane (VII) with Zinc.—Dibromide VII, 65 mg., and zinc activated with ammonium chloride, 500 mg., were mixed with 25 ml.

(33) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

of 95% ethanol and refluxed for 3 days. The mixture was filtered to remove unreacted zinc, concentrated, diluted with water, and extracted with chloroform. The chloroform extracts were washed with water, dried, and evaporated. Chromatography of the residue on neutral alumina gave 27 mg. (54%) of [2.2]paracyclophane monoolefin (II), m.p. 187–192°. One crystallization of the material from benzene-hexane gave m.p. 195.0–196.2°, not depressed by admixture with an authentic sample.

Attempted Reaction of [2.2]Paracyclophane Monoolefin with Butadiene.—In a number of attempted reactions, 50 mg. of monoolefin, 0.3 ml. of butadiene and 2.5 ml. of benzene were heated in a sealed tube for 24 hours. In all cases, only starting material and polymer were obtained.

4-Dimethylamino[2.2]paracyclophane (XIV).—The amino compound XVII, 100 mg., and 3 ml. of methyl iodide were heated in a sealed tube at 100° for 2.5 hours. The methyl iodide was evaporated, dilute sodium hydroxide solution was added, and the mixture was extracted with chloroform. The chloroform layer was washed with water, dried, and evaporated to give a green solid which was adsorbed on a column of activity I alumina.³³ Elution of the column with 10% ether-pentane gave 50 mg. (45%) of XIV, m.p. 113.6–114.2°. For analysis, a small sample was twice recrystallized from ethanol-water, m.p. 114.4–115.0°.

Anal. Calcd. for C₁₅H₂₁N: C, 86.00; H, 8.42. Found: C, 86.01; H, 8.47.

N,N-Dimethyl-*p*-bromobenzylamine.—Dimethylamine, 65 ml., dissolved in 75 ml. of benzene, was introduced into a 500-ml. 3-necked flask equipped with a Dry Ice condenser, stirrer and dropping funnel. To this stirred mixture was added 100 g. of *p*-bromobenzyl bromide³⁴ in 150 ml. of benzene at such a rate that the reaction was modulated. The mixture was stirred at room temperature for an additional hour, filtered to remove the precipitated hydrobromides, and extracted with 6 *N* hydrochloric acid. The extracts were made basic while at 0°, and extracted with ether. The ether layer was washed with water, dried, and distilled to give 63 g. (74%) of product, b.p. 121–122° (20 mm.), *n*_D²⁰ 1.5406. For analysis, a small sample was converted to the solid methiodide, m.p. 227° dec.

Anal. Calcd. for C₁₀H₁₅NBrI: C, 33.73; H, 4.25. Found: C, 33.91; H, 4.20.

Treatment of the [2.2]Paracyclophane with Palladium.—A small amount of [2.2]paracyclophane was placed in a sublimation apparatus and heated with 10% palladium-on-carbon at 300° for a few minutes. The pressure was then reduced and most of the material sublimed out. The residue was a dark, viscous tar which was not investigated further. The sublimate was chromatographed on neutral alumina to give a mixture of the [2.2]paracyclophane and 1,2-bis-(*p*-tolyl)-ethane (m.p. 79–80° undepressed by admixture with an authentic sample).

[2.2]Paracyclophane Diolefin III.—The crude dibromide obtained from the preparation of the monobromide, 1.0 g., was dissolved in 50 ml. of 1 *M* potassium *t*-butoxide solution, and the solution was refluxed for 2 hours. At the end of this time, the mixture was cooled, poured into 300 ml. of ice-water, and extracted twice with ether. The ether extracts were combined, washed with water, dried, and evaporated to dryness. The residue was taken up in benzene and adsorbed on a column of neutral alumina of activity I.³³ Elution of the column with pentane gave 150 mg. of III, m.p. 220–225°. Elution of the column with ether gave no further material. For analysis, a small sample of III was twice recrystallized from benzene-hexane, m.p. 230.0–231.0°.

Anal. Calcd. for C₁₆H₁₂: C, 94.08; H, 5.92; mol. wt., 204. Found: C, 93.97; H, 6.04; mol. wt. (Signer), 210.

Catalytic Hydrogenation of the [2.2]Paracyclophane Diolefin.—The diolefin, 12.0 mg., was dissolved in 20 ml. of ethanol and hydrogenated with 3 mg. of platinum oxide. After 15 min., 98.5% of the theoretical amount of 2 molar equivalents was absorbed. The platinum was filtered, and the filtrate was concentrated and cooled to give 8.0 mg. of the [2.2]paracyclophane, m.p. 283–286°. A mixed-melting point with an authentic sample of m.p. 286–288° was 285–287°. The infrared spectra of the compounds were identical. Rate data for the hydrogenation of this compound in ethyl acetate is given in Table III.

TABLE III^a

Time, min.	Volume, ml.	Time, min.	Volume, ml.
0	0.0	16	3.9
2	0.8	18	4.1
4	1.5	20	4.3
6	2.2	22	4.5
8	2.6	24	4.6
10	3.0	26	4.7
12	3.3	28	4.8
14	3.6	30	4.9

^a Data for 18.0 mg. of diolefin, 2.0 mg. of platinum oxide (pre-reduced) and 20 ml. of ethyl acetate at 22° and 745 mm.

1,2,9,10-Tetrabromo[2.2]paracyclophane (XXVI).—To 75 mg. of diolefin III in 10 ml. of carbon tetrachloride was added slowly 140 mg. of bromine in 7 ml. of carbon tetrachloride. The solution was allowed to stand overnight, and then was poured through a column of neutral alumina to give 140 mg. (73%) of XXVI, m.p. 235–260°. For analysis, a small sample was recrystallized 3 times from benzene-hexane to give a discrete isomer, m.p. 270° dec.

Anal. Calcd. for C₁₆H₁₂Br₄: C, 36.68; H, 2.31. Found: C, 36.38; H, 2.45.

The other possible isomer could not be isolated in a pure state.

Treatment of 1,2,9,10-Tetrabromo[2.2]paracyclophane (XXVI) with Zinc.—Tetrabromide XXVI, 60 mg., activated zinc, 700 mg., and 30 ml. of 95% ethanol were refluxed overnight. The mixture was filtered to remove zinc, concentrated, diluted with water, and filtered. The solid was taken up in benzene and adsorbed on a column of neutral alumina of activity I.³³ Elution of the column with pentane gave 22 mg. (94%) of [2.2]paracyclophane diolefin (III), m.p. 228–229°, not depressed by admixture with an authentic sample.

[2.2]Paracyclophane Tetrabromides XVIII and XIX.—A mixture of [2.2]paracyclophane (5.0 g., 24 mmoles), *N*-bromosuccinimide (20.0 g., 112 mmoles), dry carbon tetrachloride, 250 ml., and a trace of benzoyl peroxide were refluxed with ultraviolet radiation for 38 hours. At the end of this time the hot mixture was filtered to remove succinimide, and the filtrate was evaporated on a steam-bath. The residue was mixed with ether and filtered to give 1.4 g. (11%) of [2.2]paracyclophane tetrabromide (XVIII), m.p. 222.5–224.5°. For analysis, a small sample was recrystallized from benzene-hexane, m.p. 220.4–221.2°.

Anal. Calcd. for C₁₆H₁₂Br₄: C, 36.68; H, 2.31. Found: C, 36.75; H, 2.27.

The ethereal solution was evaporated, dissolved in benzene, and adsorbed on a column of 500 g. of neutral alumina of activity I.³³ The chromatogram was eluted with 15% ether-pentane and a total of 20 400-ml. fractions were collected with the following melting points: 1, 158–197°; 2, 185–195°; 3, 190–198°; 4, 193–198°; 5, 189–198°; 6, 187–194°; 7, 183–196°; 8, 168–173°; 9, 154–157°; 11, 155–159°; 13, 165–170°; 15, 171–175°; 17, 174–176°; 20, 184–185°.

Fractions 1–8 were combined to give 5.0 g. of material, which upon fractional crystallization from benzene-hexane gave 2.9 g. (23%) of [2.2]paracyclophane tetrabromide (XIX), m.p. 213–214°. For analysis, a small sample was sublimed and twice recrystallized from benzene-hexane, m.p. 213.8–214.4°.

Anal. Calcd. for C₁₆H₁₂Br₄: C, 36.68; H, 2.31. Found: C, 36.85; H, 2.46.

Fractions 9–11 were combined to give 0.5 g. of material which melted at 162.8–163.8° upon repeated recrystallization. Analysis showed this material to be mainly a tribromide with smaller amounts of tetrabromide present. In a previous run, however, this fraction yielded a pure tribromide, m.p. 164.6–165.0°.

Anal. Calcd. for C₁₆H₁₃Br₃: C, 43.18; H, 2.94. Found: C, 43.03; H, 2.99.

Fractions 13–20 were combined to give a total of 1.5 g. of material, recrystallization of which from benzene-hexane gave 0.70 g. (5%) of [2.2]paracyclophane pentabromide, m.p. 179–180°. For analysis, a small sample was recrystallized repeatedly from benzene-hexane, m.p. 188.6–189.0°.

(34) J. B. Shoemaker and R. H. Stater, *J. Chem. Soc.*, 211 (1926).

Anal. Calcd. for $C_{16}H_{11}Br_5$: C, 31.86; H, 1.84. Found: C, 31.82; H, 2.05.

Another run with 12.0 g. of [2.2]paracyclophane and 51.0 g. of *N*-bromosuccinimide gave the following results: tetrabromide XVIII, 5.5 g. or 18% yield; tetrabromide XIX, 8.6 g. or 28% yield; pentabromide, 1.1 g. or 3% yield.

Reduction of [2.2]Paracyclophane Tetrabromides to [2.2]Paracyclophane.—When treated in a solution of refluxing acetone and sodium iodide, tetrabromide XVIII did not oxidize the iodide, and only starting material and polymer were obtained. When treated with zinc, tetrabromide XIX gave [2.2]paracyclophane as follows. A mixture of 500 mg. of XIX, 10 g. of activated zinc and 100 ml. of dibutyl ether was held at reflux for one hour. The resulting mixture was filtered, and the filtrate was washed with water, dried and evaporated *in vacuo*. When pentane was added to the residue, 140 mg. (71%) of [2.2]paracyclophane separated, m.p. 280–284°, not depressed by admixture with an authentic sample.

To 500 mg. of tetrabromide XVIII dissolved in 100 ml. of a mixture of isopropyl alcohol–benzene (4:1) was added 2.3 g. of sodium over a period of 1 hour. The mixture was further refluxed until the solution of sodium was complete and was then cooled and diluted with 4 volumes of water. The benzene layer which separated was diluted with ether and the phases were separated. The aqueous phase contained 92% of the theoretical amount of bromide ion. The benzene–ether layer was evaporated to give 195 mg. of material, m.p. 220–250°. This substance was fractionally sublimed to give 27 mg. (13.5%) of [2.2]paracyclophane, m.p. ca. 290°; 120 mg. of material, m.p. 175–265°; and 19 mg. of residue. The middle fraction was chromatographed on neutral alumina of activity I³³ and shown to be essentially the [2.2]paracyclophane, containing small amounts of partially-reduced bromide, and a trace of substance, m.p. >300°.

1,9-Diketo[2.2]paracyclophane (XX).—Tetrabromide XVIII, 960 mg., silver acetate, 1.28 g., and 300 ml. of dry acetic acid were refluxed for 1.5 hours. A small amount of water was added, and the hot mixture was filtered to remove silver bromide. The filtrate was evaporated *in vacuo* and the residue was crystallized from benzene to give 295 mg. (68%) of XX, m.p. ca. 270° dec. For analysis, a small sample was twice recrystallized from benzene–hexane.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12; mol. wt., 236. Found: C, 81.42; H, 5.19; mol. wt., (Signer) 247.

A 2,4-dinitrophenylhydrazone derivative of this compound was prepared in ethanol by the usual method, m.p. >>300°. Analysis showed it to be the mono derivative.

Anal. Calcd. for $C_{22}H_{16}N_4O_5$: N, 13.45. Found: N, 13.16.

1,10-Diketo[2.2]paracyclophane (XXI).—Tetrabromide XIX, 2.5 g., was treated as above to give 665 mg. (63%) of product, m.p. 222–226°. For analysis, a small sample was recrystallized 3 times from benzene–hexane, m.p. 234.4–235.4°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12; mol. wt., 236. Found: C, 81.25; H, 5.39; mol. wt. (Signer), 227.

1,9-Dihydroxy[2.2]paracyclophane (XXII).—Diketone XX, 580 mg., was placed in a Soxhlet extractor with 1.0 g. of lithium aluminum hydride and 400 ml. of ether, and refluxed for 3 days. Ethyl acetate was added to destroy the excess hydride, followed by sufficient dilute hydrochloric acid to dissolve the complex. The phases were separated and the aqueous phase extracted with two more portions of ether. The combined ether extracts were washed, dried, and evaporated. Crystallization of the residue from ethanol–water gave 470 mg. (81%) of diol XXII, m.p. 200–203°. For analysis, a small sample was twice recrystallized from ethanol–water, m.p. 200.4–202.4°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.84; H, 6.55.

1,10-Dihydroxy[2.2]paracyclophane (XXIII).—Diketone

XXI, 495 mg., was treated as above to give 480 mg. (96%) of XXIII, m.p. 194–197°. For analysis, a small sample was recrystallized three times from benzene–hexane, m.p. 199–204°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.05; H, 6.92.

1,9-Ditosyloxy[2.2]paracyclophane (XXIV).—Diol XXII, 160 mg., *p*-toluenesulfonyl chloride, 320 mg., and 2.0 ml. of dry pyridine were mixed and allowed to stand overnight. The mixture was then heated at 50° for 8 days, cooled, and diluted with 50 ml. of chloroform. The mixture was stirred for 15 min. and then acidified with cold, dilute sulfuric acid. The chloroform layer was separated, washed with sodium bicarbonate, water and dried. The chloroform was concentrated and diluted with hexane to give 220 mg. (60%) of product, m.p. 141° dec. For analysis, a small sample was twice recrystallized from chloroform–hexane, m.p. 138° dec.

Anal. Calcd. for $C_{30}H_{28}O_6S_2$: C, 65.67; H, 5.14. Found: C, 65.45; H, 5.09.

1,10-Ditosyloxy[2.2]paracyclophane (XXV).—Diol XXIII, 510 mg., was treated as above to give 995 mg. (85%) of XXV, m.p. 165° dec. For analysis, a small sample was twice recrystallized from chloroform–hexane, m.p. 153° dec.

Anal. Calcd. for $C_{30}H_{28}O_6S_2$: C, 65.67; H, 5.14. Found: C, 65.65; H, 5.40.

Treatment of 1,9-Ditosyloxy[2.2]paracyclophane (XXIV) with Potassium *t*-Butoxide.—Ditosylate XXIV, 215 mg., and 10 ml. of 1 *M* potassium *t*-butoxide solution were refluxed for 45 min. The cooled solution was poured into 100 ml. of water and extracted with ether. The ether was washed, dried, evaporated, and the residue chromatographed on neutral alumina of activity I³³ to give 65 mg. (81%) of the [2.2]paracyclophane diolefin (III), m.p. 225–229°. One recrystallization of the substance brought the melting point to 229–230°, not depressed upon admixture with an authentic sample.

Treatment of 1,10-Ditosyloxy[2.2]paracyclophane (XXV) with Potassium *t*-Butoxide.—Ditosylate XXV, 1.0 g., was treated as above to give 225 mg. (61%) of the [2.2]paracyclophane diolefin (III), m.p. 226°, not depressed by admixture with an authentic sample.

Treatment of 1,10-Diketo[2.2]paracyclophane (XXI) with Hydrazoic Acid.—Diketone XXI, 225 mg., was dissolved in 4 g. of trichloroacetic acid and held at 65°. Sodium azide, 200 mg., was then added, followed by an additional 50-mg. portion after 0.5 hour. The mixture was heated another 0.5 hour, cooled, diluted with water, and neutralized with ammonium hydroxide. The solid which formed was collected and dried. For analysis, a small sample was recrystallized 3 times from benzene–hexane, m.p. >300°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: N, 10.52. Found: N, 10.44.

All the available solid was combined, mixed with 3 ml. of 6 *N* sulfuric acid, and refluxed for one hour. The mixture was cooled, basified with dilute sodium hydroxide solution, and continuously extracted with ether for 30 hours. The ether was dried and evaporated in a 10-ml. flask. To this flask was added 0.2 ml. of dry pyridine, followed by 100 mg. of *p*-toluenesulfonyl chloride in 0.1 ml. of pyridine. The mixture was swirled at room temperature for 5 min. and diluted with 7 ml. of water. The flask was cooled in an ice-bath, swirled until the oil solidified, and filtered. The orange solid was recrystallized from ethanol–water with the aid of charcoal to give 23 mg. (5.7%) of the bis-*p*-toluenesulfonamide of *p*-phenylenediamine, m.p. 274°. One more recrystallization gave material, m.p. 276°, undepressed by admixture with an authentic sample. The infrared spectra of the two samples were identical.

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